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**Transformation and Transport of Nitrogen in a
Subalpine Catchment -
Effects of Elevated Nitrogen Deposition**

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presented by

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Abstract

Forests in large areas of Europe and North America are subjected to high nitrogen (N) deposition. As a consequence, the forest ecosystem may reach the status of N saturation when elevated N inputs exceed the N retention capacity. Increased nitrate (NO_3^-) leaching is regarded as the main symptom of N saturated forests. This thesis aimed to gain insight into the N cycle in a subalpine forest with Gleysols in Central Switzerland. The main objectives were (i) to estimate whether enhanced NO_3^- leaching is caused by N saturation or by rapid transport of elevated N inputs through the soil; (ii) to identify the role of flow paths for N transformation; (iii) to study the significance of dissolved organic nitrogen (DON) in this ecosystem, and (iv) to investigate the effects of redox conditions and runoff processes on the mobility of dissolved organic nitrogen and carbon (DOC).

N deposition was experimentally increased by applying $30 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1} \text{ y}^{-1}$ to a spruce forest simultaneously and proportionally to rainfall. The response of N transformation and leaching to the increased N inputs was studied at four different spatial scales: (1) at the mm^2 scale with micro suction cups; (2) in plots of 20 m^2 by sampling soil solution, measuring N mineralisation, and denitrification; (3) in the runoff from experimental sub-catchments of 1500 m^2 ; and (4) in the stream water of a headwater catchment of 0.7 km^2 .

Three years of N additions neither affected vegetation nor N-pools in the soil such as bulk soil N, microbial N, and K_2SO_4 -extractable N. In contrast, N losses from the ecosystem due to denitrification and NO_3^- leaching increased significantly. There are strong indications that the rapid change in NO_3^- leaching is mainly hydrologically driven. During storms, discharge and NO_3^- concentration of the catchment runoff responded to rainfall within minutes. The water chemistry of the catchments runoff indicated that a large portion of the runoff derives directly from precipitation and from water which had interacted only with the topsoil. This is consistent with the results of the study at the microscale. The response of 50 micro suction cups to dye tracer, sulfate, and chloride (Cl) applications demonstrates that a large portion of the soil volume

does not come in direct contact with the infiltrating rainwater. As a consequence, the contact time of the rain water with the soil matrix is insufficient for a complete retention of NO_3^- . Thus, the increased NO_3^- leaching due to elevated N inputs is caused by the bypassing of the soil matrix and the root system rather than to 'N saturation'.

Locations along flow paths, which were identified based on the response of micro suction cups to the dye tracer addition, showed a stimulated N transformation compared to that of the soil matrix. This was indicated by higher NO_3^- concentrations and larger temporal variations of the $\text{NO}_3^-/\text{Cl}^-$ ratios along flow paths.

DON was the dominant form of dissolved N in the soil water. Below 30 cm depth, all of the dissolved N occurred in the organic form. DON export from all catchments was approximately $6 \text{ kg N ha}^{-1} \text{ y}^{-1}$, which corresponds to 60% of the total N export and to 35% of the ambient N deposition. DON was mobilised by leaching from organic matter as water passed through the forest canopy and the upper soil compartments. The retention of DON in the ecosystem appears to be controlled by abiotic mechanisms such as sorption to soil surfaces and runoff processes rather than by biotic processes.

The redox environment of the Gleysol had a pronounced impact on DOC and DON mobility. In the mineral soil, DOC and DON concentrations in the soil solution were considerably higher under reducing than under oxidizing conditions. The close correlation of DOC and DON with dissolved iron concentrations suggests that the reductive dissolution of Fe(III)-oxides was the major reason for the low retention under reducing conditions.

Runoff processes had a large effect on the transport and properties of DOC and DON. During storms, concentrations of DOC and DON increased substantially compared to base flow in both subsurface flow and catchment runoff. In the subsurface flow, the elevated DOC concentrations at high flow velocities indicate that DOC was preferentially transported to the subsoil at high discharge. In the catchments, temporal variations of DOC and DON concentrations were mainly caused by changes in hydrological pathways. An end-member mixing analysis based on inorganic chemistry shows that the catchment runoff at high discharge originated mainly from the topsoil which explains the increased DOC and DON concentrations during storms.

Kurzfassung

Die derzeit hohen Stickstoffeinträge übersteigen häufig das Aufnahmevermögen von Waldökosystemen. Dies führt zur einer N-Sättigung. Erhöhte Nitratauswaschung ist eine Folge der N-Sättigung. Ziel dieser Arbeit war es, Einblicke in den N-Kreislauf eines Gleybodens in einem Fichtenwald der Schweizer Voralpen zu gewinnen. Die wichtigsten Fragestellungen waren: (1) Inwieweit ist eine erhöhte NO_3^- -Auswaschung eine Folge der N-Sättigung oder des schnellen Transports des eingetragenen Nitrats durch den Boden? (2) Welche Rolle spielen Fließwege bei der N-Umsetzung im Boden? (3) Welche Bedeutung hat der gelöste organische N (DON) im Ökosystem? (4) Welche Auswirkungen haben Redoxbedingungen und Abflussprozesse auf die Mobilität von DON und gelöstem organischen Kohlenstoff (DOC)?

Die N-Deposition wurde experimentell erhöht, indem $30 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1} \text{ a}^{-1}$ mit Hilfe eines automatischen Sprinkelsystems während natürlichen Regenereignissen im Wald verteilt wurden. Ich untersuchte die Auswirkungen des erhöhten N-Eintrags auf 4 verschiedenen Skalen: 1. Im Kleinstbereich weniger mm^2 mittels Mikroaugkerzen, 2. in Flächen von je 20 m^2 , in denen ich die N-Mineralisierung und die Denitrifikation mass sowie Bodenlösung sammelte, 3. in durch Gräben abgegrenzten Klein-Einzugsgebieten von 1500 m^2 Fläche, 4. im Bachwasser des gesamten Einzugsgebietes mit einer Grösse von 0.7 km^2 .

Drei Jahre erhöhter N-Eintrag wirkten sich weder auf die Vegetation noch auf die N-Pools des Bodens aus. Weder der gesamte N, der mikrobielle N noch der K_2SO_4 -extrahierbare N nahmen zu. Im Gegensatz hierzu erhöhten sich die N-Verluste aus dem Ökosystem durch Denitrifikation und NO_3^- -Auswaschung signifikant. Folgende Hinweise deuten darauf hin, dass das schnelle Ansprechen der NO_3^- -Auswaschung hydrologisch bedingt ist. Der Abfluss aus den Einzugsgebieten und dessen NO_3^- -Konzentrationen reagierten innerhalb von Minuten auf Niederschläge. Die chemische Zusammensetzung zeigte, dass ein Grossteil des Abflusses direkt aus dem Niederschlag stammte oder nur kurz mit dem Boden in Kontakt kam. Dies wird von der Untersuchung im mm^2 -Bereich unterstützt. Farbtracer sowie Chlorid- und Sulfat-Gaben zeigen, dass ein grosser Teil des Bodens von dem infiltrierenden Wasser umflossen wurde. Eine nur kurze Kontaktzeit des Niederschlagswassers mit der Bodenmatrix ist die Folge. So kann NO_3^- im Ökosystem nicht vollständig aufgenommen werden.

Die erhöhte NO_3^- -Auswaschung ist daher nicht auf eine N-Sättigung, sondern in erster Linie auf einen schnellen Transport des eingetragenen Nitrats zurückzuführen.

Die Fließwege im Boden, die anhand der Reaktion der Mikrosaugkerzen auf den Farbtracer identifiziert wurden, zeigten eine gesteigerte N-Umsetzung im Vergleich zur Bodenmatrix. Die Bodenlösung der Fließwege hatte höhere NO_3^- -Konzentrationen. Zudem wies das $\text{NO}_3^-/\text{Cl}^-$ Verhältnis entlang von Fließwegen grössere zeitliche Schwankungen auf als dasjenige der Bodenmatrix.

Die quantitativ wichtigste Form des gelösten Stickstoffs im Bodenwasser war DON. Unterhalb von 30 cm Tiefe lag der gelöste N vollständig in organischer Form vor. Der DON-Export aus den Einzugsgebieten lag bei ca. $6 \text{ kg N ha}^{-1} \text{ a}^{-1}$. Dies entsprach 60% des gesamten N-Austrags und 35% der Nass- und Trocken-Deposition. Die Mobilisierung von DON erfolgte im Bestand und im Oberboden durch Auswaschung aus der organischen Substanz. Die Retention von DON im Ökosystem scheint nicht von biotischen, sondern vielmehr von abiotischen Prozessen, wie Sorption am Boden und Abflussprozessen, abzuhängen.

Die Redoxbedingungen beeinflussen die Mobilität von DOC und DON. Unter reduzierenden Verhältnissen waren die DOC und DON Konzentrationen des Bodenwassers im Mineralboden deutlich höher als unter oxidierenden Bedingungen. Die enge Beziehung zwischen DOC sowie DON und gelöstem Eisen deutet auf die reduktive Auflösung von Fe(III)-Oxiden als Hauptursache für die geringe Sorption des DOC und DON hin.

Abflussprozesse spielen eine entscheidende Rolle beim Transport des DOC und DON. Die Eigenschaften dieser Komponenten verändern sich bei Abflussereignissen stark. Im Abfluss aller Einzugsgebiete und im Zwischenabfluss in 30 bis 60 cm Tiefe nahmen die DOC und DON Konzentrationen während Abflussereignissen deutlich zu. Die erhöhten DOC Konzentrationen im Zwischenabfluss weisen auf einen präferentiellen vertikalen Transport von DOC bei hohen Abflüssen hin. In den Einzugsgebieten beruhen die zeitlichen Konzentrationsänderungen auf wechselnden Beiträgen verschiedener Abflusskomponenten. Mit einer End-member mixing analysis konnte ich zeigen, dass bei hohen Abflüssen das Abflusswasser in erster Linie aus dem Oberboden stammt. Dies erklärt die erhöhten DOC und DON Konzentrationen während Abflussereignissen.

Chapter 1

General Introduction

1.1 Background: Nitrogen saturation of forest ecosystems

Human activity has greatly altered the biogeochemical cycles on Earth, generally increasing pollutant concentrations in the atmosphere and deposition rates to the surface. There is increasing concern about the nitrogen component of emissions and its potential impacts on air and water quality, and health of forest ecosystems (Aber *et al.*, 1989). The sources of nitrogen emission are fossil fuel combustion producing nitrogen oxides and intensive agriculture, leading to ammonia emission. Globally, about five times as much N was emitted to the atmosphere in 1990 through human action as by natural processes (Galloway, 1995). The high N deposition in the Northern Hemisphere may cause elevated NO_3^- concentrations in ground and streamwaters, soil acidification, eutrophication of ecosystems, and forest decline (van Breemen *et al.*; 1982; Aber *et al.*, 1989; Schulze, 1989).

Under low N deposition, plant growth in temperate forests is mostly limited by nitrogen availability (Keeney, 1980), while the metabolism of free-living microbes is generally limited by carbon (or energy). The rate-limiting step in the N cycle is the mineralisation of litter and humus, and the largest pool of N in these forest systems is in soil organic matter. Forest ecosystems at low N deposition are thus characterised by 'closed' N cycles in which inputs and outputs of the system are small in relation to the amounts cycling between soil and vegetation (Miller *et al.*, 1979).

The high atmospheric N deposition of the last decades has led to increased leaching of NO_3^- , indicating that forest ecosystems have a limited capacity to

retain nitrogen in vegetation and soil (Kahl *et al.*, 1993; Dise & Wright, 1995). This state of the ecosystem is referred to as N saturated (Aber *et al.*, 1989). Various definitions of N saturation have been proposed. They usually focus on the inability of an ecosystem to retain more N and the absence of any further increase in primary production (Ågren & Bossata, 1988; Aber *et al.*, 1989). Enhanced NO_3^- leaching is usually regarded as the main symptom of N saturation of forest ecosystems (Ågren & Bossata, 1988; Aber *et al.*, 1989; Stoddard, 1994).

This thesis was part of the NITREX project (NITROgen saturation EXperiments, (Wright & Rasmussen, 1998). NITREX focused on the impact of N deposition on forest ecosystems, in particular on the factors and processes affecting N saturation. The NITREX project entailed large-scale manipulation of N deposition to whole forests at eight sites in Europe (Wright & Rasmussen, 1998). Nitrogen was added at sites with low to intermediate ambient N deposition and removed with roofs at sites with high deposition.

The research site of the Swiss part of NITREX, Alptal, is located in Central Switzerland. It receives an ambient annual N input by dry and wet deposition of $18 \text{ kg N ha}^{-1}\text{y}^{-1}$ (Fischer-Riedmann, 1995). This represents an N deposition typical for the Swiss Northern Prealps (Flückiger & Braun, 1998) and is an intermediate N input compared to other European forest stands (Dise & Wright, 1995). In the NITREX project at Alptal, the N deposition to the forest ecosystem was experimentally increased by $30 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1}\text{y}^{-1}$ (Schleppi *et al.*, 1998). Thereby, the N input was raised above the critical threshold of about $25 \text{ kg N ha}^{-1}\text{y}^{-1}$ at which the cycling of N is thought to become uncoupled and significant N leaching losses generally occur (Dise & Wright, 1995). The objective of NITREX was to study the response of the whole forest ecosystem to the elevated N deposition. Changes in vegetation were monitored (Müller, 1997, Schleppi *et al.*, 1999a; Schleppi *et al.*, 1999b), and the impact on denitrification was measured (Mohn, 1999). This dissertation focuses on the transformations and on the transport of experimentally increased N inputs in the soil.

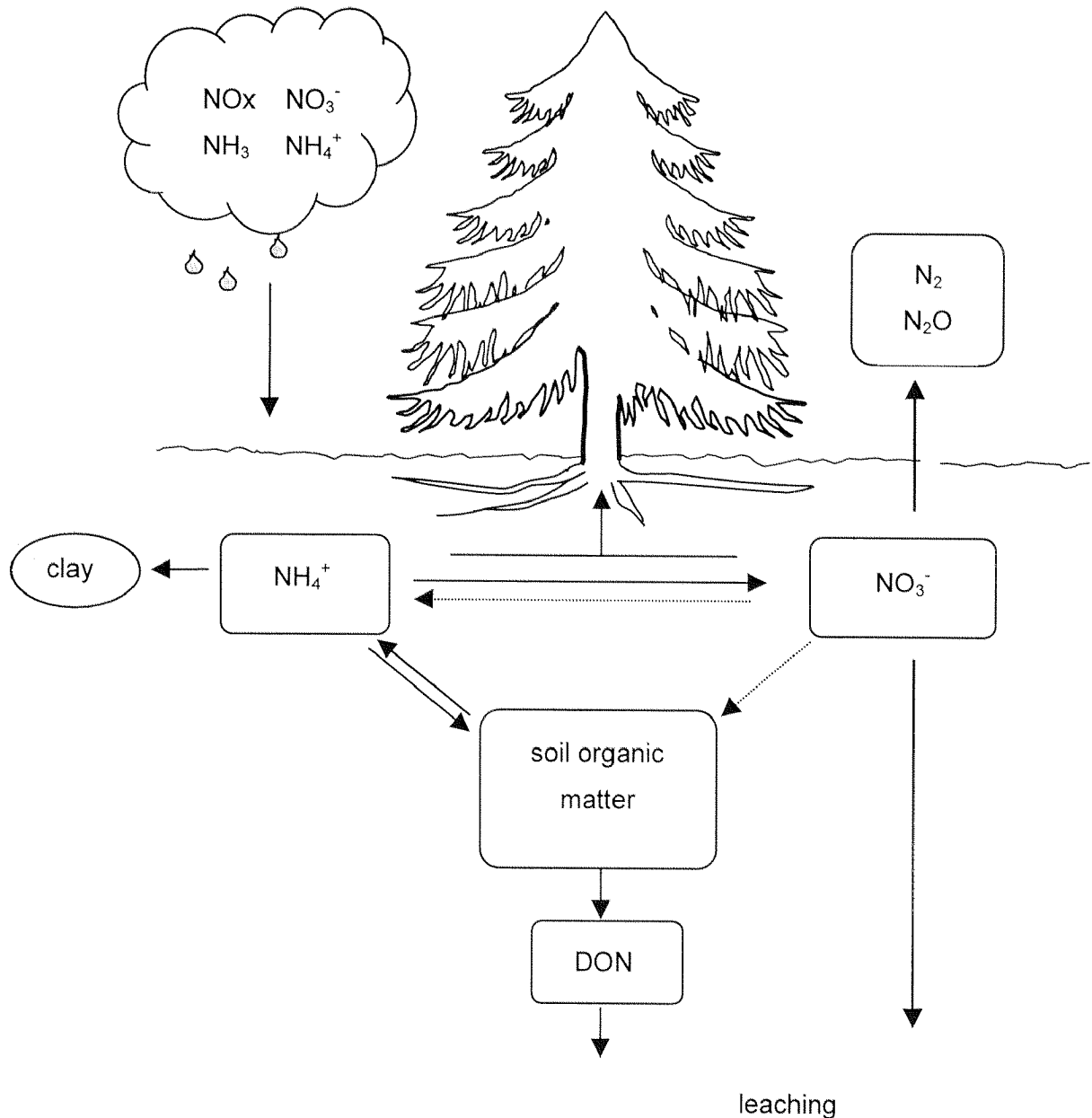


Figure 1.1: Major processes and pools of the N cycle in forest ecosystems. Nitrogen bound in soil organic matter can be decomposed by microorganisms to NH_4^+ (N mineralisation). NH_4^+ can be microbially oxidised to nitrite (NO_2^-) and further to NO_3^- , a process called *nitrification*. Moreover, NH_4^+ can be adsorbed on negatively charged soil surfaces and fixed by clay minerals. Both NH_4^+ and NO_3^- serve as a substrate for *plant uptake*. N mineralisation is counteracted by N immobilisation by which inorganic N is microbially incorporated into soil organic matter. Losses of N from the ecosystem can either occur by *leaching* of NO_3^- and DON or by *denitrification*, leading to the emission of the gaseous compounds N_2 and N_2O .

1.2 Nitrogen transformation and leaching

The early theory about the time course of N saturation assumed that plant processes that are mainly N-limited change first in response to chronic N inputs (Aber *et al.*, 1989). Soil microbial processes such as N mineralisation and nitrification that are mostly carbon-limited were thought to change subsequently in response to alterations in litter input and quality, and to the saturation of plant demand for inorganic N. Aber *et al.* (1989) postulated that NO_3^- leaching from the forest ecosystem, as a result of an accelerated nitrification rate does not occur until inorganic N is in excess of total plant demand.

However, the experimental manipulation of N deposition to forest ecosystems in the NITREX experiments, the addition and removal of N, showed an immediate response of NO_3^- leaching within the first year of treatment, whereas responses in vegetation and soil were delayed (Gundersen *et al.*, 1998). The unpredicted fast response in NO_3^- leaching after N addition and removal suggests that the change in NO_3^- leaching is hydrologically driven rather than reflecting a change in nitrogen saturation of the forest ecosystem.

The flow pathways of solutes in soils are often highly irregular. In well-structured soils, water may move along cracks, fissures and earthworm burrows (Lawes, 1882; Ehlers, 1975; Beven & Germann, 1982; Edwards *et al.*, 1993). In unstructured sandy soils, an infiltrating water front may become unstable and split into 'fingers' (Hillel, 1980). These flow phenomena occurs in most soils and are referred to as preferential flow (Luxmoore *et al.*, 1990; Flury *et al.*, 1994; Stagnitti *et al.*, 1995). It is a transport mechanism by which relatively large amounts of water flow through a small proportion of the whole soil volume. Travel times of solutes are shorter than expected based on the convective-dispersive flow assumption (Stamm *et al.*, 1998). Only a small proportion of the reactive sites within the soil gets in contact with the percolating water. A consequence of preferential flow is that even strongly sorbing solutes like pesticides and phosphorus are rapidly transported to deep

groundwaters (Flury *et al.*, 1995; Stamm *et al.*, 1998). With respect to the fate of elevated N deposition in forest ecosystems, preferential flow may cause increased NO_3^- leaching before the assimilation capacity of the ecosystem is exceeded.

Chapter 2 and 3 of this thesis focus on the relationship between nitrogen transformation in the soil and predominant transport mechanisms. In chapter 2, I investigate the response of nitrogen transformation and NO_3^- leaching to elevated N deposition at the plot scale (20 m^2) and at the sub-catchment scale (1500 m^2). In chapter 3, I present the results of an experiment carried out at the microscale (mm^2) with micro suction cups and discuss the role of flow paths for N transformations.

Objectives of chapter 2 and 3:

- (1) to investigate whether increased NO_3^- leaching due to elevated N deposition is primarily hydrologically driven or whether it reflects N saturation of the forest ecosystem;
- (2) to identify the spatial distribution of NO_3^- concentrations and their relation to the main flow paths in the topsoil; and
- (3) to investigate the N transformation within reach of flow paths and in the soil matrix.

1.3 Role of dissolved organic nitrogen

Until recently, dissolved organic nitrogen (DON) was an unrecognised form of N. However, in undisturbed forests, DON typically accounts for 50 to 95% of the total dissolved nitrogen leached from the forest floor to the mineral soil (Qualls *et al.*, 1991; Arthur & Fahey, 1993; Currie *et al.*, 1996). Moreover, the exports of DON from unpolluted ecosystems can exceed those of inorganic N (Hedin *et al.*, 1995, Arheimer *et al.*, 1996; Adamson *et al.*, 1998).

There have been numerous studies about the origin, the composition, and the fate of dissolved organic carbon (DOC) in forest ecosystems (McDowell & Likens, 1988; Guggenberger & Zech, 1993). Little is known about the N component of DOC, the DON (Northup *et al.*, 1995). Fractionation reveals that most of this DON is not composed of free amino acids or proteins, but is rather associated with humic substances such as protein-tannin complexes (Qualls *et al.*, 1991, Northup *et al.*, 1995). Thus, DON does not appear to be readily available to most soil microorganisms and plants and cannot easily be converted into inorganic forms (Northup *et al.*, 1995). This is supported by biodegradation experiments showing that there is no preferential decay of DON compared to DOC (Qualls & Haines, 1992). These findings suggest that the mobility of DON and DOC are linked to each other, which enables us to transfer knowledge about the origin and fate of DOC to DON.

The forest floor is the major source of soluble organic substances, leading to an input to the mineral soil of up to 400 kg DOC ha⁻¹ y⁻¹ (McDowell & Likens, 1988; Guggenberger & Zech, 1993). However, the output from the mineral soil and consequently the export of DOC by streams is often less than 50 kg DOC ha⁻¹ y⁻¹ (Tate & Meyer, 1983; Guggenberger & Zech, 1993), indicating that DOC is effectively retained in subsoils. Retention of DOC is generally attributed to the sorption by Al- and Fe-oxides and clay (Guggenberger & Zech, 1993, Kaiser & Zech, 1998). Biodegradation is thought to play a minor role (Qualls & Haines, 1992, Jandl & Sollins, 1997).

Gleysols are at the interface between terrestrial and aquatic ecosystems and are strongly influenced by the groundwater. Subsoils of Gleysols are characterised by reducing conditions leading to the reductive dissolution of Mn- and Fe-oxides to Mn^{2+} and Fe^{2+} . As these oxides are important sorbents of DOC (Tipping, 1981), it is likely that DOC is more mobile under reducing than under oxidising conditions.

Another important factor regulating the transport of DOC through the ecosystem is the flow process. Jardine *et al.* (1990) showed that preferential flow may cause a considerable vertical transport of DOC through the soil. In catchments, storms are identified to account for a substantial proportion of the total DOC export (Hinton *et al.*, 1997). Changes in water flow paths contributing to the stream are considered to explain temporal variations of DOC in stream water (Tate & Meyer, 1983; Sedell & Dahm, 1990). Highest DOC concentrations usually occurring at high flow are attributed to the largest contribution of DOC-rich topsoil water.

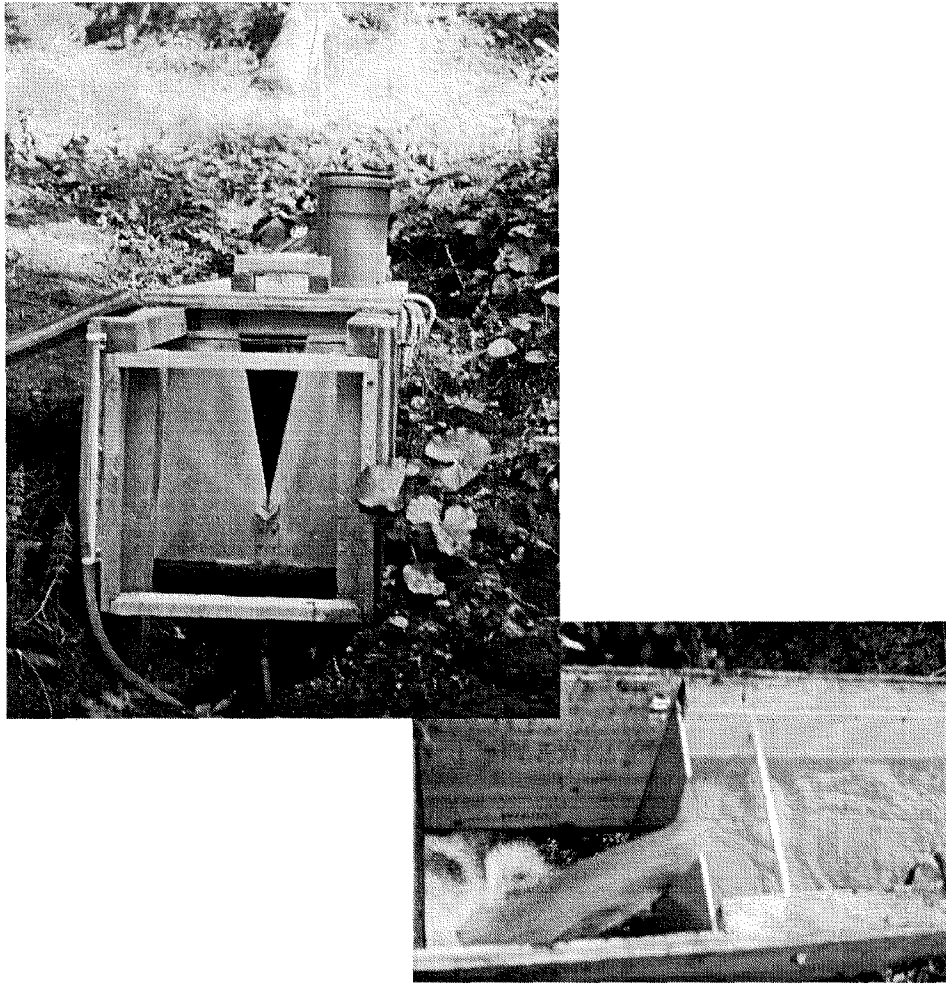
Chapter 4 addresses on the origin and fate of DOC and DON in a Gleysol. Chapter 5 focuses on the regulating mechanisms of the DOC and DON export from sub-catchments of 1500 m² and from a headwater catchment of 0.7 km².

Objectives of chapter 4 and 5:

- (1) to assess the effects of redox conditions on DOC and DON dynamics;
- (2) to estimate the role and regulating factors of DON mobility in the soil and in the catchments; and
- (3) to identify the significance of flow processes for the DOC and DON transport through the Gleysol and for the DOC and DON export from the catchments.

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Chapter 2



Rapid flow processes limit the ability of a forest soil to retain atmospheric N

with

P. Schleppi, J. Mohn, J.B. Bucher, and H. Flüeler

submitted to *Water, Air and Soil Pollution*

2.1 Abstract

The responses of nitrogen transformations and nitrate (NO_3^-) leaching to experimentally increased N deposition were studied in forested sub-catchments (1500 m^2) with Gleysols in Central Switzerland.

Three years of continuous N addition at a rate of $30 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1} \text{ y}^{-1}$ had effects neither on bulk soil N, on microbial biomass N, nor on K_2SO_4 -extractable N concentrations in the soil. In contrast, N losses from the ecosystem through denitrification and NO_3^- leaching increased significantly. Nitrate export from the control sub-catchment was $4 \text{ kg N ha}^{-1} \text{ y}^{-1}$ at an ambient N deposition of $18 \text{ kg N ha}^{-1} \text{ y}^{-1}$. The export from the treated sub-catchment was $8 \text{ kg N ha}^{-1} \text{ y}^{-1}$. Highest NO_3^- leaching occurred during snowmelt. Ammonium was effectively retained within the uppermost centimeters of the soil as shown by the complete absence of NH_4^+ from the soil solution collected with micro suction cups.

Discharge and NO_3^- concentrations of the sub-catchment runoff responded to rainfall within minutes. The water chemistry of the sub-catchment runoff showed that during storms, a large part of the runoff derives directly 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 the soil. As a consequence, the contact time of the water with the soil matrix is insufficient for a complete retention of NO_3^- . Increased NO_3^- leaching due to elevated N inputs is due to the bypassing of the soil and the root system rather than to a soil-internal N surplus.

2.2 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 an open flow system with inputs and outputs as the dominant factors (Berg & Verhoef, 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 NO_3^- leaching is usually regarded as the main symptom of N saturation (Ågren & Bossata, 1988; Aber *et al.*, 1989).

In the last years, there were many studies which experimentally manipulated the N deposition to forest ecosystems (Adams *et al.*, 1997; Aber *et al.*, 1998; Wright & Rasmussen, 1998). They showed an immediate response of 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 the 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; Stagnitti *et al.*, 1995). 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, 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 & 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 & 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 mm² scale with micro suction cups; (ii) in plots of 20 m² by sampling soil solution, measuring N mineralisation, and denitrification; and (iii) in the runoff from experimentally delineated forested sub-catchments of 1500 m².

2.3 Materials and methods

2.3.1 Study site

The study area is located in the Alptal (47°03N, 8°43E) in the Prealps of central Switzerland. Mean air temperature is 6°C and precipitation averages 2300 mm per year. The parent rock material is Flysch, from which heavy clay soils have been formed with a water table close to the surface throughout the year.

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 an anmoor 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 1.

Norway spruce (*Picea abies* (L.)) grow on the better drained mounds and *Vaccinium* *sp.* 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* and *Petasites alba* (*Equiseto-Abietum*)

under a dense tree canopy, and by *Poa trivialis* and *Carex ferruginea* (*Carici remotae-Fraxinetum*) in open patches (Muller, 1997).

Table 2.1: Selected soil properties.

| horizon (depth) | pH (CaCl ₂) | redox potential ^a [mV] | C content [g kg ⁻¹] | N content [g kg ⁻¹] | C/N | texture % clay/silt/sand |
|-------------------|----------------------------|---|---------------------------------------|---------------------------------------|-----|--------------------------------|
| mound | | | | | | |
| LF (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 (0-10 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 |

^a measured with Pt electrodes (n = 20 per depth)

2.3.2 Experimental design of NITREX sub-catchments (1500 m²)

This study was part of the NITREX project (NITRogen saturation EXperiments, Wright & Rasmussen, 1998). Two forested sub-catchments (1500 m²) were hydrologically delineated by 80 cm deep trenches to collect the exported N (Schleppi *et al.*, 1998). The N deposition of one of the sub-catchments was increased by adding 30 kg NH₄NO₃-N ha⁻¹ y⁻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 NH_4NO_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).

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, USA) at a rate of one sample per 0.9 mm.

The water balance, calculated on a yearly basis for the sub-catchments, showed differences between inputs and outputs not exceeding 7% (Schleppi *et al.*, 1999c). The budget of Cl, a conservative tracer negligibly interacting with the soil solids nor taken up by biota, was balanced. This indicates that element budgets of the experimentally delineated catchments may be estimated from precipitation and from the element concentrations of runoff samples.

2.3.3 Nitrogen transformation in soil plots (20 m²)

Nitrogen transformation was studied in detail in 5 plots (20 m²) with and in 5 plots without increased N deposition in a replicated design. Soil solution was sampled using horizontally installed porous glass filter plates (Ø 90 mm, max. pore radius <16 μm) 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.

Denitrification was measured by the acetylene inhibition technique using a static core system (Ø 6.3 cm, 10 cm) (Ryden *et al.*, 1987, details see Mohn, 1999).

2.3.4 Mineralisation monitoring boxes

The mineralisation monitoring boxes (MMB) 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 NO_3^- containing solution from the shallow groundwater to penetrate the MMB.

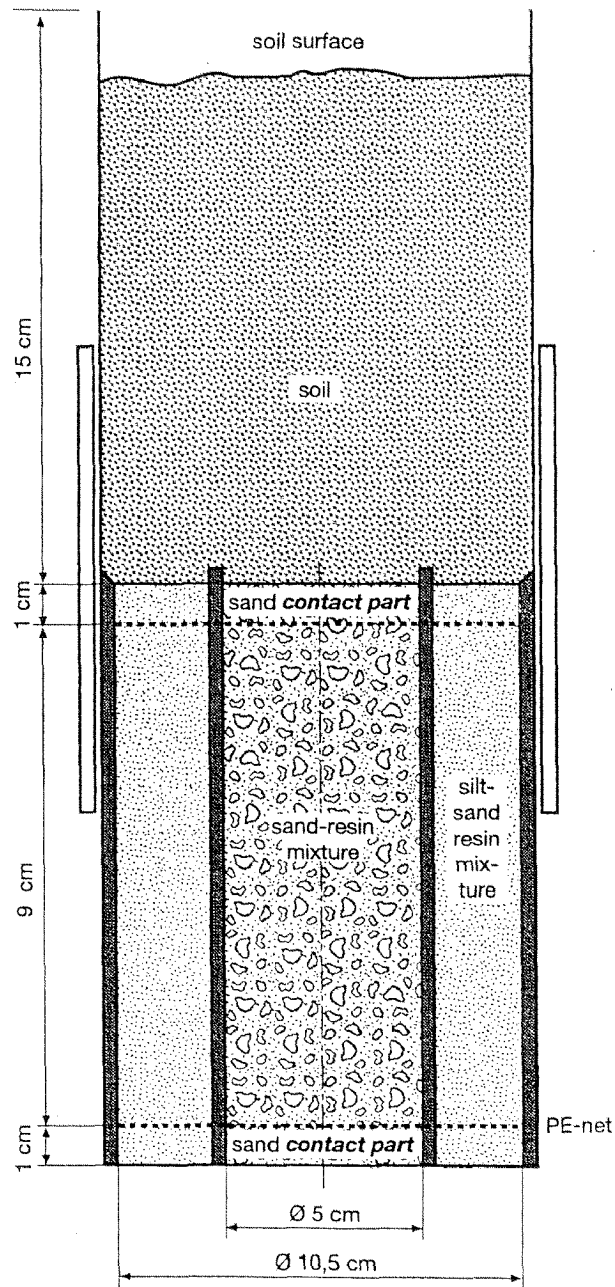


Figure 2.1: Construction of mineralisation monitoring boxes.

The MMB consisted of two parts, a soil core on top of an ionic exchange layer (Fig. 2.1). The soil core was obtained by pushing a PVC tube (length 15 cm, inner \varnothing 10.5 cm) gently into a pre-cut circle in the soil. During each incubation period, three soil cores per plot were sampled. Two cores were taken to the laboratory for immediate extraction for initial inorganic N determinations. The other 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 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, H⁺ form; DOWEX 1X8, Cl⁻ form saturated with OH⁻) was intended to capture any NO₃⁻ and NH₄⁺ percolating through the column. The silt-resin tubes were prepared by mixing 25 ml of each resin with industrial pure SiO₂ silt. For the sand-resin, 20 ml of each resin were mixed with industrial pure SiO₂ sand. Both silt and sand were rinsed with deionised water before use. Mixing the resin with sand and silt modified the hydraulic conductivity according to that 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, 1999). The artificially packed silt-resin mixture had a low hydraulic conductivity ($K_s < 0.2 \text{ cm h}^{-1}$), whereas the sand-resin mixture had a high conductivity ($K_s \approx 80 \text{ cm h}^{-1}$). 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.

In order to distinguish between NO₃⁻ derived from the incubated soil and NO₃⁻ 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.

The MMBs were incubated for four weeks in the field during the snowfree season (May to November 1996). During the winter, MMBs were sampled only once in December and once in April.

As an internal standard, NH_4NO_3 equivalent to 30 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.

2.3.5 Transformation of NH_4^+ and NO_3^- at the mm^2 scale

50 micro suction cups (surface 12 mm^2) 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, NH_4^+ and NO_3^- were added one after the other to investigate the individual transformation of both N forms.

First, a pulse of $2.5 \text{ mmol } (\text{NH}_4)_2\text{SO}_4$ was applied with a backpack sprayer during a simulated rainfall event of 14 mm. Then, after a drainage period of ten days, 5 mmol KNO_3 and 5 mmol KCl were added onto the plot with an automatic sprinkling device (described in detail by Flury *et al.*, 1994). Since this experiment was designed to study the NO_3^- transformation in the topsoil, rapid leaching was avoided by applying NO_3^- at the end of the simulated rainfall of 18 mm. The addition of both NH_4^+ and NO_3^- corresponded approximately to the mean N input of 2 weeks ($= 18 \text{ kg N ha}^{-1}\text{y}^{-1}$). 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 μl 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.

2.3.6 Sample preparation and analyses

Within 36 h after soil sampling, the roots were removed, the soil was homogenised, and shaken for 1 h with 0.5 M K_2SO_4 at a 1:4 soil/solution ratio. All fractions of the exchange resin layer from the MMB were extracted with 0.5 M K_2SO_4 . The upper section of the sand-resin mixture was shaken with 200 ml for 12 h, followed by an 1 h extraction with another 100 ml. The middle and the lower section of the sand-resin column were shaken for 12 h with 100 ml, and finally all silt-resin columns with 200 ml for 12 h. Microbial biomass in the soil was estimated with the chloroform fumigation-extraction procedure according to Brooks *et al.* (1985).

Determination of NO_3^- in the filtrates (filter: Schleicher & Schuell 589/3) was conducted photometrically at 210 nm according to Norman & 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 μm filter (Schleicher & Schuell ME25) within the next 48 h and were stored at 4°C. Subsamples were acidified to 2.5 % HNO_3 by volume for cation analyses. Water samples were analysed for major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Mn_{tot} , Fe_{tot} , Al_{tot}) by induced-coupled plasma atomic emission spectrometry (Perkin Elmer ICPAES OPTIMA 3000), and anions (Cl^- , NO_3^- , SO_4^{2-} , $H_2PO_4^-$) 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 (Solorzano & Sharp, 1980; details see chapter 4). 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 (Cl^- , NO_3^- , SO_4^{2-}) were measured using a pyromellitic acid buffer system adjusted to pH 8 with TEMED (Fluka) (Göttlein & Blasek, 1996). Analyses of cations (Ca^{2+} , Mg^{2+} , K^+ , NH_4^+) were

performed with a metal buffer system (5 mM metal, 5 mM ascorbic acid, 2 mM 18-crown-6). Separation was conducted at 20°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 μM for Cl^- , NO_3^- , and SO_4^{2-} , and 10 μM for NH_4^+ . Due to the minimal available volumes, samples were not filtered prior to analysis.

2.3.7 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, as in the present case, Ca^{2+} in the B horizon, DOC in the topsoil and Cl^- in precipitation. Solute concentrations were normalised relative to their standard deviations. Calculations were performed with the non-negative least square fitting procedure of MATLAB.

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 (Fig. 2.10), which allowed us to consider the precipitation as a short pulse with constant element concentrations.

2.4 Results and discussion

2.4.1 K_2SO_4 -extractable NO_3^- and NH_4^+ concentrations

Increased N deposition caused no increase of K_2SO_4 -extractable N in the soil, neither of NO_3^- nor of NH_4^+ (Fig. 2.2). Nitrate concentrations in the N-treated plots were even lower than those of the control plots, which was probably due to their higher water tables and consequently lower redox potentials. Both, NH_4^+ and NO_3^- showed a seasonal pattern with highest concentrations during the winter and during dry summer periods. The highest NH_4^+ concentrations

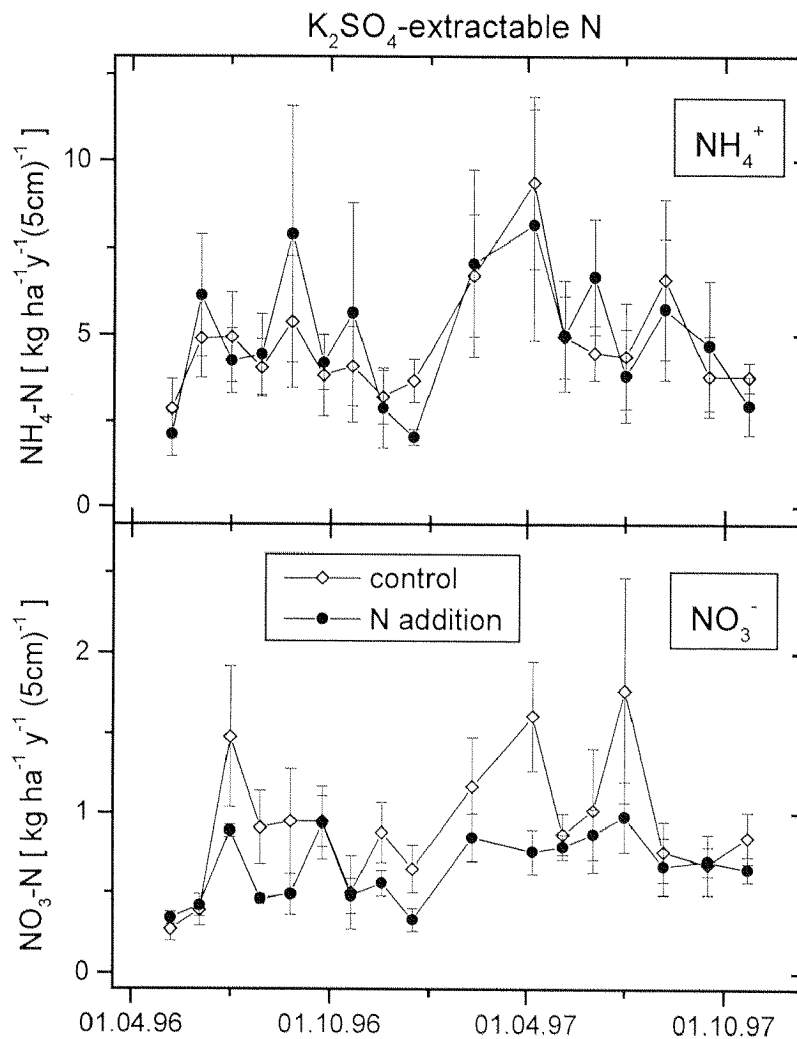


Figure 2.2: K_2SO_4 -extractable NH_4^+ and NO_3^- concentrations. Means and standard errors of 5 plots per treatment.

in the late winter were probably due to a stimulated mineralisation by frost and thaw cycles (DeLuca *et al.*, 1992). The high NO_3^- concentrations in dry and cold periods suggest a reduced biological assimilation, which is in accordance to the lowest denitrification rates and highest redox potentials during these periods (Mohn, 1999).

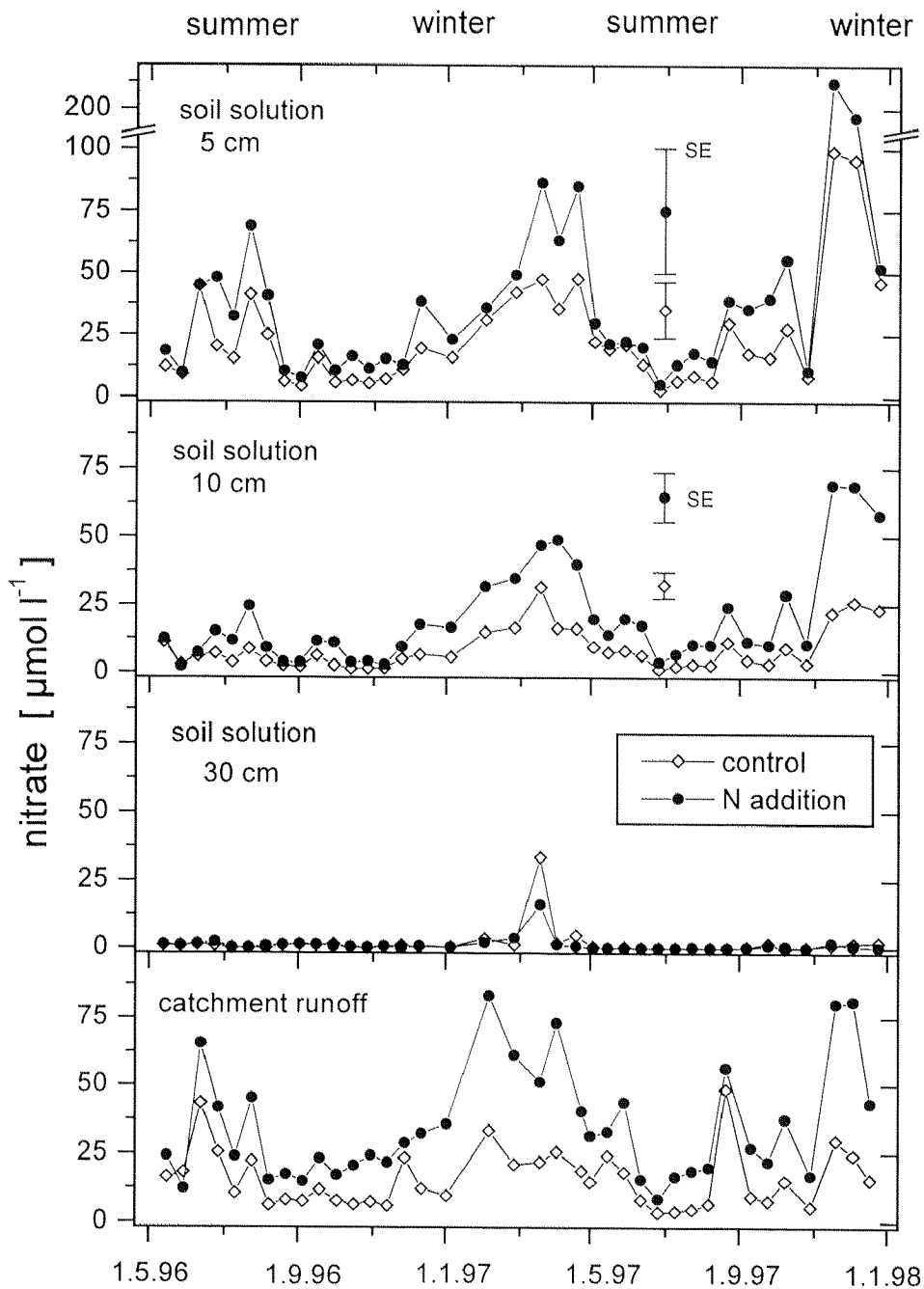


Figure 2.3: Nitrate concentrations in the soil solution and in the sub-catchment runoff. Means of 5 plots per treatment. Error bars indicates the mean standard errors of all sampling dates.

2.4.2 Soil solution

Nitrogen concentrations of the soil solution were low (Fig. 2.3). At 30 cm soil depth, NO_3^- concentrations were already below the detection limit of $0.8 \mu\text{M}$ NO_3^- , except during snowmelt periods. NH_4^+ concentration of the soil solution were even lower than NO_3^- concentrations (data not shown). Below the 5 cm depth, NH_4^+ concentrations were lower than the detection limit of $0.9 \mu\text{M}$ NH_4^+ . In contrast to the K_2SO_4 -extractable NO_3^- , two years of elevated NH_4NO_3 input increased the NO_3^- concentration of the soil solution at 5 and 10 cm depths (Fig. 2.3; $p < 0.03$). Both, the effect of N addition as well as the absolute NO_3^- concentrations were highest during the dormant season and during dry periods. In spring and summer, elevated N deposition did not increase NO_3^- concentrations significantly.

2.4.3 Transformation of NH_4^+ and NO_3^- at a small scale

In order to study the *in situ* transformation of NH_4^+ and NO_3^- in the soil, both N forms were separately applied onto one of the plots in a depression and soil solution was sampled with micro suction cups. The breakthrough of NH_4^+ and NO_3^- demonstrates that the form of N deposition is important for the N fluxes and the N transformation in the soil. The NH_4^+ pulse addition was not reflected in the soil solution at all (Fig. 2.4), not even at the 1 cm depth. In contrast, NO_3^- applied at the end of a rainfall event was rapidly leached beyond the 20 cm depth (data not shown, see Figure 2.5 for 5 cm depth). These findings indicate that NH_4^+ is immediately removed from the percolating rainwater, whereas the mobile NO_3^- anion is rapidly leached. The extremely rapid retention of NH_4^+ suggests that abiotic rather than biotic processes dominate. Abiotically, NH_4^+ is either exchanged as a cation to negatively charged surfaces and/or incorporated into organic matter through chemical reactions (Nomnik, 1970; Schimel & Firestone, 1989; Thorn & Mikita, 1992). Both processes are promoted by topsoil characteristics such as high carbon content (14%) combined with a high pH.

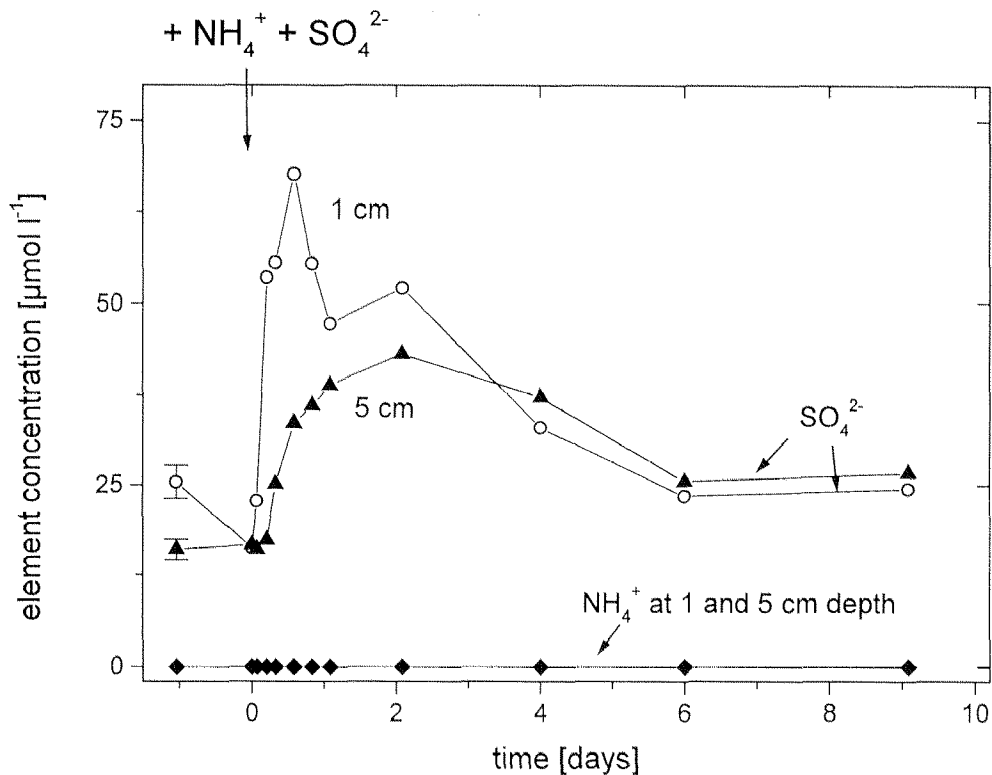


Figure 2.4: Ammonium and SO_4^{2-} concentrations in the soil solution sampled with micro suction cups at 1 and 5 cm depth. Standard errors were estimated from 10 micro suction cups at the beginning of the experiment.

The comparison of NO_3^- with the inert Cl^- concentrations indicates that NO_3^- was assimilated until the third day after the rainfall event. Denitrification measurements (data not shown here, Hagedorn *et al.*, 1999) showed that the reduced NO_3^- to Cl^- ratio was mainly due to denitrification caused by water saturation. The 3-day time span for net NO_3^- immobilisation is probably the maximum rate in this ecosystem since at this time temperatures were the highest in this season (11.5 °C at 20 cm depth). Net nitrification, here indicated by an increase of NO_3^- relative to Cl^- , did not start until a drainage period of 5 days. However, such conditions are not common at this research site as only 2 rainless weeks occurred during the summers 1996 and 1997.

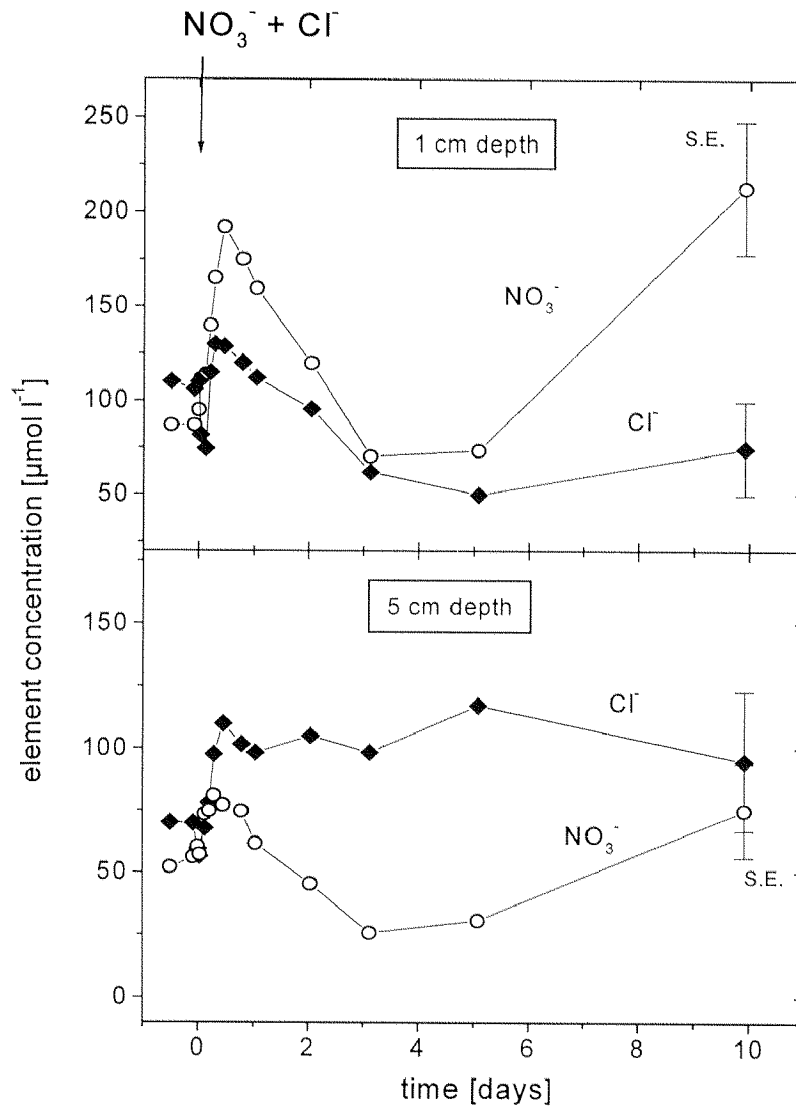


Figure 2.5: Nitrate and Cl^- concentrations in the soil solution sampled with micro suction cups at 1 and 5 cm depth. Standard errors were estimated from 10 micro suction cups per depth at the end of the experiment.

2.4.4 NO_3^- leaching

Figure 2.6 shows the cumulative NO_3^- leaching measured by the MMBs and based on the concentrations of the runoff from the NITREX sub-catchments. Both methods yielded approximately the same NO_3^- export and no NH_4^+ leaching was detected. The addition of $30 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1}\text{y}^{-1}$ caused an increase of NO_3^- leaching by approximately $3.9 \text{ kg N ha}^{-1} \text{ y}^{-1}$ during the second

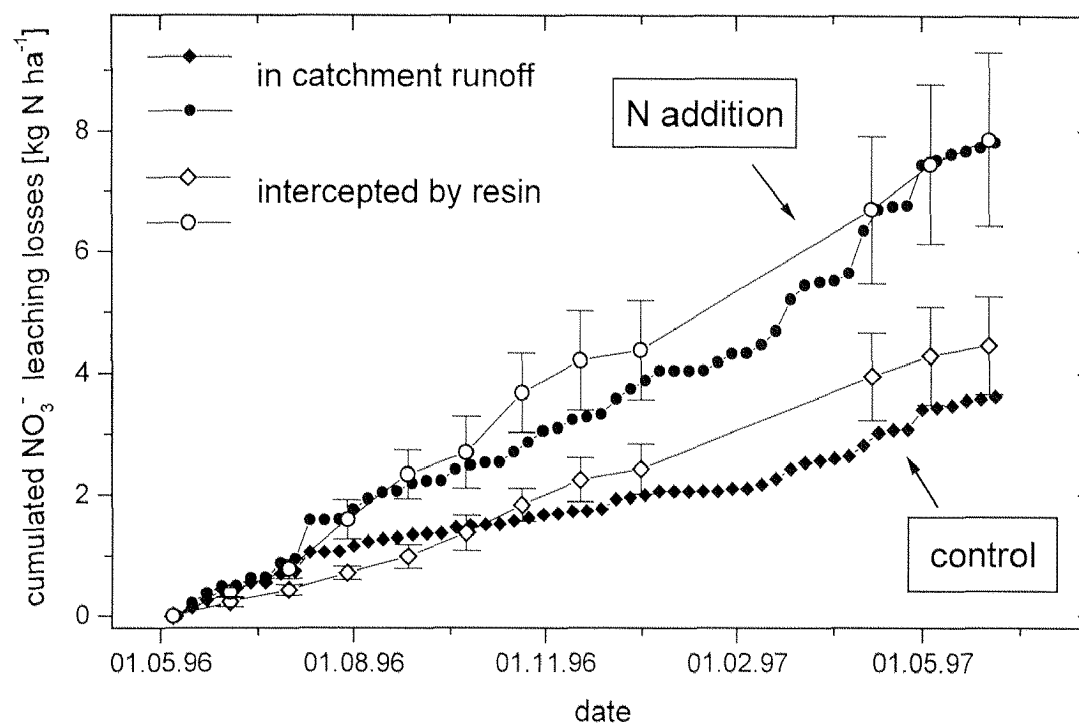


Figure 2.6: Cumulative NO_3^- leaching losses measured by the sub-catchment runoff and by the mineralisation monitoring boxes at 10 cm depth. Means and standard errors of 5 plots per treatment.

year of treatment ($p < 0.05$ for MMBs). Within the MMBs, NO_3^- was only captured by the coarser sand-resin mixture with its higher saturated conductivity.

The topography affected NO_3^- leaching. Nitrogen addition led to more NO_3^- leaching on the mounds than in the depressions as indicated by both the MMBs and the suction plates (Fig. 2.7).

The higher NO_3^- leaching on the mounds suggest a lower NO_3^- assimilation in the aerobic and acidic mor humus than in the anaerobic depressions with neutral pH. This is in accordance with the generally low potential of forest floors to immobilise nitrate (Clinton *et al.*, 1995; Downs *et al.*, 1996; Tietema, 1998). Particularly, mor type organic layers, which develop on Spodosols and Inceptisols with low pH and high C/N ratios, appear to have little capacity to assimilate NO_3^- (Kahl *et al.*, 1993; Downs *et al.*, 1996). Our results show that NO_3^-

concentrations of the mor layer were not significantly correlated to temperature, suggesting that biological assimilation played a minor role.

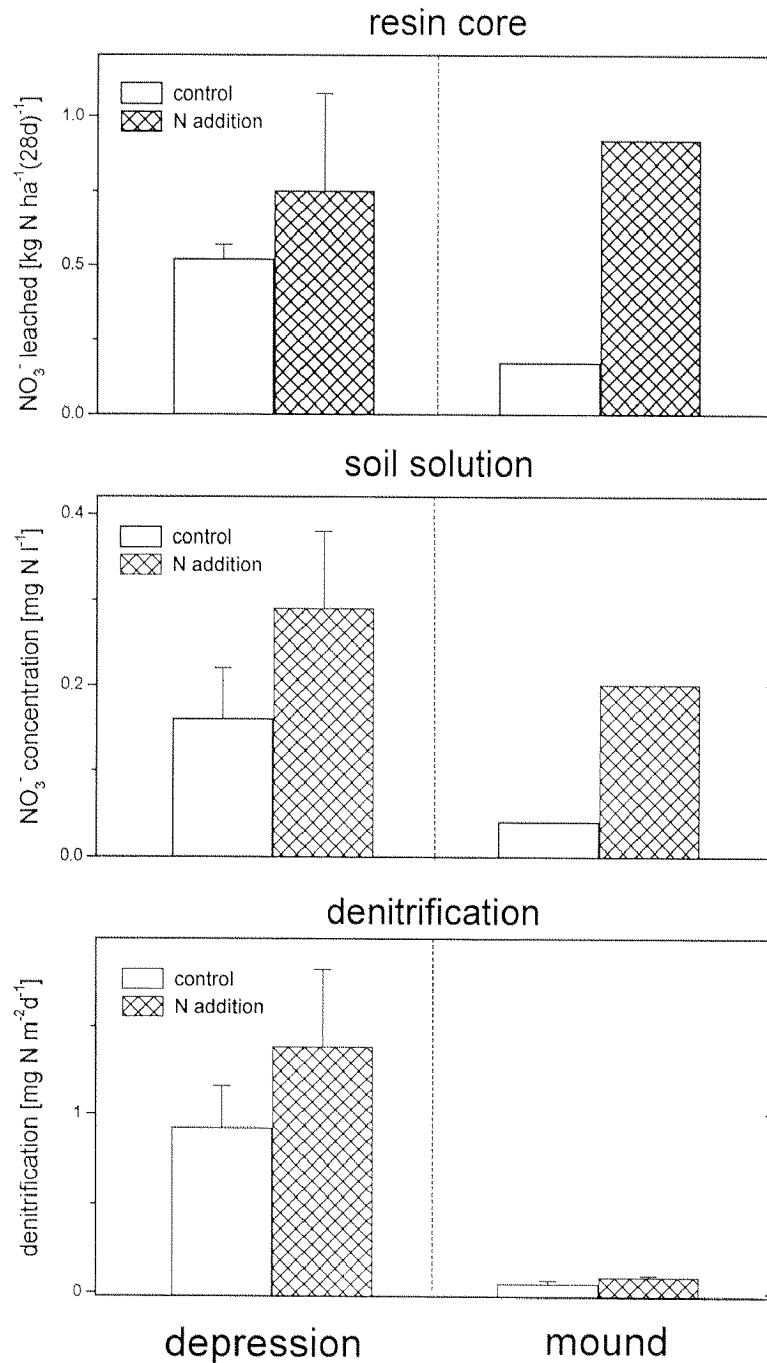


Figure 2.7: Leached NO_3^- from the mound and the depression measured by the mineralisation monitoring box, NO_3^- concentrations sampled by suction plates at 10 cm depth and denitrification rates. Means and standard errors (4 plots per treatment for the depressions and 1 plot per treatment for mounds).

In contrast, the NO_3^- concentrations in the depressions, with temporarily anaerobic conditions, were significantly negatively correlated to temperature ($r = -0.62^{***}$, $n=38$) and positively correlated to the measured redox potentials ($r = +0.57^{***}$, $n=38$). In the depressions, significant losses of N by denitrification were measured (Fig. 2.7), which shows that waterlogged depressions had a higher capacity to assimilate NO_3^- than aerobic mounds. This resulted in a smaller increase in NO_3^- leaching.

2.4.5 Runoff processes

Considering soil solution data only (as done in most studies), it seems that N deposition affect only the topsoil, and that NO_3^- leaching from the rooting zone was not increased by elevated N inputs (Fig. 2.3). The runoff data show, however, that NO_3^- export from the sub-catchments (1500 m^2) was increased. Absolute concentrations and seasonal variations of NO_3^- in the runoff corresponded closely to that of the soil solution at 5 cm depth (Fig. 2.3). This suggests that the runoff is more likely topsoil water 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 (Fig. 2.10), which points to a rapid water movement through the soil system and/or surface runoff. 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 (Fig. 2.8). It rapidly declined within the following 10 hours. 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 h 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.

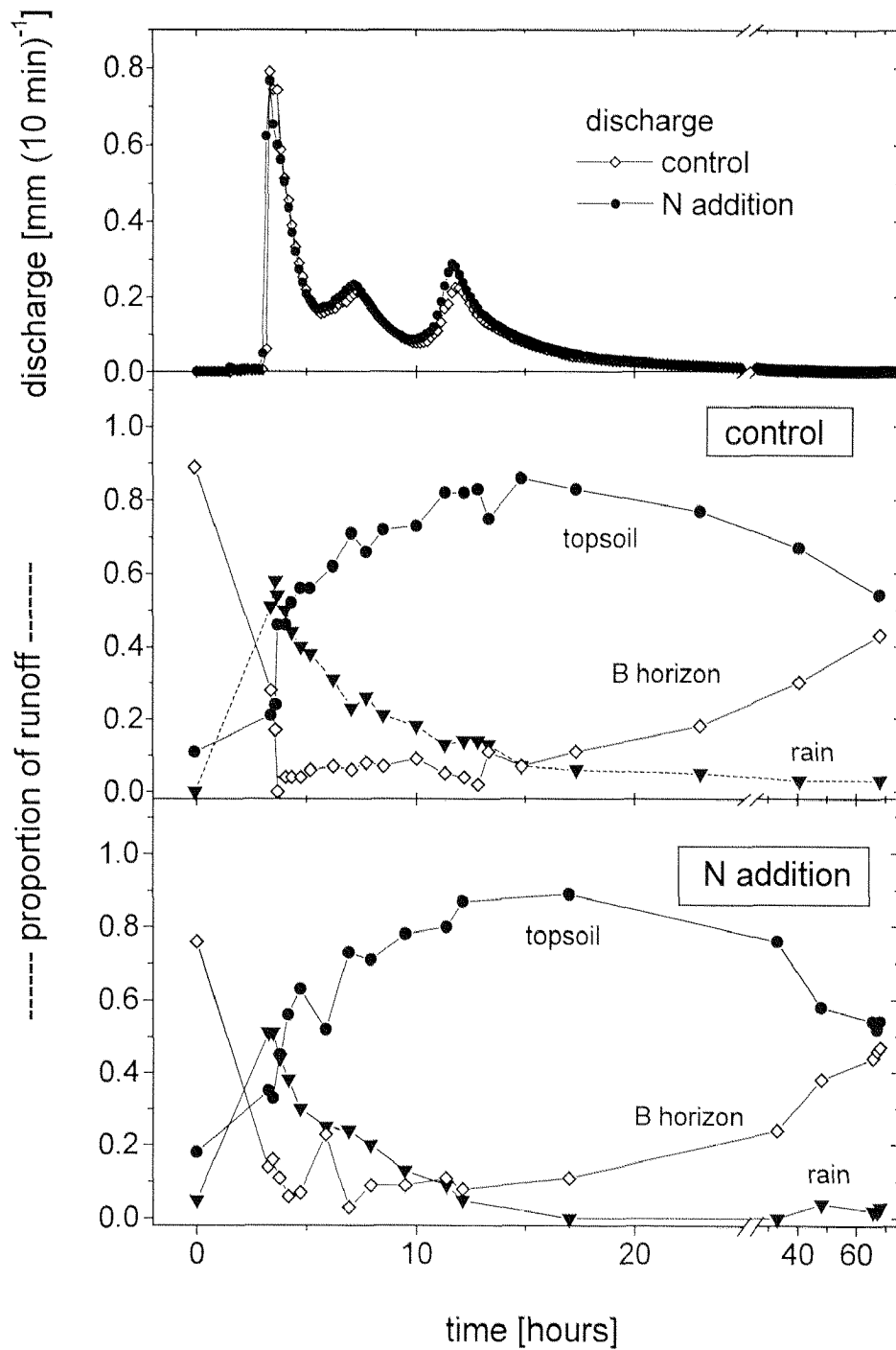


Figure 2.8: Discharge and contribution of end-members (rain, B horizon, topsoil at 5 cm depth) to the runoff from the control and N addition sub-catchment. The EMMA was calculated with Ca^{2+} , Cl^- , and DOC concentrations.

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 EMMA. Finally, the contributions of end-members using Ca^{2+} , DOC, and Cl^- concentrations were used to predict NO_3^- concentrations in the runoff. Predicted and measured NO_3^- concentrations were significantly correlated (Fig. 2.9).

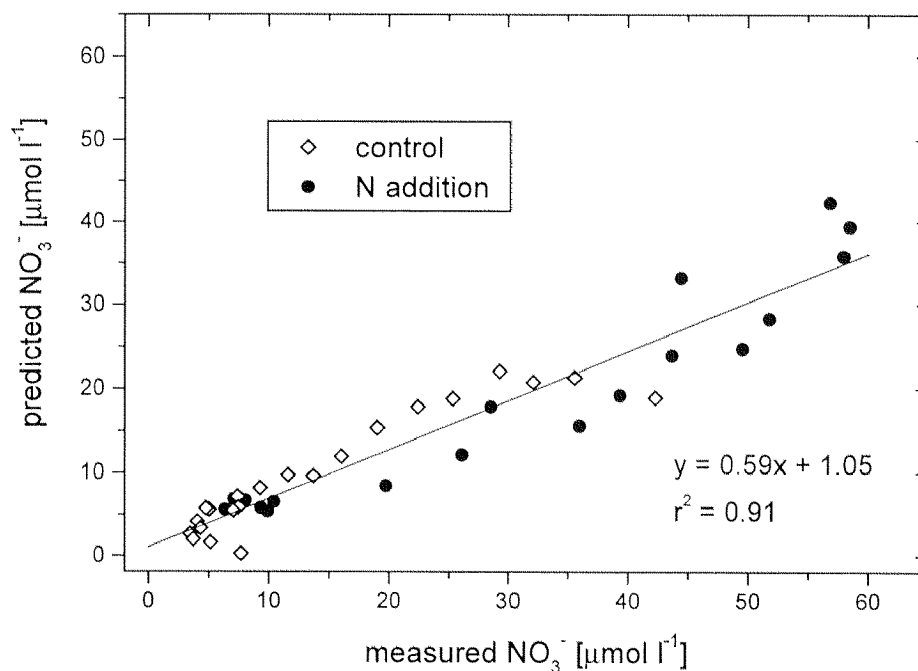


Figure 2.9: Measured and predicted NO_3^- concentrations by the EMMA calculated with Ca^{2+} , Cl^- , and DOC concentrations.

EMMA clearly shows that a large proportion of the runoff had limited contact with the subsoil and originated directly 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, 1999). Since NO_3^- concentrations were highest in the rainwater and decreased with depth in the soil, the highest NO_3^- concentrations occurred at peak flow when precipitation had the largest contribution to the runoff (Fig. 2.10). The

consequence was, that most of the NO_3^- was exported directly after rainfall in all of the four monitored events.

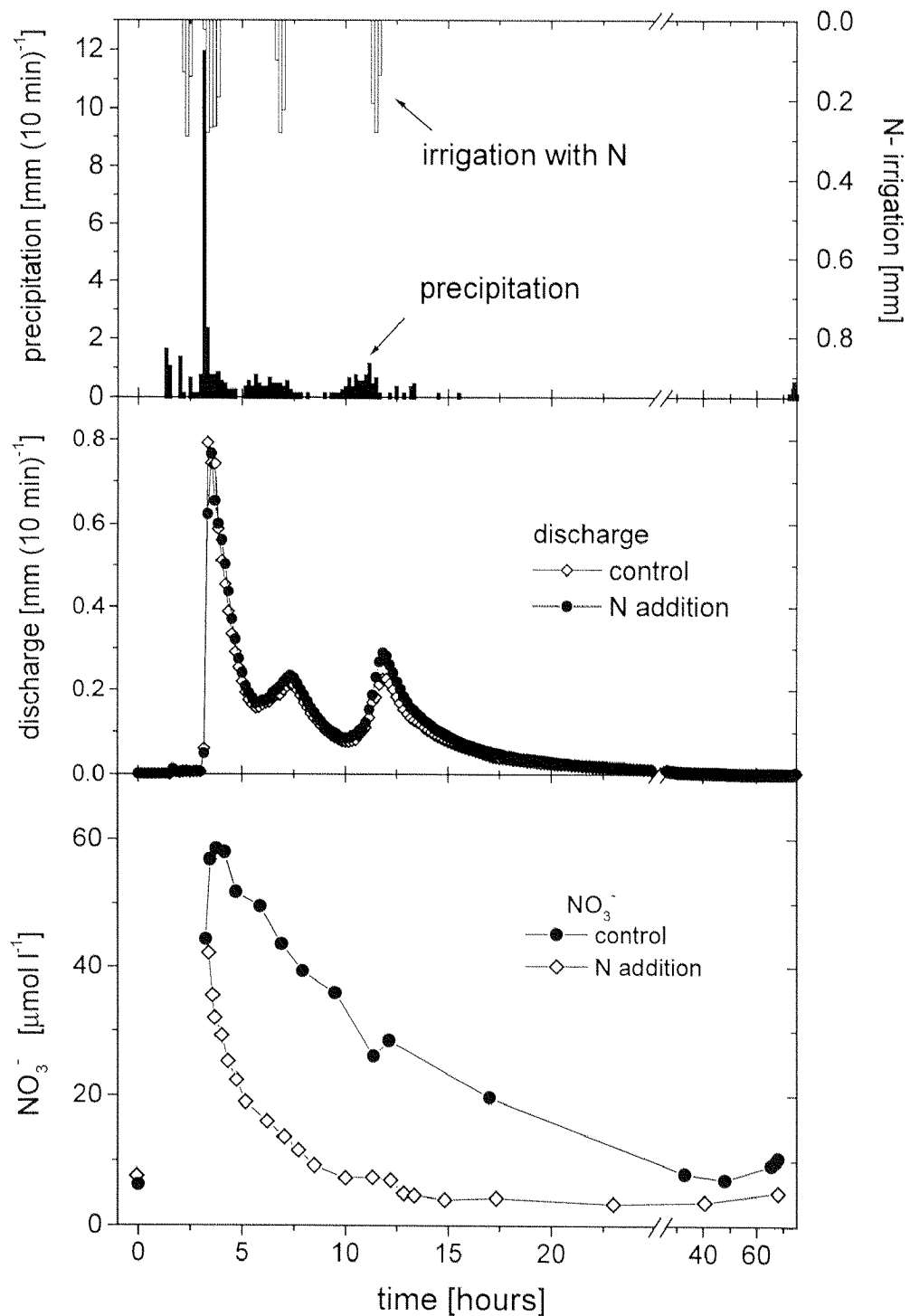


Figure 2.10: Precipitation, N-irrigation, discharge, and NO_3^- concentrations of the sub-catchments runoff. Irrigated water had a $\text{NH}_4\text{NO}_3\text{-N}$ concentration of 17 mg N l^{-1} .

The pronounced impact of hydrological processes on NO_3^- leaching was also observed on a larger temporal scale. The weekly NO_3^- export from the sub-catchment, expressed as percentage of the weekly NO_3^- input, was closely related to the discharge of the sub-catchment (Fig. 2.11). The higher the discharge, the more NO_3^- was exported. However, the relative effect of discharge on the NO_3^- export was lower in summer during wet periods when anaerobic conditions prevail.

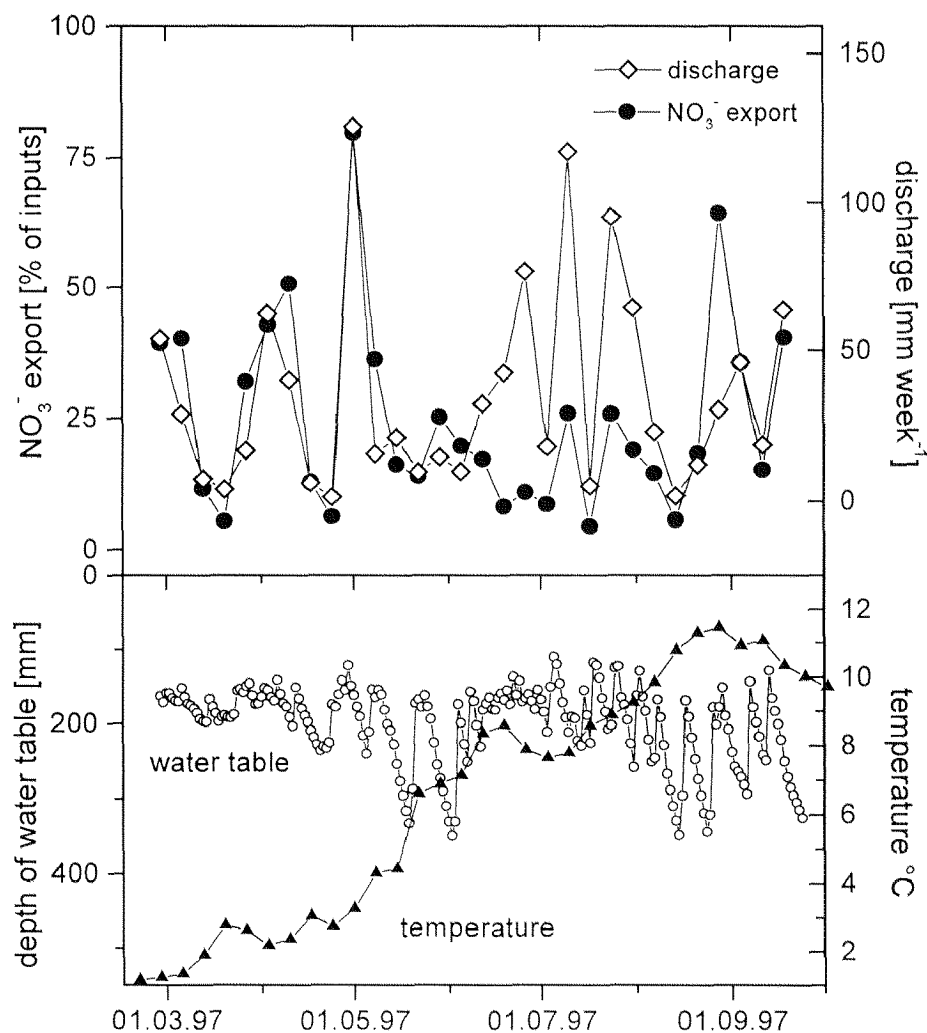


Figure 2.11: Nitrate export (expressed as the percentage of the inputs) from the sub-catchment with N additions during the 3rd year of treatment. Runoff and throughfall samples were bulked weekly. Water table and soil temperature at 20 cm depth were measured within the sub-catchment.

2.4.6 N balance

Quantifying the N fluxes of the forest ecosystem showed that the system retained most of the added N (80%, Table 2.2). This agrees well with the results of a ^{15}N study, which showed that one year after the 12 months of continuous ^{15}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}N . The high N retention in the soil at the Alptal site is consistent with a survey of NO_3^- leaching in response to N deposition in over 65 forest stands in Europe, which showed that approximately 70% of the inorganic N input was retained (Dise & Wright, 1995).

N retention in the soil is generally related to (1) NH_4^+ adsorption to cation exchange sites and fixation by clay minerals, (2) microbial immobilisation (Clinton *et al.*, 1995; Tietema, 1998), (3) abiotic incorporation of inorganic N into organic matter through chemical reactions (Nomnik, 1970; Schimel & Firestone, 1989; Thorn & Mikita, 1992), or (4) mycorrhizal assimilation (Aber *et al.*, 1998).

The negligible effect of N deposition on K_2SO_4 -extractable NH_4^+ (Table 2.2) 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 NH_4^+ in the organic layer, the direct fixation of deposited NH_4^+ by clay minerals is hindered by the minimal travel distance of NH_4^+ , but it is probably responsible for the non-detectable NH_4^+ concentrations in the subsoil. Microbial biomass was also not a dominant sink for the added N (Table 2.2), which is in accordance to the findings of a rapid NH_4^+ and NO_3^- disappearance from soil solutions with no parallel increase in CO_2 efflux as reported by Aber *et al.* (1995). 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 NH_4^+ (Nomnik, 1970; Clinton *et al.*, 1995; Thorn & 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 years. Since the C/N ratio of the Alptal is close to that of N saturated forest stands in the Netherlands and Wales (Gundersen *et al.*, 1998) long-term effects can be expected.

Table 2.2: 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 ⁻¹ y ⁻¹ | kg N ha ⁻¹ y ⁻¹ | kg N ha ⁻¹ y ⁻¹ |
| bulk deposition | | | |
| NO ₃ ⁻ | 6.0 | 19.9 | 13.9 |
| NH ₄ ⁺ | 6.6 | 20.5 | 13.9 |
| DON | 2.5 | 2.5 | 0 |
| dry deposition ¹ | 4.6 | 4.6 | 0 |
| total input | 19.7 | 47.4 | 27.7 |
| soil N pools (0-5 cm) | | | |
| total nitrogen | 1400 ± 180 | 1230 ± 150 | -170 (n.s.) |
| ² exchangeable NH ₄ ⁺ | 4.8 ± 1.5 | 5.1 ± 2.2 | 0.3 (n.s.) |
| ² exchangeable NO ₃ ⁻ | 1.1 ± 0.4 | 0.8 ± 0.1 | -0.3 (n.s.) |
| ³ microbial biomass N | 68.1 ± 15 | 62.4 ± 13 | -5.7 (n.s.) |
| N-output | | | |
| ⁴ denitrification | 2.2 (11%) | 3.8 (8%) | 1.6 (6%) |
| NO ₃ ⁻ - export | 4 (23%) | 8 (17%) | 4 (14%) |
| NH ₄ ⁺ - export | 0 | 0 | 0 |
| DON export* | 5.5 (28%) | 5.5 (11%) | 0 |
| apparent N retention | 8 (40%) | 30 (64%) | 22 (80%) |

¹ according to Fischer-Riedmann (1995)

² average of 16 samplings in 1996-1997

³ measured by chloroform fumigation extraction using a $k_{en} = 0.54$ (Brooks *et al.*, 1985), mean of 6 samplings in 1996-97

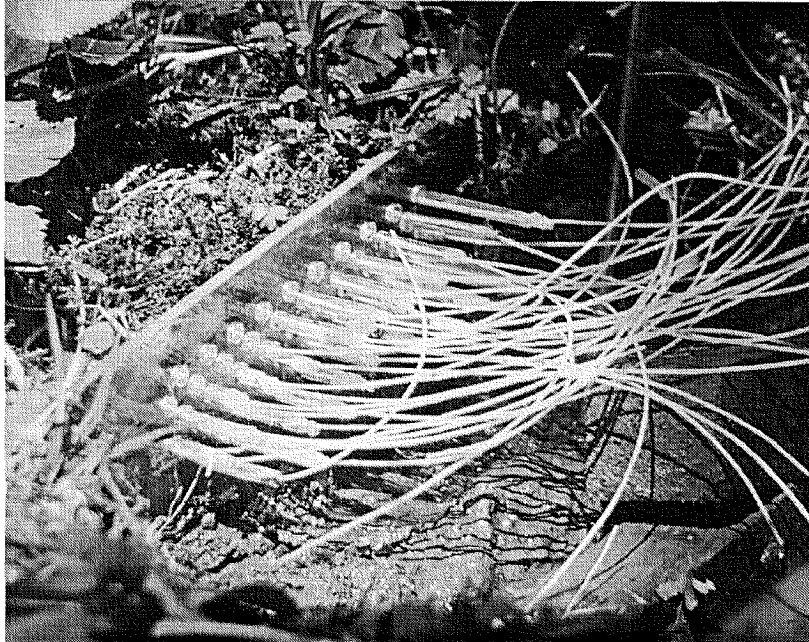
⁴ Mohn (1999), 0-10 cm

n.s.: not significant

2.5 N saturation ?

Nitrate leaching is usually regarded as the main symptom of N saturation (Aber *et al.*, 1989; Gundersen *et al.*, 1998). However, despite a slight N deficiency of the trees and no effects of N additions on vegetation at the research site in the first 3 years (Schleppi *et al.*, 1999b), NO_3^- leaching was increased due to elevated N deposition. This is consistent with findings of other NITREX experiments which have shown that NO_3^- leaching responded within the first year of manipulating N inputs, whereas responses in vegetation and soil were delayed (Gundersen *et al.*, 1998). Our results demonstrate that the rapid changes in NO_3^- leaching were mainly hydrologically driven. The rapid response of discharge and 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 is insufficient for a complete retention of NO_3^- . Enhanced NO_3^- leaching is due to the bypassing of the soil and root system rather than to a soil-internal N surplus. Thus, the increased NO_3^- leaching is hydrological driven and does not reflect a change in nitrogen saturation of the forest ecosystem. However, the N balance shows that most of the deposited N was retained in the soil. Therefore, long term effects can be expected due to a continuous accumulation of N in the soil.

Chapter 3



**The role of rapid flow paths for nitrogen
transformation in a forest soil –
a field study with micro suction cups**

with

J. Mohn, P. Schleppi, and H. Flüher

Soil Science Society of America Journal (in press)

3.1 Abstract

Preferential flow is a common phenomenon in soils. This study was conducted to investigate the significance of rapid flow paths for nitrogen transformation in a forested Humaquept in Central Switzerland. Fifty micro suction cups, each with a surface area of 12 mm², were installed in a regular grid in the uppermost 5 cm. First, the location of each 'micro-cup' relative to main flow paths was estimated based on the response to a dye, a SO₄²⁻, and a Cl⁻ application. Then, a N addition experiment was carried out to study the N transformation at locations along flow paths and within the soil matrix. Only 23 out of 50 'micro-cups' responded to the application of the dye within the first 24 h which indicates that a large portion of the soil volume does not get in direct contact with the infiltrating rainwater. Those 'micro-cups' which responded to the added dye were regarded to be located along 'flow paths'. At depths below 2 cm, under temporarily reducing conditions, sampling locations in or near flow paths had higher NO₃⁻ concentrations (20-25 μM) than those of the soil matrix (below 12 μM). Within 24 h after a simulated rainfall the NO₃⁻/Cl⁻ ratio decreased more in the flow paths (between -2.4 and -4.9 mol/mol) than in the soil matrix (-0.7 to -0.8 mol/mol), which indicates an enhanced denitrification at these locations. In the subsequent dry period, nitrification started 2 days earlier and was more pronounced along flow paths. The results of this case study suggest that flow paths are microhabitats with an increased N transformation compared to the soil matrix.

3.2 Introduction

Forests in large areas of Europe and North America are subjected to elevated nitrogen deposition which may impair the functioning of these ecosystems. Increased N inputs may cause 'N saturation' when the retention capacity of the system is exceeded (Aber *et al.*, 1989). Nitrogen saturation is associated with increased leaching of nitrate from the soil compartment (Aber *et al.*, 1989; Gundersen *et al.*, 1998). Generally, nitrogen saturation and thus NO₃⁻ leaching from forests is thought to occur when inorganic N is in excess of total plant and microbial demand. However, the ability of forest soils to retain increased N deposition additionally depends on the flow regime in the soil compartment. Field studies have shown that solutes bypass a large portion of the soil matrix (Flury *et al.*, 1994; Stagnitti *et al.*, 1995; Stamm *et al.*, 1998). Travel times of solutes may be shorter than a priori expected (Stamm *et al.*, 1998). Only a small part of the soil may come in contact with the infiltrating rainwater.

Analogous to the heterogeneous nature of solute movement in the soil, soil biologists point out that microbial activity is heterogeneously distributed in the soil. This is attributed to the patchy distribution of organic matter (Parkin, 1987), to soil aggregation (Tiedje *et al.*, 1984; Cambardella & Elliot, 1993; Chotte *et al.*, 1998), and to the distribution of pore sizes (Juma, 1993), which lead to manifold microhabitats for soil biota. In this field study, we investigated how preferential flow paths are linked to locations of preferred N transformation in the soil. Habitats near or in flow paths are likely to provide a better supply of N and since flow paths are more permeable, they drain more rapidly and are better aerated than the rest of the soil matrix.

Studies focusing on microscale variability of microbial processes are either visual (Morgan *et al.*, 1991, Stamatiadis *et al.*, 1990) or destructive by incubation of spatially separated soil material (e.g. Cambardella & Elliot, 1993; Nishio, 1994; Abbasi & Adams, 1998). Another approach is the *in situ* measurement of oxygen concentrations (Bakker & Bronswijk, 1993) and redox potentials (Cogger *et al.*, 1992; Flessa & Beese, 1995) using microelectrodes. However, these two

methods only provide information about the physico-chemical conditions of microhabitats, but not on the transformation of nutrients. Micro suction cups combined with a recently developed analytical technique, capillary electrophoresis, enables collecting and analysis of small samples of soil solution (Göttlein *et al.*, 1996; Göttlein & Matzner, 1997). In contrast to destructive spatial separation of soil, micro suction cups allow the temporal dynamic of the *in situ* nutrient transformation to be estimated at a small scale. Using a dye, Cl^- and SO_4^{2-} as tracers, we located the micro suction cups relative to flow paths.

The objectives of this study were:

- (i) to identify the spatial distribution of NO_3^- concentrations and their relation to the main flow paths in the uppermost 5 cm of a Humaquept;
- (ii) to investigate the N transformations within the reach of flow paths and the soil matrix;
- (iii) to explore the significance of microscale variability for the effects of increased N deposition on NO_3^- leaching at a plot scale.

3.3 Materials and methods

3.3.1 Study site

The study area is located in the Alptal (47°03N, 8°43E) in the Prealps of central Switzerland. Mean annual air temperature is 6°C and precipitation averages 2300 mm per year. The parent rock material is Flysch, from which heavy clay soils, mainly Humaquepts, have formed with a water Table close to the surface throughout the year.

Vegetation and soil types form a mosaic pattern, which is closely related to the micro-topography. Norway spruce (*Picea abies* (L.)) grow on the mounds where the water table is below 40 cm depth. Soils on the mounds have an oxidised Bw horizon and a forest floor. In the depressions, the water table frequently reaches the surface, leading to a muck topsoil with a high carbonate content. The mineral soil is a permanently reduced Bg horizon (Table 3.1). The

experiment with the micro suction cups was conducted in a depression with a dense ground floor vegetation (mainly *Caltha palustris*, *Petasites alba*, and *Poa trivialis*). Selected soil properties are given in Table 3.1.

Table 3.1: Selected soil properties.

| horizon (depth) | bulk density ^a [kg dm ⁻³] | texture ^b % clay/silt/sand | C content [g kg ⁻¹] | redox potential [mV] | pH ^c |
|-----------------|---|--|------------------------------------|---------------------------|-----------------|
| LF (0-2 cm) | | | 430 | 550 | |
| A (2-5 cm) | 0.27 | 51/45/4 | 148 | 40 ± 221 | 7.4 |
| AB (5-10 cm) | 0.33 | 44/44/11 | 127 | 260 ± 226 | 7.4 |
| Bg (10-50 cm) | 0.72 | 43/42/15 | 16 | 45 ± 88 | 7.5 |

^a measured with undisturbed soil cores (n=4).

^b data from Schleppe *et al.* (1998).

^c measured in the soil solution.

3.3.2 Nitrogen addition experiments at the plot scale

This study on microscale N transformations was part of the NITREX project (NITrogen saturation EXperiments, Wright & Rasmussen, 1998). Two forested sub-catchments (1500 m²) were hydrologically delineated by 80 cm deep trenches to collect the N exported from the forest (Schleppe *et al.*, 1998). Rainwater was collected with a plastic sheet (300 m²) next to the forest stand and applied by sprinklers in addition and simultaneously to the precipitation onto the two sub-catchments. The N deposition of one of the sub-catchments was increased by adding 30 kg NH₄NO₃-N ha⁻¹ y⁻¹ to the sprinkled rainwater. The ambient N input was 12 and 17 kg N ha⁻¹ year⁻¹ in bulk and throughfall deposition, respectively.

The water discharge from the sub-catchments was measured with V-notch weirs. Runoff proportional samples, bulk deposition and throughfall were collected weekly (Schleppe *et al.*, 1998).

Additionally, soil solution was sampled on 5 plots (20 m²) of each with and without increased N deposition. Nitrogen was sprinkled simultaneously to the NITREX sub-catchments. Horizontally installed porous glass filter plates (diameter (Ø) 90 mm, max. pore diameter <16 µm) were used to sample at 5, 10 and 20 cm depths, and suction cups at 30, 50 and 100 cm depths. Samples were collected weekly and bulked fortnightly.

Soil cores (Ø 5.5 cm, 10 cm) were taken monthly for measuring extractable N. Roots were removed, the soil homogenised, and shaken for 1 h with 0.5 M K₂SO₄ at a 1:4 soil/solution ratio. Analysis of NO₃⁻ in the filtrates (filter: Schleicher & Schuell 589/3) was conducted photometrically at 210 nm according to Norman & Stucki (1981) with a Shimadzu UV-160 spectrophotometer.

Denitrification was measured by the acetylene inhibition technique using a static core system (Ø 6.3 cm, 10 cm) (Ryden *et al.*, 1987). Polypropylene tubes were inserted into the topsoil several weeks before sampling to allow equilibration of the disturbed soil system. The tubes were transferred into jars fitted with neoprene septa, and incubated at soil temperature in an atmosphere of 10 kPa acetylene. Gas samples were taken after 2, 3.5, and 5 h. N₂O concentrations were measured with a Perkin-Elmer gas chromatograph (model 8500) with an ECD-detector. The seasonal denitrification pattern was monitored from May 1996 to October 1997. The measurements were executed every 2 weeks on all of the 10 plots.

Redox potential measurements were performed with platinum electrodes (Pfisterer & Gribbohm, 1989; Cogger *et al.*, 1992) inserted into the soil and an Ag/AgCl reference electrode placed into a piezometer within a distance of 50 cm to the redox electrodes. The Eh readings were carried out with a portable pH/mV meter (WTW pH 320). Redox electrodes were installed at 1, 2, 3, 4, 5, 10 and 20 cm depths (3 per depth), 3 weeks before the N addition experiment. All electrodes were tested with a redox buffer (K₄[Fe(CN)₆]/K₃[Fe(CN)₆]) before and after the experiment.

3.3.3 Construction and installation of micro suction cups

The micro suction cups, referred to as micro-cups, were constructed by inserting and gluing a small ceramic plate (Ø 4 mm, 1.5 mm thickness) into a pipette tip (20-200 μl) (Fig. 3.1). The small ceramic plate was obtained with a corer from a large ceramic plate. The micro-cups were connected to 1/16" teflon tubing (inner Ø 0.3 mm) and then glued on plexiglass pipes (inner Ø 5 mm; outer Ø 6.5 mm). The dead volume of the micro-cups and the teflon tubes was approximately 40 μl . All micro-cups were individually tested for leaks. In the field, micro-cups were able to maintain a suction of 40 kPa for 2 weeks. Prior to installation, all suction cups were first flushed with 1N HCl and subsequently rinsed with distilled water.

To install the micro-cups in the field, a rectangular plexiglass plate with diagonally arranged holes was attached vertically at the profile face of a shallow soil pit (Fig. 3.1). A steel pipe (outer Ø 6 mm, inner Ø 5 mm) was drilled horizontally through these holes into the soil to slightly less than the desired depth. Then the micro-cups were inserted and gently pushed 5 mm past the bottom of the hole.

Fifty micro-cups were arranged in a systematic 5 by 20 cm grid to minimise the interaction between adjacent cups (Fig. 3.1). The vertical distance between the micro-cups was 1 cm, the lateral distance was 2 cm. The uppermost row of micro-cups at 1 cm depth ($n=10$) was installed at a horizontal distance of 10 cm from the plexiglass plate. The following deeper rows of suction cups were installed 2 cm further into the soil.

Soil water samples were taken by connecting the micro-cups to an evacuation device, which allowed individual sampling from each micro-cup. The bottom of the evacuation device was filled with distilled water to produce water-vapour saturated conditions, thereby reducing evaporation losses from the samples. Sampling started in July 1997, 6 weeks after the installation. In the period from installation to the first sampling, the micro-cups were flushed and allowed to equilibrate with the surrounding soil.

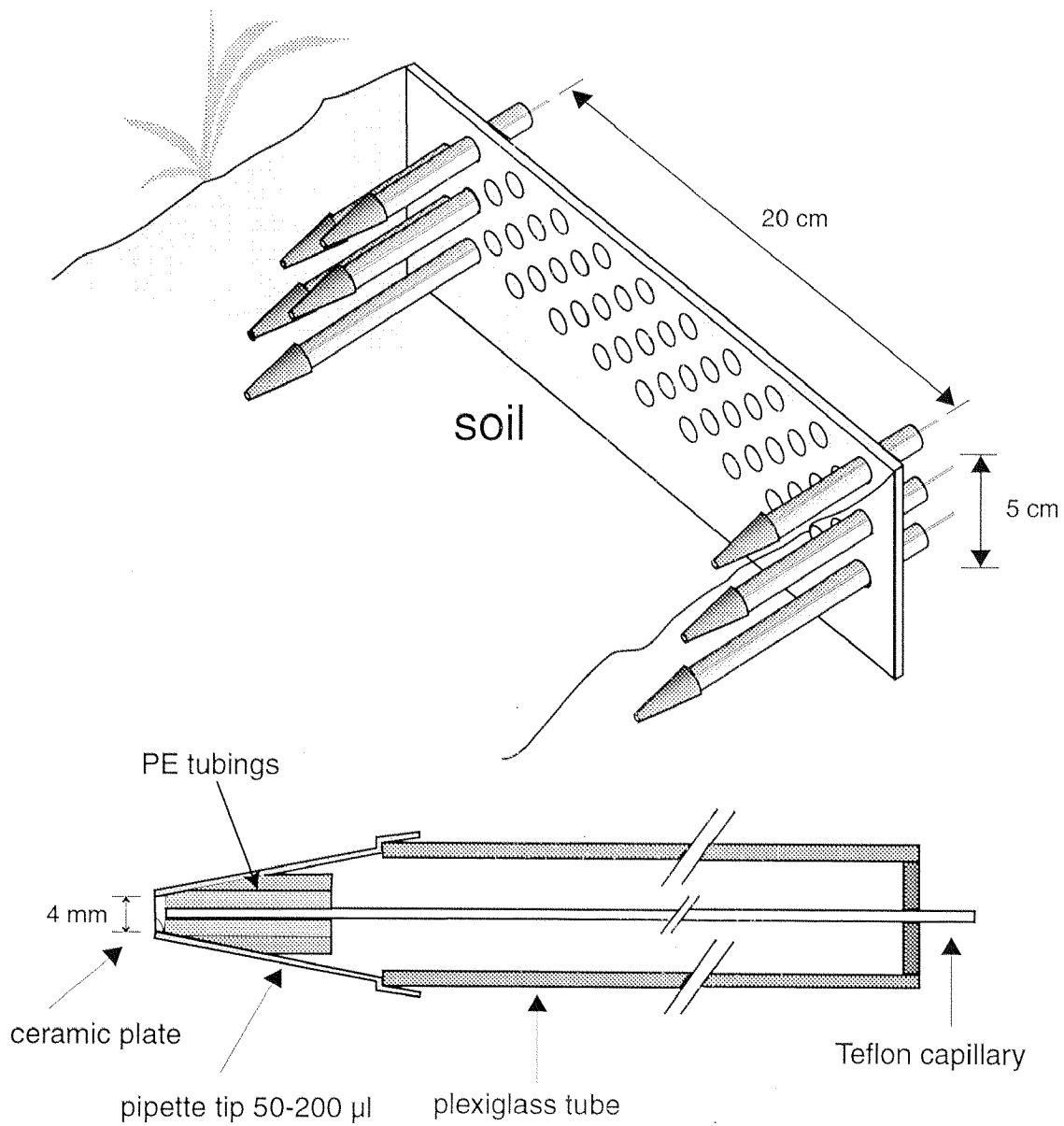


Figure 3.1: Micro suction cups: Construction and instrumental array in the field.

To estimate the microscale spatial variability, soil solution was collected for 3 consecutive weeks by applying a permanent suction of 30 kPa. The typical sample volume collected ranged from 200 μ l to 10 ml and averaged 3.7 ml of soil water. Samples were frozen and stored until analysis.

In order to evaluate the relevance of soil water sampled by micro-cups for larger scale additional suction plates were installed at 5, 10, and 20 cm depths (2 per depth) within 50 cm distance to the micro-cups.

3.3.4 Identification of the location of micro-cups with Brilliant Blue

To identify the location of each micro-cup relative to the flow paths, we observed the response to infiltrating water, spiked with a Brilliant Blue FCF solution (1 g BB l^{-1}), homogeneously sprinkled with a backpack sprayer onto an area of 50 \times 50 cm above the micro-cups. The arrival time of the Brilliant Blue FCF solution at each cup was visually observed, and the solution was collected for one day. Micro-cups with arrival times of $t < 24$ h were considered to be within reach of rapid flow paths (fast response) and those with $t > 24$ h to tap the soil matrix (slow response).

The homogeneity of tracer applications were tested with containers of 100 cm^2 placed on the ground. Five containers were used during the Brilliant Blue addition and 10 during the simulated rainfalls. The coefficient of variation were always below 10%.

3.3.5 Microscale N transformation experiment

In order to investigate the *in situ* nitrification and denitrification at a microscale, N addition experiments were carried out during August 1997.

a. NH_4^+ addition

A solution with a high NH_4^+ concentration corresponding to the mean NH_4^+ input of 2 weeks (= 18 kg NH_4^+ -N $ha^{-1}y^{-1}$) was added with a backpack sprayer onto a surface of 2 m^2 around the micro-cups. First, the plot was irrigated with 8 mm of deionised water for 4 h. Then, 2.5 mmol $(NH_4)_2SO_4 m^{-2}$ dissolved in 2 mm

water was applied within 10 minutes. During the next 2 h, an additional 4 mm of deionised water was added.

b. NO₃⁻ addition

During the second experiment, we applied Cl⁻ as a conservative tracer and NO₃⁻ with a automated sprinkling device (described by Flury *et al.*, 1994) onto a surface of 3.5 m² around the micro-cups. Since the experiment was designed to investigate the NO₃⁻ transformation in the topsoil, rapid leaching was avoided by applying NO₃⁻ at the end of the simulated rainfall. First, 15 mm of deionised water were applied within 5 h. Then, 5 mmol KNO₃ m⁻² and 5 mmol KCl m⁻² dissolved in 1.4 mm 'rainwater' were sprinkled within 10 minutes onto the plot. The NO₃⁻ addition corresponded to the mean input of 2 weeks (= 18 kg NO₃-N ha⁻¹y⁻¹). Directly after the tracer application, 2 mm of deionised water was sprinkled onto the plot to flush the sprinkling device. After these additions, the field plot was covered with a plastic sheet to prevent precipitation and additional N inputs.

A suction of 30 kPa was applied to the micro-cups and 5 kPa to the suction plates at 5, 10 and 20 cm depths during both the NH₄⁺ and the NO₃⁻ addition. The solutions of the micro-cups from each depth were grouped into flow paths and soil matrix based on the response of the micro-cups to the previous Brilliant Blue addition. To obtain sufficient volumes for the analysis the solutions were bulked (50 µl per cup) per group and depth except the first and the last sampling date where the micro cups yielded sufficient water for separate analysis. All samples were immediately frozen and stored until analysis.

Denitrification activity was measured with 3 pairs of cores during the NH₄⁺ addition and 4 pairs of cores during the NO₃⁻ addition. The cores were inserted 3 weeks before the experiment within a distance of 1.5 m to the micro-cups.

3.3.6 Laboratory analysis

Micro-cup soil solutions were analysed by capillary electrophoresis (BioFocus 3000, BioRad), which requires 5 to 10 nl per analytical run (Göttlein & Blasek, 1996). Major anions (Cl⁻, NO₃⁻, SO₄²⁻) were measured using a pyromellitic

acid buffer system (buffer: 3 mM pyromellitic acid adjusted to pH 8 with TEMED (Fluka)). Analysis of cations (Ca^{2+} , Mg^{2+} , K^+ , NH_4^+) was performed with a metal buffer system (5 mM metal, 5 mM ascorbic acid, 2 mM 18-crown-6) (Göttlein & Blasek, 1996). Separation was conducted at 20°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 μM in the case of Cl^- , NO_3^- , and SO_4^{2-} , and 10 μM for NH_4^+ . Due to the minimal available volume, samples were not filtered prior to analysis.

Brilliant Blue FCF concentration was measured photometrically at a wavelength of 630 nm with a Shimadzu UV-160 spectrophotometer.

Soil solution sampled by suction plates and suction cups were filtered (0.45 μm , Schleicher & Schuell ME25). Anions (Cl^- , NO_3^- , SO_4^{2-}) in the filtrates were measured by ion chromatography (DIONEX DX-120).

Soil carbon contents were measured with a Carlo Erba carbon/nitrogen analyser.

3.4 Results and discussion

3.4.1 Spatial distribution of NO_3^- concentrations and redox potentials

The depth and the frequency distribution of NO_3^- in the soil solution sampled by the micro-cups and bulked during 3 consecutive weeks are shown in Figure 3.2. As expected NO_3^- concentrations decreased with soil depth. The main drop of NO_3^- concentrations was found below 3 cm depth, where redox potential measurements indicated NO_3^- -reducing conditions (Fig. 3.3).

Nitrate concentrations showed an unimodal distribution at 1 and 2 cm depths and a bimodal distribution at 3 and 4 cm depths. The separation in apparently two states occurred exactly at the boundary between the organic layer and the mineral soil. This suggests that soil structure in the mineral soil leads to the coexistence of 'active' and 'inactive' locations with respect to NO_3^-

formation. The skewed distribution at 5 cm depth is typical for the dominance of NO_3^- reducing conditions with a few aerobic microsites (Flühler *et al.*, 1976). As indicated by one-dimensional variogram analysis (data not shown), NO_3^- concentrations at each depth were spatially independent.

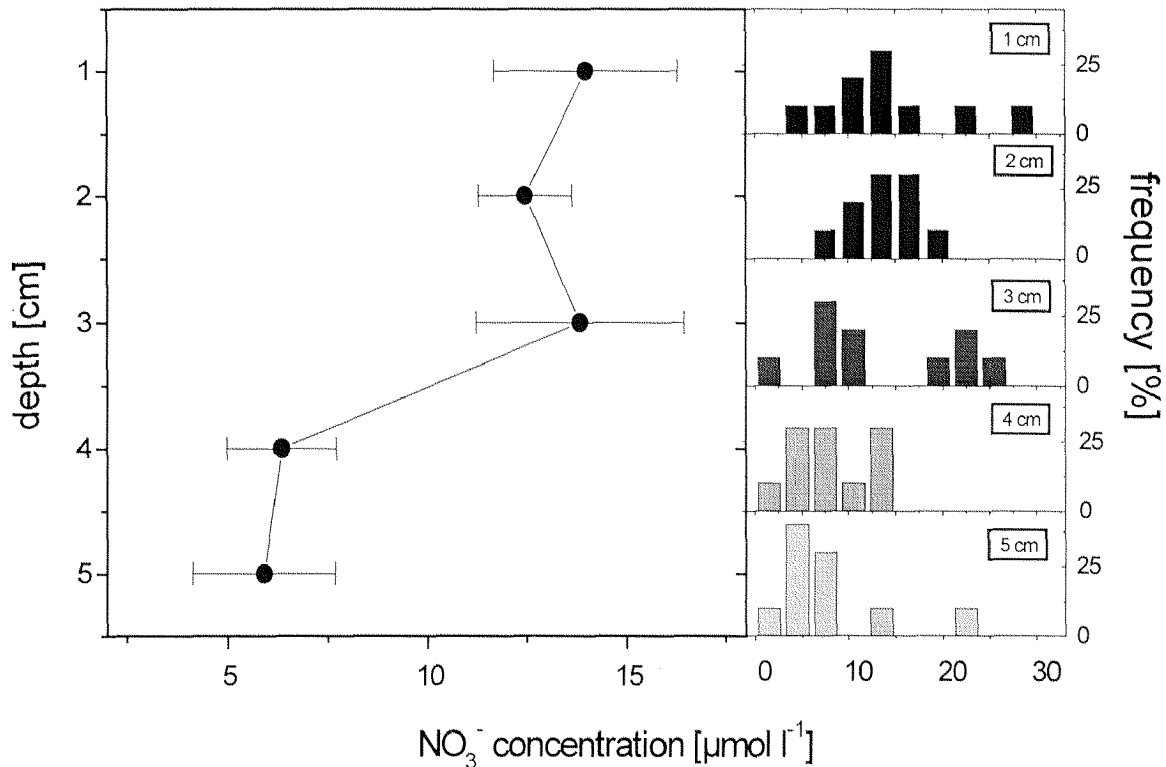


Figure 3.2: Distribution of mean NO_3^- concentrations and relative frequencies at individual depths. Means and standard errors of 3 sampling dates ($n=10$ per depth).

As observed for NO_3^- concentrations, the measured redox potentials in the mineral soil below 2 cm depth varied over a broad range, indicating the coexistence of anaerobic and aerobic microsites (Fig. 3.3). The temporal dynamic of individual electrodes shows the simultaneous occurrence of 'active' and 'inactive' microsites. At inactive locations (16 out of 21 electrodes), the redox potentials remained, whereas the redox potential at 'active' locations (5 out of 21) exhibited a pronounced temporal dynamic after rainfall events.

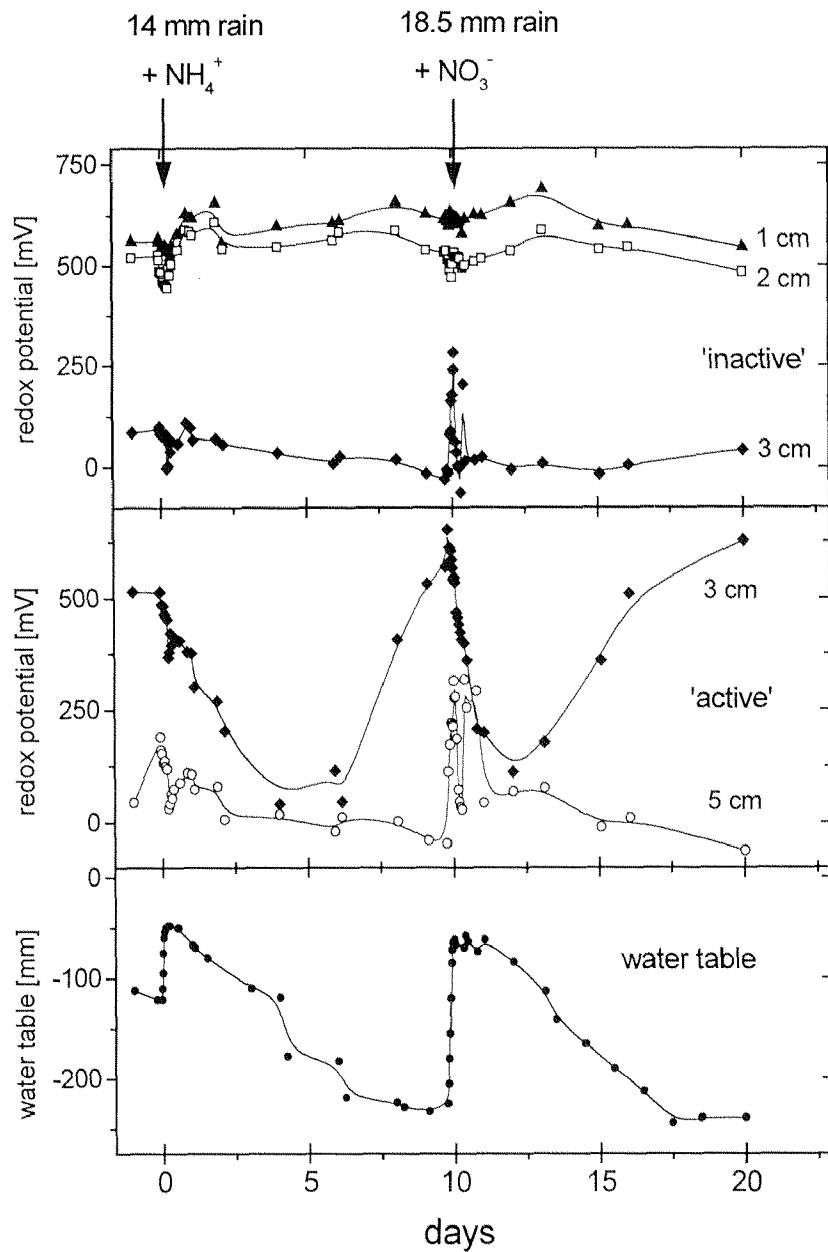


Figure 3.3: Soil redox potentials at different depths and water table position during the N addition experiment. Lines represent individual redox electrodes.

3.4.1 Flow regimes and micro-cups locations

In order to explain the microscale variability of NO₃⁻ in the topsoil, the relative location of each micro-cup with respect to flow paths was estimated by the response to a pulse input of a dye tracer. We assumed that the 'fast'

responding micro-cups showing a high recovery of the Brilliant Blue FCF solution were located within the reach of 'flow paths'. Micro-cups showing a slow response to the dye tracer input were regarded to be located within the 'soil matrix'.

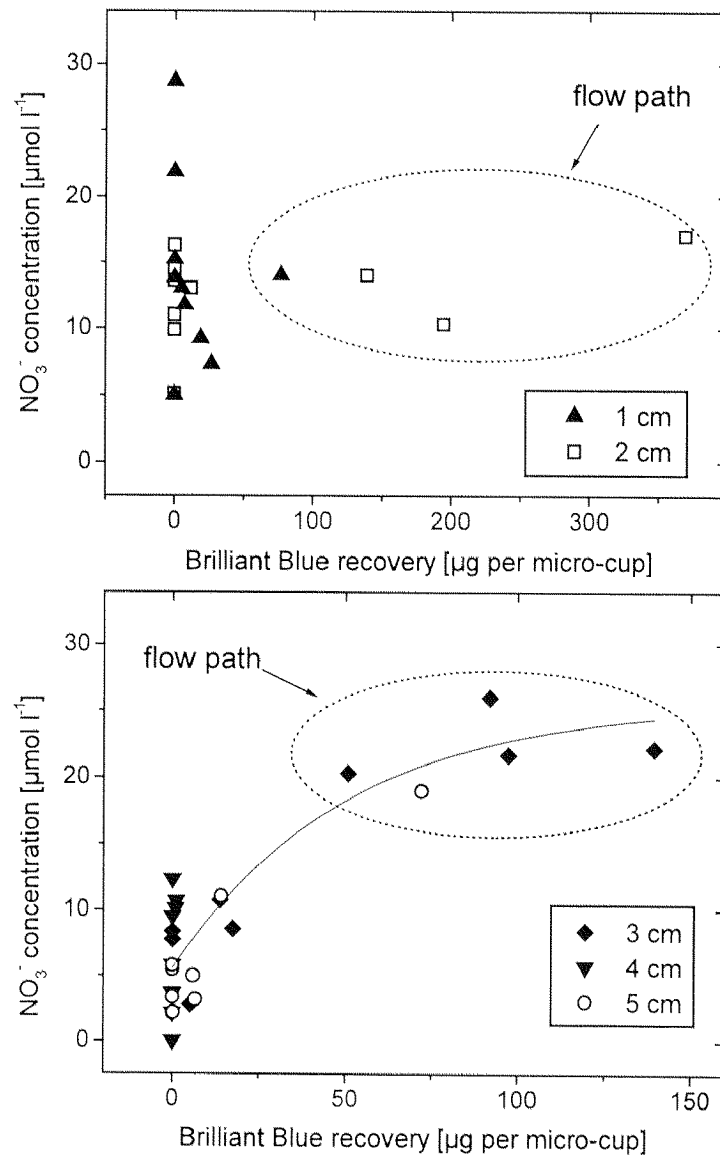


Figure 3.4: Relation of NO₃⁻ concentrations to locations of micro-cups characterised based on Brilliant Blue FCF recovery (flow path = high recovery). NO₃⁻ concentrations of each micro-cup are the mean of 3 sampling dates. Brilliant Blue recovery is the amount sampled by each micro-cup within 24 h after application.

27 out of 50 micro-cups did not respond to the dye tracing, which indicates that a large portion of the soil volume did not come into contact with the dye solution within 24 h of application. The observed infiltration pattern was surprising, since preferential flow, studied in agricultural soils, was mainly observed in subsoils (Flury *et al.*, 1994; Heijs *et al.* 1996; Stamm *et al.*, 1998). However, in these studies ground vegetation had been removed and the uppermost soil was homogenised. Our experiment shows that a large proportion of the topsoil was bypassed. One reason for this was probably the dense ground vegetation and the heterogeneity of the organic layer, which led to a redistribution of homogeneously applied rainfall. According to our observations, rainwater accumulated on foliage and dripped irregularly in space and time onto the soil surface. Additionally, water might have preferentially infiltrated along stems and roots (Dekker & Ritsema, 1996).

3.4.2 Response of flow paths and soil matrix to tracer applications

Based on the response of the micro-cups to the Brilliant Blue addition, the micro-cups were divided into two groups, flow paths and soil matrix.

Micro-cups from flow paths showed a faster SO_4^{2-} in the first and a faster Cl^- breakthrough in the second N-addition experiment than those from the soil matrix (Fig. 3.5 and 3.7), which supports the grouping based on the Brilliant Blue response.

After the peak, Cl^- concentrations decreased in flow paths, but remained constant at maximum concentrations for the next 10 days within the soil matrix. Since the tracer pulse was applied at the end of the rainfall event and the soil dried out subsequently, the Cl^- leaching pattern indicates that flow paths drained faster than the soil matrix.

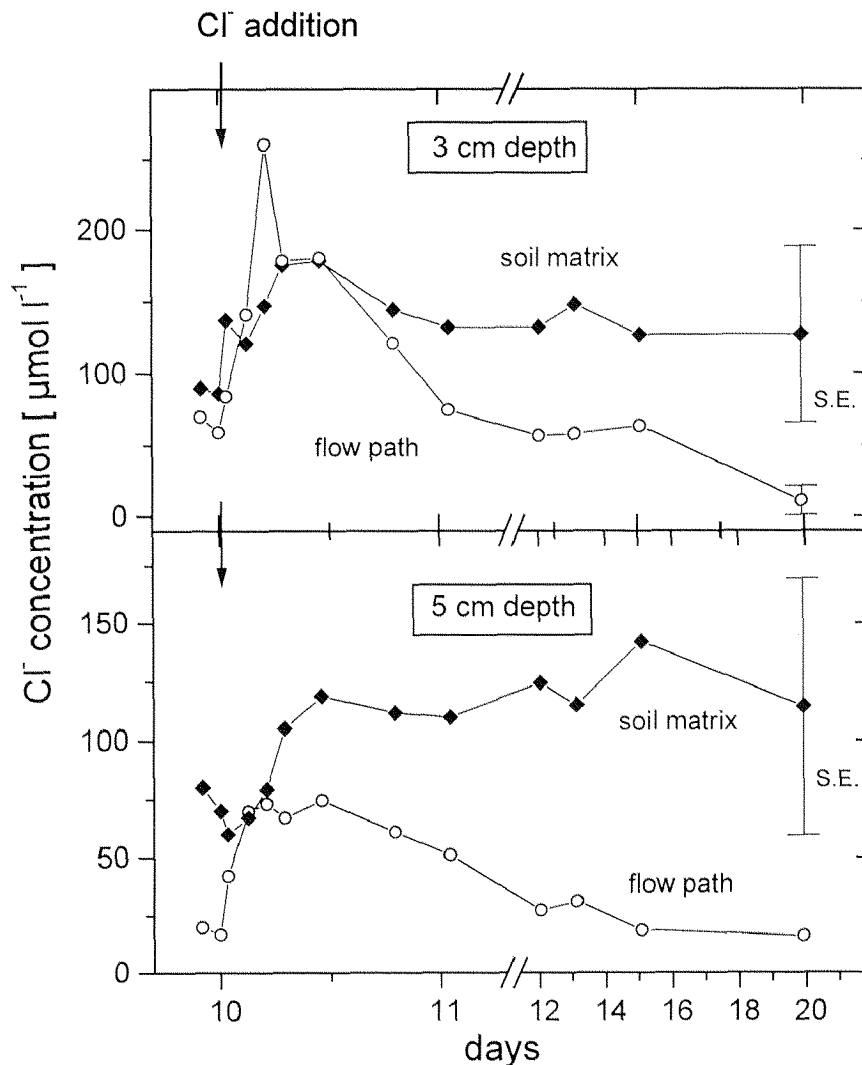


Figure 3.5: Chloride concentrations in the soil solution of flow paths and soil matrix at 3 and 5 cm depths. Due to the small sample volumes, the samples were bulked during the experiment. Standard errors represent the variability of collected solution at day 20 (3 cm soil matrix: $n = 6$; 3 cm flow path: $n = 4$; 5 cm soil matrix: $n = 8$). The 5 mM Cl^- m^{-2} have been applied at the end of the simulated rainfall of 18 mm.

3.4.3 Relation of NO_3^- concentrations to flow paths

The existence of flow paths affected the NO_3^- concentrations in the topsoil (Fig. 3.4). Nitrate concentrations of the micro-cups at 3, 4, and 5 cm depths were positively correlated with the Brilliant Blue recovery. In contrast, NO_3^- concentrations of the uppermost 2 cm were not related to the location of the micro-cups (expressed as Brilliant Blue recovery). This shows that the location

of the micro-cups influenced the NO_3^- concentration only under reducing conditions. Higher NO_3^- concentrations along flow paths under reducing conditions were probably due either to a shorter contact time of NO_3^- with the soil in the flow paths, too short for denitrification, and/or more favourable conditions for net nitrification. Our results suggest that both mechanisms hold true. A shorter residence time of the solution sampled along flow paths was shown by the shorter breakthrough time of Cl^- , SO_4^{2-} , and Brilliant Blue. The more favourable conditions for nitrification along flow paths compared to the soil matrix were indicated by the shorter tailing of Cl^- breakthrough curve in flow paths. This suggests that flow paths are better drained and warrant a better oxygen supply (Dziejowski *et al.*, 1997).

3.4.4 Temporal NO_3^- dynamics in flow paths and soil matrix

In order to investigate the temporal dynamics of N transformations N was added onto the surface above the micro-cups under controlled conditions. First, NH_4^+ was applied during a simulated rainfall. Then, after 10 days of drying, NO_3^- was added at the end of a rainfall of 18 mm.

The NO_3^- concentrations of the soil solution were related to the Cl^- concentrations to account for concentration effects. Assuming that Cl^- is inert in the soil system, an increase of the $\text{NO}_3^-/\text{Cl}^-$ ratio suggests a net mobilisation or production of NO_3^- , whereas a decrease of the $\text{NO}_3^-/\text{Cl}^-$ ratio suggests a NO_3^- consumption.

After the simulated rainfall of the NO_3^- addition, the $\text{NO}_3^-/\text{Cl}^-$ ratio decreased at all depths below 2 cm and remained constant in the upper 2 cm for the following 3 days (Fig. 3.6). Since no water was applied within this period, this suggests that denitrification occurred below 2 cm depth, but not within the uppermost 2 cm. This is supported by the corresponding redox potential measurements (Fig. 3.3). The measured denitrification showed an analogous temporal pattern as the $\text{NO}_3^-/\text{Cl}^-$ ratio. It peaked immediately after the NO_3^- application and then decreased drastically within the next 24 h (Fig. 3.8).

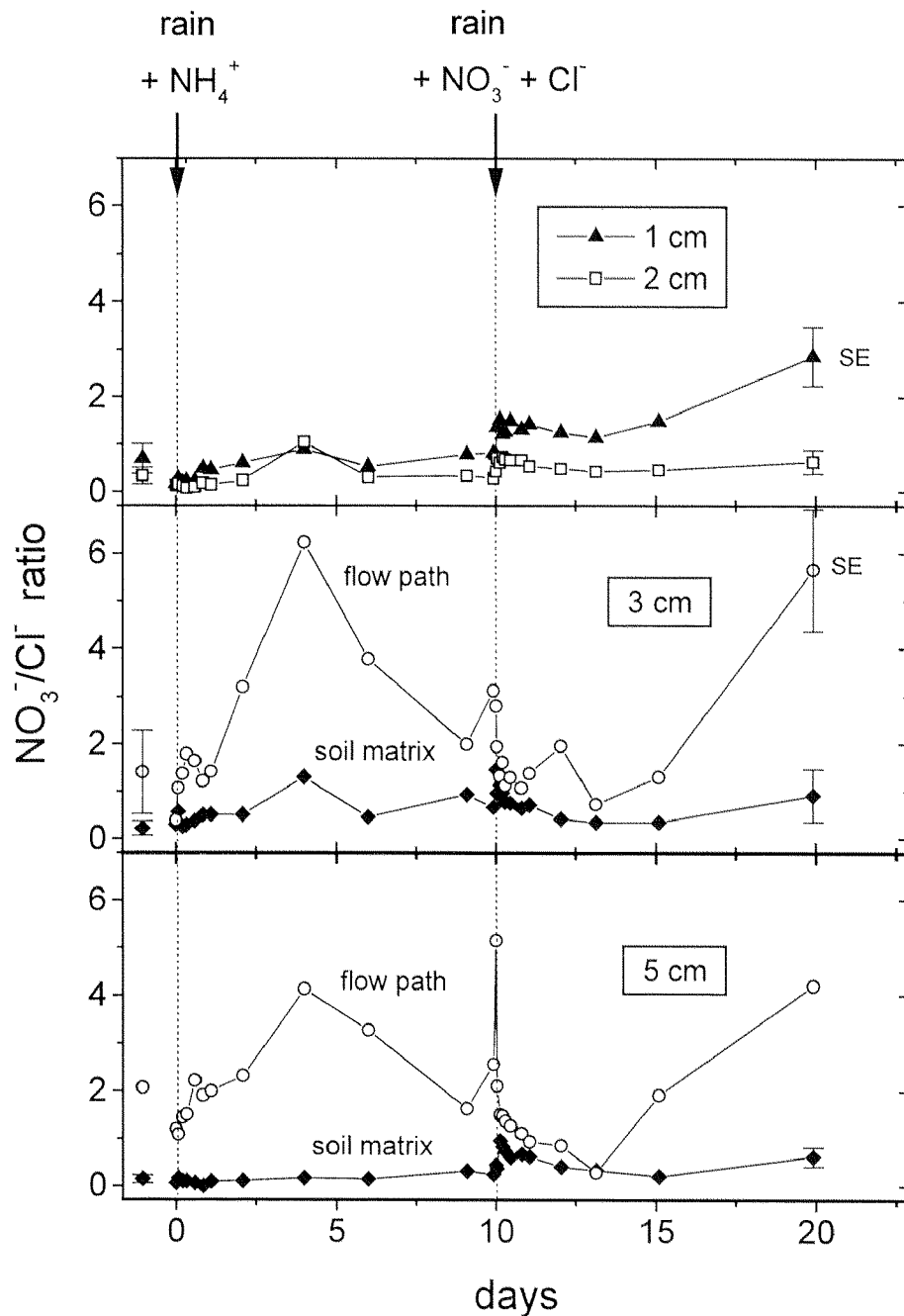


Figure 3.6: $\text{NO}_3^-/\text{Cl}^-$ ratio in the soil solution during the N-addition experiment. Due to the small sample volumes, the samples were bulked. Standard errors were estimated at the first and the last sampling date.

Soil solution collected within reach of flow paths showed a more pronounced temporal variation of the $\text{NO}_3^-/\text{Cl}^-$ ratio than that of the soil matrix (Fig. 3.6). Directly after the rainfall, the decrease of the $\text{NO}_3^-/\text{Cl}^-$ ratio was stronger in the

flow paths than in the soil matrix, suggesting that more of the applied NO_3^- was denitrified at these locations. In the subsequent dry period, the $\text{NO}_3^-/\text{Cl}^-$ ratio increased again; 3 days after the rainfall in the flow paths and 2 days later in the soil matrix (Fig. 3.6). This suggests that favourable (aerobic) conditions for net nitrification reappeared faster in flow paths than in the soil matrix.

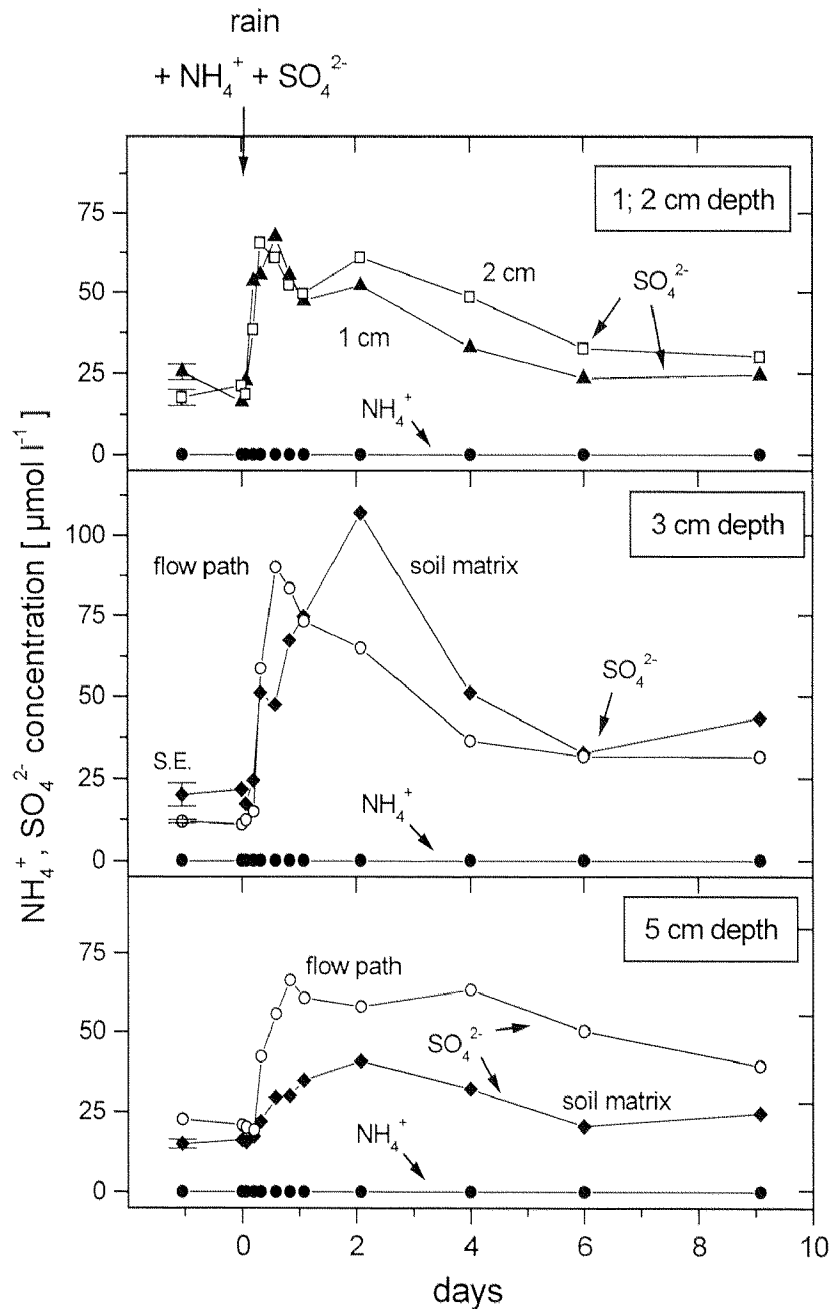


Figure 3.7: Breakthrough curves of NH_4^+ and SO_4^{2-} at various depths. $5 \text{ mM NH}_4^+ \text{ m}^{-2}$ and $2.5 \text{ mM SO}_4^{2-} \text{ m}^{-2}$ were applied after 8 mm of rain, followed by an additional 6 mm of rain. This resulted in a concentration of $360 \text{ } \mu\text{M NH}_4^+$ and $180 \text{ } \mu\text{M SO}_4^{2-}$ in the rainwater. The detection limit of NH_4^+ was $10 \text{ } \mu\text{M}$.

3.4.5 Retention of NH_4^+ and its consequences for nitrification-denitrification

In contrast to NO_3^- , NH_4^+ concentrations showed no differences between flow paths and soil matrix. The added NH_4^+ pulse corresponding to a two-week ambient input did not show up in the soil solution at all, in contrast to the simultaneously applied SO_4^{2-} (Fig. 3.7). None of the samples from micro-cups nor suction plates indicate increased NH_4^+ concentrations on any sampling date. At most locations, they remained below the detection limit of $10 \mu\text{M NH}_4^+$. Ammonium was immediately immobilised at its first soil contact. The extremely efficient retention of NH_4^+ suggests that abiotic rather than biotic processes are responsible. Ammonium can either be adsorbed to cation exchange sites and/or incorporated into organic matter through chemical reactions (Schimel & Firestone, 1989). Both processes are promoted by the high carbon (14%) and clay content (50%) of the topsoil, combined with a high pH (Table 3.1). Strong retention of NH_4^+ may also limit the direct nitrification of elevated atmospheric NH_4^+ inputs, as suggested by the low increase of NO_3^- in the soil solution after the NH_4^+ application (Fig. 3.6 and 3.8).

This is consistent with the denitrification pattern: denitrification did not increase after the NH_4^+ application (Fig. 3.8). However, the simulated rainfall after 10 days of drying caused an increased denitrification, even before NO_3^- was added.

Combining the denitrification pattern with the high $\text{NO}_3^-/\text{Cl}^-$ ratio in flow paths during dry periods and its rapid drop after rainfalls suggests the following process: nitrate is mainly produced in aerobic flow paths during rainless periods. The subsequent rainfall displaces this NO_3^- into anoxic parts. The NO_3^- enriched flow paths become anaerobic due to waterlogging. Both processes combined with an additional NO_3^- input through infiltrating rainwater along flow paths stimulates denitrification. However, NO_3^- is rapidly depleted and denitrification activity decreased drastically within 24 h (Fig. 3.6 and 3.8). In this gleyic topsoil, nitrification and denitrification appears to occur temporally separated and to be not as closely coupled as reported in other studies (Abbasi & Adams, 1998; Nielsen & Revsbech, 1998). However, the

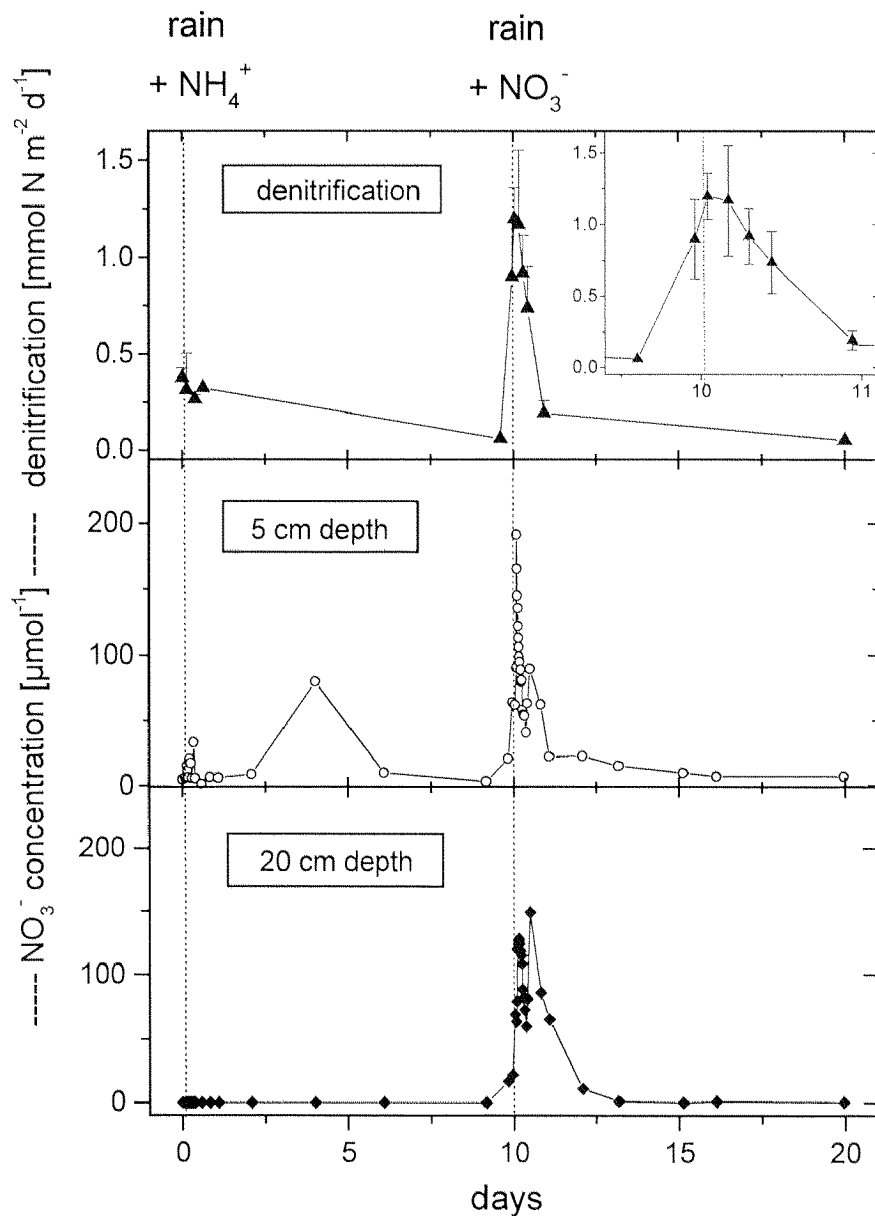


Figure 3.8: Denitrification rate and NO_3^- concentrations at 5 and 20 cm depth of the soil solution sampled by suction plates. Denitrifying activity was measured with 3 pairs of cores during the NH_4^+ addition and with 4 pairs of cores during the NO_3^- addition. NO_3^- concentrations are the mean of 2 suction plates, installed within 50 cm of the micro-cups.

quoted studies were carried out with NH_4^+ -rich aerobic soils in which local enrichments of organic materials cause an increased respiration producing anaerobic microsites (Christensen *et al.* 1991; Flessa & Beese, 1995; Nielsen &

Revsbech, 1998). Our results suggests that in the water saturated topsoil, NH_4^+ is very immobile and net nitrification can only start after a period of drying. The produced NO_3^- is not denitrified until the next rain, which leads to NO_3^- transport into anaerobic spots and to the formation of anaerobic conditions in formerly aerobic parts.

3.4.6 Significance of microscale variability for processes at the catchment scale

The observed bypassing of a large portion of the soil volume by infiltrating rainwater and the increased NO_3^- concentrations along flow paths may help to explain effects of N deposition on the catchment scale.

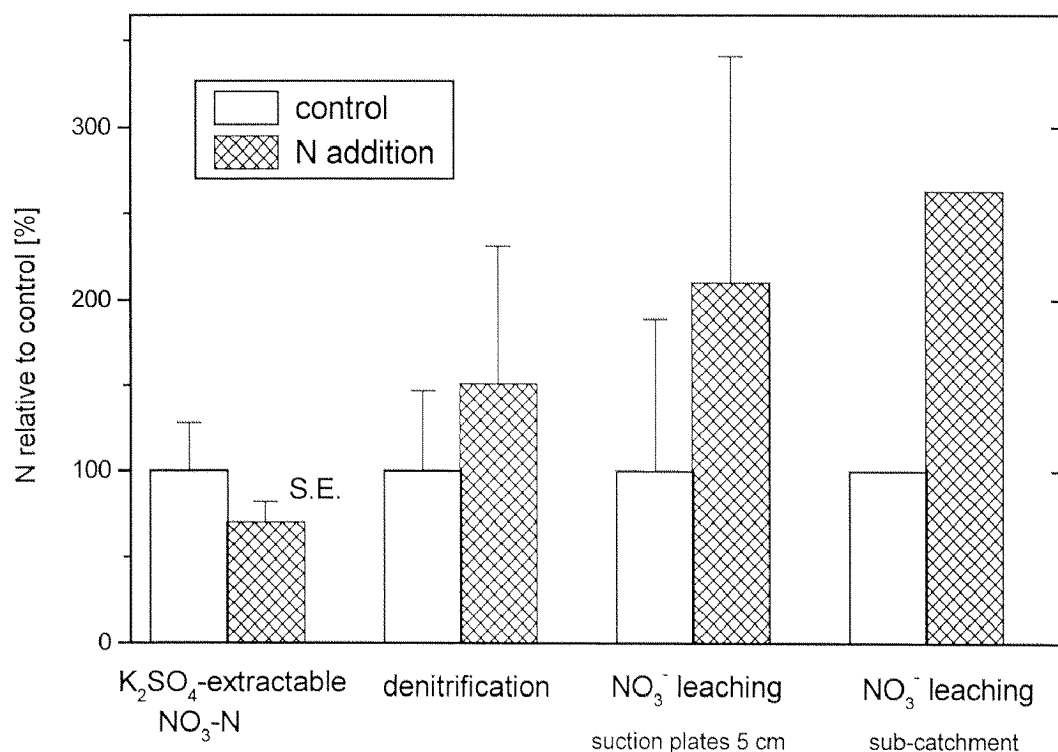


Figure 3.9: K_2SO_4 -extractable NO_3^- concentrations of the bulk soil (0-5 cm), and fluxes within the soil compartment. Mean and mean spatial standard errors of 5 plots from May 1996 to November 1997. Sampling dates: $n = 15$ (K_2SO_4 -extractable); $n = 28$ (denitrification); $n = 30$ (leached NO_3^-); NO_3^- export from sub-catchments (1500 m^2), 1997.

Three years of continuous addition of $30 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1} \text{ y}^{-1}$ increased the NO_3^- exported from the sub-catchment ($+ 4 \text{ kg N ha}^{-1} \text{ y}^{-1}$), the NO_3^- leaching at 5 cm depth ($p < 0.03$), and N loss via denitrification ($+ 1.6 \text{ kg N ha}^{-1} \text{ y}^{-1}$, $p < 0.01$), but not the K_2SO_4 -extractable NO_3^- of the bulk soil ($-0.3 \text{ kg N ha}^{-1} \text{ y}^{-1}$, n.s.) (Fig. 3.9). This appears to be a contradiction. Measurements of bulk soil samples integrate over large volumes and, as indicated by the micro-cups, a large proportion of the soil does not get in direct contact with the infiltrating rainwater. The bypassing probably affects both NO_3^- leaching and denitrification. Only a small proportion of the soil solution collected by micro-cups appears to be relevant for NO_3^- leaching and NO_3^- export from the sub-catchment, namely the soil solution from flow paths. This was suggested by the comparison of NO_3^- and Cl^- concentrations of different soil waters (Fig. 3.10, Table 3.2). The concentrations of the runoff from the sub-catchment and of the soil water collected by suction plates were closer related to samples from flow paths than to those from the soil matrix.

Table 3.2: Simple Pearson correlation coefficients of micro suction cups with suction plates at 5 cm depth (sampling dates = 24).

| Location | NO_3^- | Cl^- |
|------------------|-----------------|---------------|
| 1 cm | 0.42 | 0.16 |
| 2 cm | 0.62** | 0.17 |
| 3 cm soil matrix | 0.66*** | 0.29 |
| 3 cm flow path | 0.66*** | 0.59** |
| 4 cm | 0.62** | -0.47 |
| 5 cm soil matrix | 0.52* | -0.07 |
| 5 cm flow path | 0.83*** | 0.64*** |

* significance; $p < 0.05$; ** significance; $p < 0.01$; *** significance; $p < 0.001$

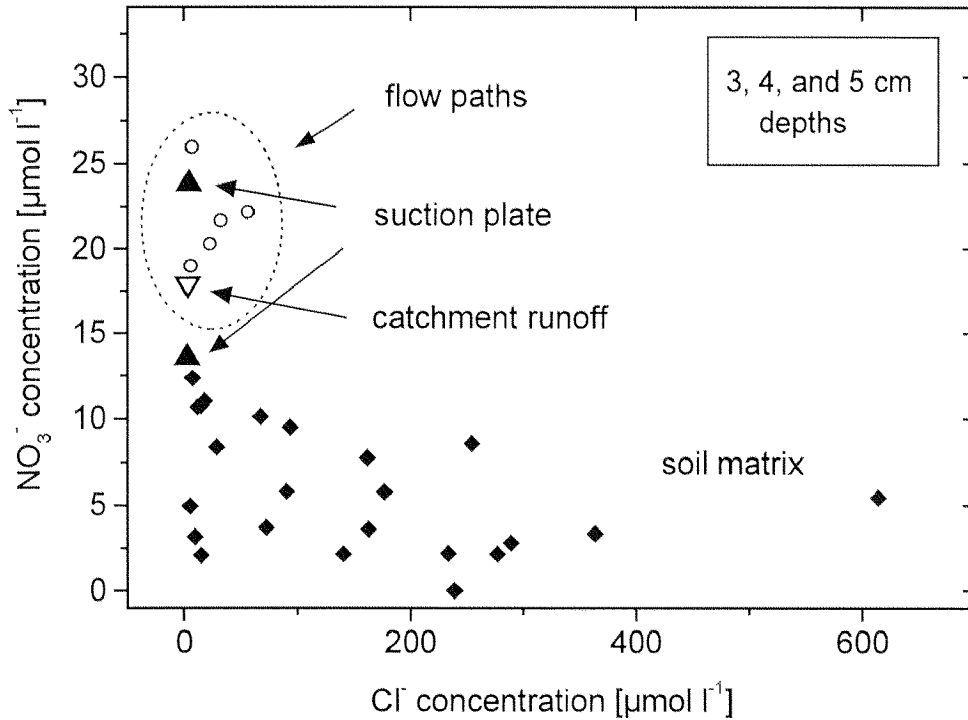


Figure 3.10: Comparison of solute concentrations from flow paths and soil matrix locations to solutes at 5 cm depth sampled by suction plates and to solutes of the runoff from the sub-catchment. Suction plates were installed within a distance of 50 cm to the micro-cups. Data points represent mean concentrations of 3 weeks.

Similarly to NO_3^- leaching, denitrification peaked only immediately after rainfall events, a time span too short for a contact of the NO_3^- rich rainwater with most of the soil matrix. Since flow paths had the highest NO_3^- supply and showed the largest decrease in the NO_3^- to Cl^- ratio after rainfalls, they were very likely the locations with the highest denitrification activity.

The results of our case study suggested that NO_3^- leaching and denitrification took place in a relatively small volume, here represented by 6 out of 30 micro-cups below 2 cm. Consequently, the capacity of the soil to retain elevated N deposition will be lower than expected by bulk soil extracts.

3.5 Conclusions

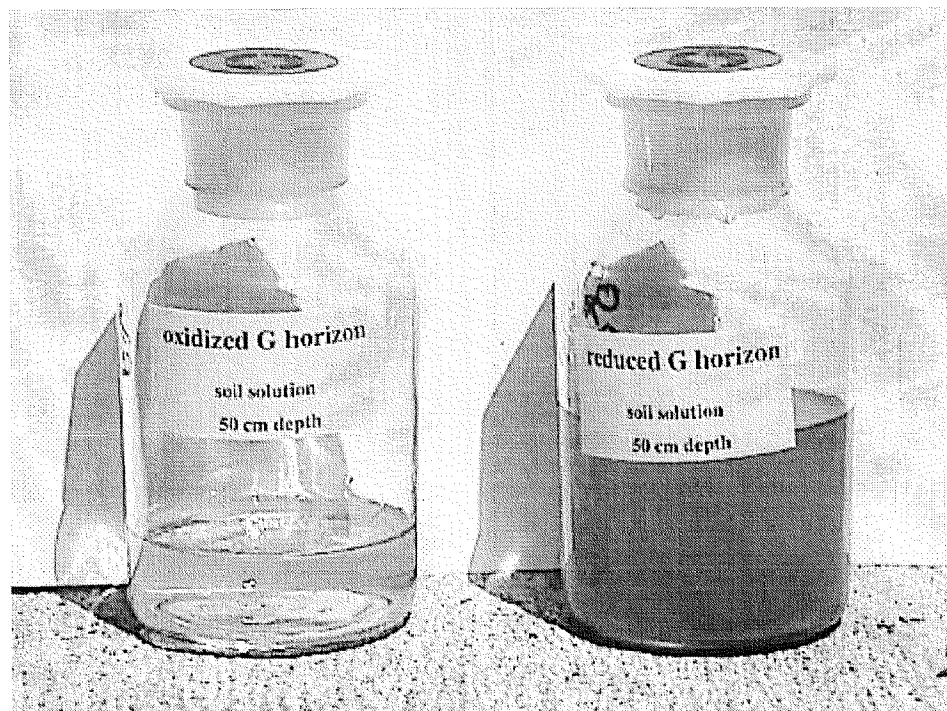
Both the soil solution sampled by micro-cups and the redox potential measurements reveal that only the uppermost 2 cm of the forest Humaquept were aerobic. Below 2 cm soil depth, aerobic and anaerobic microsites coexisted.

Only 23 out of 50 micro-cups responded to the application of the dye tracer Brilliant Blue FCF, which indicates that a large portion of the soil volume is not in direct contact with the infiltrating rainwater. The micro-cups which responded to the dye were regarded to be located within reach of flow paths. These microsites were more active with respect to the transformation of N than the 'non-responding' cups in the soil matrix. The active sites along flow paths had higher NO_3^- concentrations at depths below 2 cm, showed an increased denitrification activity after rainfalls and an earlier and enhanced net nitrification after drying. Locations within reach of flow paths are probably microhabitats that are characterised by a better nutrient as well as oxygen supply, and are more exposed to drying and wetting than the soil matrix. Additional research, however, is necessary to transfer our findings regarding the importance of flow paths for N transformation to other soils and conditions.

The observed heterogeneous distribution of N transformation at a microscale may explain the effects of increased N deposition at the catchment scale: a large proportion of the soil was bypassed by the infiltrating rainwater. This probably reduces the capacity of the soil to retain N deposition. As a consequence, elevated N inputs increase the N fluxes within the ecosystem (denitrification, NO_3^- leaching, and NO_3^- export from the sub-catchment) without increasing the K_2SO_4 -extractable NO_3^- of the bulk soil.

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Chapter 4



Effects of redox conditions and flow processes on the mobility of dissolved organic carbon and nitrogen in a forest soil

with

K. Kaiser, H. Feyen, and P. Schlegli

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4.1 Abstract

In forest ecosystems, fluxes of organic solutes play prominent roles in pollutant and nutrient transport. This study, conducted in subalpine forested Humaquepts in Switzerland, aimed to (i) investigate the influence of the redox environment on the mobility of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) and to (ii) identify the significance of flow processes for the DOC transport.

The redox environment had a pronounced impact on DOC and DON mobility. Concentrations of DOC in the soil solution of the mineral soil were higher under reduced than under oxidized conditions. In the reduced mineral soil at 100 cm depth, they averaged to 1.2 mmol DOC l⁻¹. The apparently low retention of DOC under reducing conditions, particularly of the lignin-derived DOC fraction, was probably caused by a lack of strong sorption of DOC. A close correlation between dissolved Fe and DOC concentrations ($r^2=0.83^{***}$) suggests that reductive dissolution of Fe-oxides was the controlling factor. However, during the aerobic sampling of soil solution from the reduced mineral soil, DOC co-precipitated with Fe. This suggests that the DOC input from reduced mineral soils to aerobic stream water is lower than expected from the high DOC concentrations in the soil.

Organic N was the major form of the total dissolved N in the soil solution at all soil depths. In the reduced subsoil, dissolved N was completely organically bound. This was probably due to both, an immobilisation of inorganic N and a low retention of DON under reducing conditions.

In the subsurface flow at 30 to 60 cm depth, DOC concentrations increased rapidly with increasing discharge. At peak flow, DOC concentrations were doubled compared to base flow. The molar UV absorptivity of DOC in the subsurface flow corresponded closely to that of the topsoil. These findings suggest that DOC concentrations and properties are sensitive to flow velocities and that DOC is preferentially transported to the subsoil at high discharge.

4.2 Introduction

Fluxes of organic solutes play important roles in pollutant transport, nutrient mobility and pedogenesis in forest soils (Qualls *et al.*, 1991; Guggenberger & Zech, 1993). The forest floor is the major source of soluble organic substances, leading to an input of up to 40 g DOC m⁻² y⁻¹ into the mineral soil (Guggenberger & Zech, 1993; Currie *et al.*, 1996). However, since DOC is effectively retained in many subsoils, the output from the mineral soil and consequently the export of DOC by streams is typically less than 5 g DOC m⁻² y⁻¹ (Tate & Meyer, 1983; Guggenberger & Zech, 1993). Retention of DOC is generally attributed to the sorption by Al and Fe oxides and clay (McDowell & Wood, 1984; Guggenberger & Zech, 1993; Kaiser & Zech, 1998). Biodegradation is thought to play a minor role (Qualls & Haines, 1992; Jandl & Sollins, 1997).

In many respects, DON plays a quantitatively more important role in the N cycle than DOC does in the C cycle. In undisturbed forests, DON typically accounts for 50 to 95 % of the total dissolved nitrogen (TDN) leached from the forest floor to the mineral soil (Sollins & McCorison, 1981; Qualls *et al.*, 1991; Currie *et al.*, 1996). Relatively little is known about the fate of DON in the mineral soil (Marcus *et al.*, 1998). Qualls & Haines (1992) found no preferential decay of DON compared to DOC, which suggests that the mobility of DON is closely linked to that of DOC.

Most of the field-based studies with dissolved organic matter (DOM) have been conducted in Spodosols or Inceptisols (e.g., Cronan & Aiken, 1985; Guggenberger & Zech, 1993), which have a high sorption capacity for DOM in the subsoil (Moore *et al.*, 1992; Kaiser *et al.*, 1996). However, both field and laboratory experiments indicate that under reducing conditions DOM retention is small (McLaughlin *et al.*, 1994; Kaiser & Zech, 1997b). The reason for this finding seems to be the reductive dissolution of Fe and Mn oxides. As they are important sorbents of DOM (Tipping, 1981; Tipping & Heaton, 1983), the mobility of DOM in the mineral soil consequently increases. Aquic mineral soils with reducing conditions can be significant components of forested catchments.

Since they are at the interface between terrestrial and aquatic ecosystems, those soils may represent a major source of DOM for groundwaters.

Another important factor regulating the mobility of DOM in the soil is the flow process. Jardine *et al.* (1990) noticed a considerable vertical transport of DOM during storm events caused by preferential transport. In column experiments, Weigand & Totsche (1998) showed that DOM sorption was sensitive to flow variations, indicative of chemical non-equilibrium conditions.

In this study we investigated the mobility of DOC and DON in subalpine forested Humaquepts. The objectives were (i) to assess the effects of redox conditions on DOC dynamics, (ii) to estimate the contribution of DON to the soil's N-cycle, and (iii) to identify the significance of flow processes for DOC transport through the soil.

4.3 Materials and methods

4.3.1 Study site

The study area is located at 1200 m a.s.l. in the Alptal (47°03N, 8°43E), a south-north oriented valley in the Prealps of central Switzerland. The mean air temperature is 6°C. The average annual precipitation is 2300 mm with a maximum in June (270 mm) and a minimum in October (135 mm). The parent rock material is Flysch, consisting of alternating calcareous sandstones with argillite and bentonite schists. The weathering of these rocks has resulted in heavy clayey soils of low permeability with a water table close to the surface throughout the year.

Vegetation and soil form a mosaic pattern closely related to the micro-topography (Fig. 4.1). The mounds (water table below 40 cm depth) have oxidized Bw horizons overlain by mor layers, consisting of an Oi, an Oe and an Oa-layer (clayey Typic Humaquepts, Soil Survey Staff, 1996). In the depressions, the water table frequently reaches the surface, leading to muck topsoils with high carbonate contents. The mineral soil consists mainly of a

permanently reduced Bg horizon, with a BA horizon in better drained parts. Partly decomposed wood and root fragments are common in the reduced mineral soil. The mineral soil is oxidized along cracks, and contains lepidocrocite (Disserens, 1992). Selected soil properties are given in table 4.1.

Table 4.1: Selected properties of the soils.

| horizon (depth) | pH ^a | C content [g kg ⁻¹] | N content [g kg ⁻¹] | Fe ^b [g kg ⁻¹] | Al ^c [g kg ⁻¹] | texture % clay/silt/sand |
|-------------------|-----------------|------------------------------------|------------------------------------|--|--|-----------------------------|
| mound | | | | | | |
| LF (0-5 cm) | 3.3 | 423 | 19 | 15 | 5 | |
| A (5-10 cm) | 4.6 | 70 | 4.1 | 47 | 13 | 47/47/6 |
| Bw1 (10-20 cm) | 5.2 | 27 | 1.8 | 35 | 15 | |
| Bw2 (20-50 cm) | 5.9 | 14 | 0.9 | 25 | 12 | 46/46/5 |
| depression | | | | | | |
| LF (0-2 cm) | | 423 | 19 | 4 | 1.5 | |
| A (2-10 cm) | 5.4 | 156 | 8.5 | 23 | 10 | 51/45/4 |
| BwA (5-10 cm) | 6.1 | 86 | 4.8 | 30 | 13 | 44/44/11 |
| Bg (10-50 cm) | 6.9 | 16 | 0.8 | 26 | 13 | 43/42/15 |

^a measured in the soil solution

^b extracted with 2M HNO₃

^c from Schleppe *et al.* (1998)

Norway spruce (*Picea abies* (L.)) is growing only on the drier mounds. *Vaccinium sp.* is the dominant plant species of the understory vegetation. In the depressions, the ground vegetation consists mainly of *Caltha palustris* and *Petasites alba* (*Equiseto-Abietum*) under a dense tree canopy, and of *Poa trivialis* and of *Carex ferruginea* (*Carici remotae-Fraxinetum*) in open patches.

The study site was within the Erlenbach headwater catchment which covers 0.7 km² and consists of 40% forest and 60% grassland. In the framework of the NITREX project (NITrogen saturation EXperiments), two forested and one

grassland sub-catchment (1500 m^2 each) have been hydrologically delineated by 80 cm deep trenches (Schleppi *et al.*, 1998). The sampling of the runoff was coupled to the permanent runoff measurements with a V-notch weir. Flow-proportional samples were automatically taken, bulked and collected weekly.

4.3.2 Soil solution, throughfall, and redox potentials

Soil solution samples were collected from 12 plots (Fig. 4.1). Three plots were located on mounds and 9 plots in wet depressions. Ten plots were circular and had an area of 20 m^2 each. The other two plots, one on a mound and one in a depression, were angular and delineated with trenches (see next section). Five of the circular plots, one on a mound and four in depressions, received additional N inputs ($30 \text{ kg NH}_4\text{NO}_3\text{-N ha}^{-1}\text{y}^{-1}$) simultaneously added to rainfalls by sprinklers (Schleppi *et al.*, 1998). The other plots received an equivalent amount of unaltered rainwater. This additionally applied water increased the throughfall by 10%.

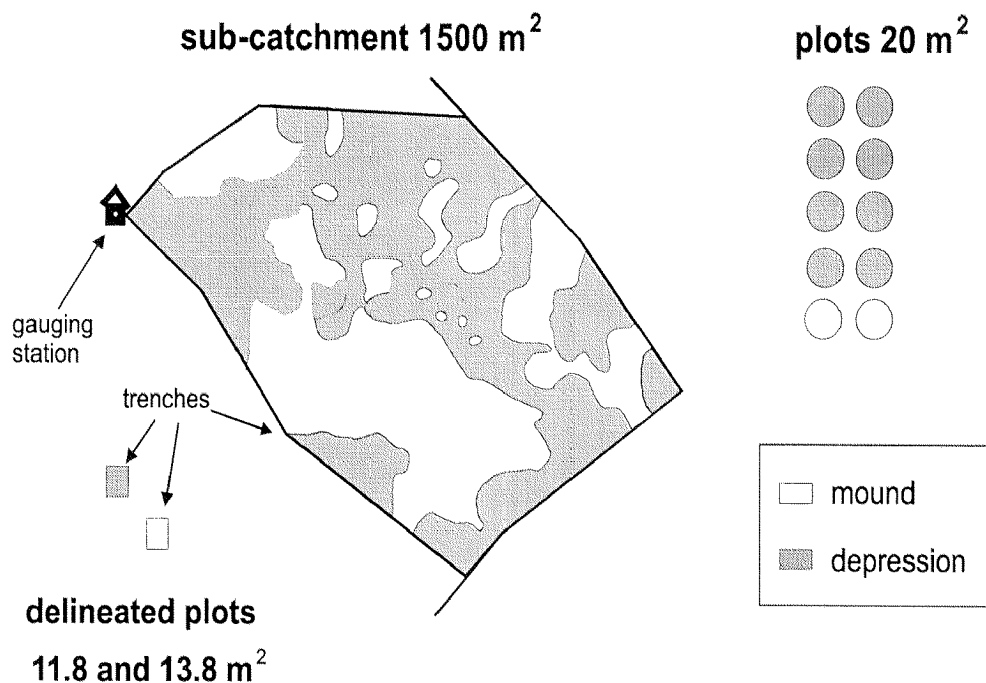


Figure 4.1: Spatial distribution of mounds and depressions in the forest sub-catchment (1500 m^2), in the circular plots (20 m^2), and in the delineated plots (11.8 m^2 and 13.8 m^2).

Horizontally installed porous glass filter plates (90 mm diameter, max. pore radius $16\ \mu\text{m}$) were used to sample soil solution from depths of 5 and 10 cm below the soil surface. The suction plates were mounted on grooved plexiglass plates and installed laterally from a soil pit by inserting them into a 20 cm deep pre-cut slit. The suction plates were placed slightly inclined and the outlet connected to a 100 cm³ glass bottle, which was placed in the pit and subsequently covered with soil. Additionally, ceramic suction cups installed at a 45° angle to the soil surface sampled the soil solution at 30, 50 and 100 cm depths. Two suction devices were used per depth in the depressions plots and 4 of them in the mound plots. They were installed during the winter of 1995/96, about 4 months before the first sampling. Prior to their installation, all suction devices were flushed with 1 N HCl, then with distilled water and finally with soil solution.

To avoid a permanent flow to the suction devices, which would alter the surrounding redox conditions, suction was applied only once a week and just sufficient to collect enough sample volume for 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 30 kPa. Sampling was performed weekly and bulked bi-weekly per plot and depth.

Throughfall was collected in all plots with polyethylene (PE) funnels (15 cm diameter) connected to 500 cm³ PE bottles. Samples were taken weekly and bulked bi-weekly.

Water tables were measured with PVC tubes, 5 cm in diameter and 1.0 m long, that were installed in a hole made with a 5 cm hand auger in each plot. Measurements were carried out once or twice a week with a ruler. Redox potentials (Eh) were measured with platinum electrodes (Cogger *et al.*, 1992) inserted into the soil and an Ag/AgCl reference electrode placed into a piezometer. Redox electrodes were installed at 5, 10, 30 cm (20 per depth), 50 and 100 cm depths (10 per depth) within a distance of 50 cm to the piezometer.

The Eh readings were carried out with a portable pH/mV meter (pH 320, WTW, Weilheim, Germany).

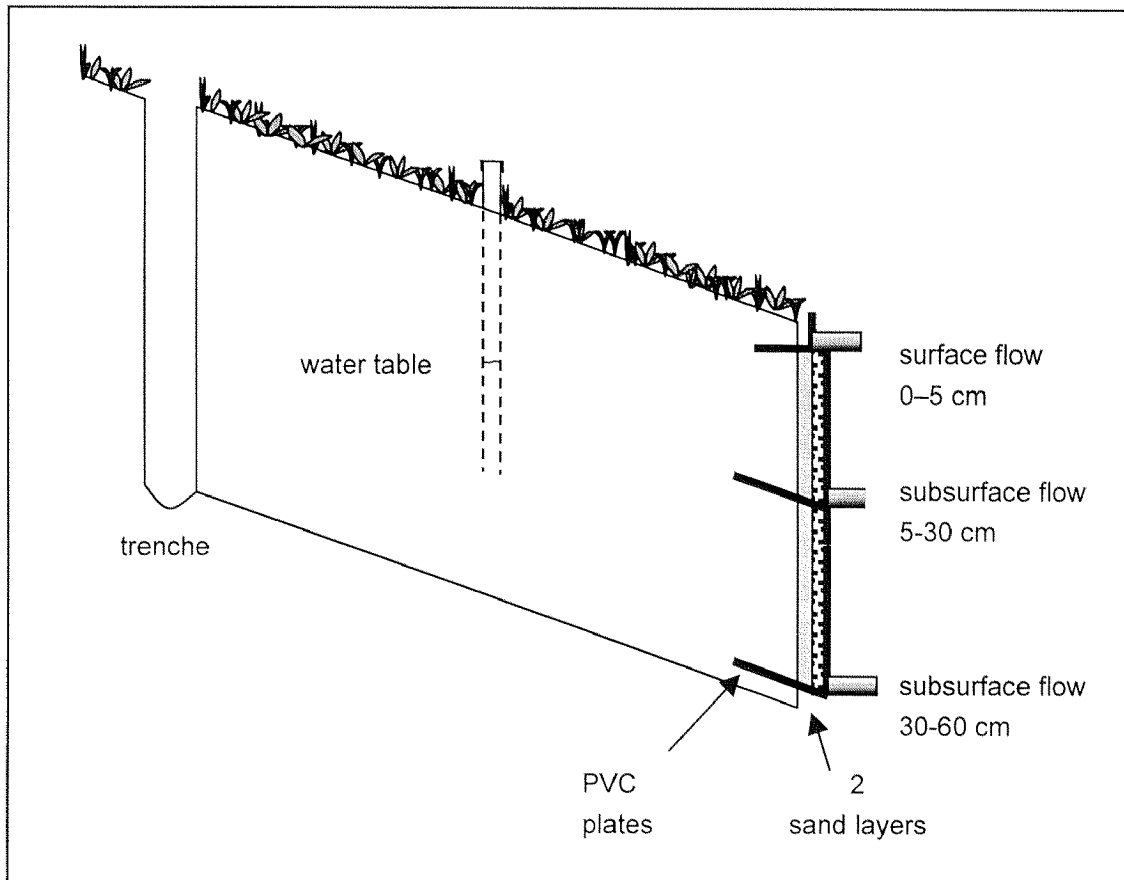


Figure 4.2: Profile view of the delineated plots which were used to measure and to sample surface and subsurface flow.

4.3.3 Surface and subsurface flow

In order to estimate the water transport through the soil and to quantify the solute transport by surface and subsurface flow, the two angular soil plots were hydrologically delineated by 80 cm deep trenches (Fig. 4.2). One of the delineated plots was located on a mound and covered 11.8 m². The other one was in a depression and had an area of 13.8 m². The slope of both delineated plots was 20%. The water entering the trenches was directed away from the plots. Surface and subsurface flow of the delineated plots was collected by 'runoff gutters' at the lower end of the plots at 0-5 cm, 5-30 cm, and 30-60 cm

depths. The 2 m wide 'runoff gutters' were inserted 25 cm into the soil profile. To preserve the flowlines of water within the soil and to maintain a minimal suction at the profile face, the runoff gutters were filled with two sand layers (0.3-0.9 mm for the layer in contact with the soil and 3-5 mm for the next). The outflow from the gutters was continuously measured by tipping-buckets (100 ml bucket volume) connected to a datalogging system (CR10, Campbell Scientific, Inc., Logan, UT). Surface and subsurface flow were flux-proportionally sampled.

4.3.4 Simulated rainfall events

The response of the surface and subsurface flow and DOC transport to rainfall was estimated by irrigating the two delineated plots with a mobile sprinkling device (Feyen, 1998). The sprinkler consisted of a spray bar with 16 nozzles (TEEJET 110015LP, Spraying System Co., Wheaton, IL) mounted at a height of 30 to 40 cm above the ground. First, tap water ($< 0.5 \text{ mg DOC l}^{-1}$, $< 1.5 \text{ mg NO}_3^- \text{ l}^{-1}$, $< 0.8 \text{ mg Cl l}^{-1}$) was applied as a step pulse with an intensity of 1.26 mm min^{-1} for 23 minutes on the mound, and of 1.94 mm min^{-1} for 16 minutes in the depression. Then, after the runoff generation had stopped, tap water was irrigated for 2 h at a constant rate of 0.15 mm min^{-1} on the mound and 0.20 mm min^{-1} in the depression. The uniformity of the irrigation was measured with square cups ($10.6 \text{ cm} \times 10.6 \text{ cm}$) placed on the ground. The coefficient of spatial variation was 4% for the irrigation on the mound and 11% for the depression.

Samples of the surface and subsurface flow ($\sim 10 \text{ ml}$) were taken every 2.5 l of outflow from the delineated plots with a fraction collector (Retriever II, ISCO, Lincoln, NE).

4.3.5 Sample preparation and analyses

All solution samples were collected in acid-washed PE bottles, filtered ($0.45 \mu\text{m}$, cellulose acetate membranes Schleicher & Schuell, Keene, NH) within 48 h

and stored at 4°C. For elemental analyses, sub-samples were acidified with concentrated HNO₃ to a final concentration of 2.5% HNO₃. If time until analysis exceeded 1 month, samples were stored frozen. Since the Fe-rich subsoil solution contained precipitates, we acidified subsamples to 10% per volume with HNO₃ for elemental and DOC analyses in order to dissolve the precipitate prior to filtration. DON was measured directly in unfiltered samples.

All samples were analyzed for major elements (Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe_{tot}, Al_{tot}, S_{tot}) by induced-coupled plasma atomic emission spectrometry (ICPAES OPTIMA 3000, Perkin Elmer, Norwalk, CT), anions (Cl⁻, NO₃⁻, SO₄²⁻, H₂PO₄⁻) by ion chromatography (DX-120, Dionex, Sunnyvale, Ca), and NH₄⁺ colorimetrically by automated flow injection analysis (PE FIAS-300, Perkin-Elmer).

Dissolved organic carbon (DOC) was measured with a TOC-500 analyzer (Shimadzu Corp., Tokyo, Japan). Hydrophilic and hydrophobic DOC were separated by the use of columns filled with Amberlite XAD-8 macroporous resin (Aiken & Leenheer, 1993). The DOC adsorbing at pH 2 on XAD-8 resin is operationally defined as hydrophobic, while hydrophilic DOC passes through the columns.

Total dissolved N was estimated by alkaline peroxodisulfate digestion converting all N to nitrate (NO₃⁻). In contrast to the original procedure (Solorzano & Sharp, 1980), which recommends leaving the cap of the autoclave bottles loose, the caps were closed tightly. This improved the reproducibility of the method considerably. Nitrate was then measured either photometrically at 210 nm (UV-160, Shimadzu Corp., Tokyo, Japan) for iron free samples or by ion chromatography with Fe-rich (subsoil) samples. Both measurement methods gave comparable results. The DON was calculated by subtracting the concentration of inorganic species from TDN. Recovery of the standards glycine, purine, pyridine and humic acid (Fluka Chemie AG, Buochs, Switzerland) was found to be between 95 and 101%. The coefficient of variation of the TDN measurements for a reference soil solution (n=10) was found to be below 3%. However, the detection limit for DON depends on the background of

inorganic N. In bulk deposition and stream water during snowmelt, both typically with high inorganic N and low DON concentrations, the detection limit was about 10 $\mu\text{mol DON l}^{-1}$. In the soil solutions of the subsoil, which contained no mineral N, DON measurements were reproducible down to concentrations of 5 $\mu\text{mol DON l}^{-1}$.

To obtain information on the characteristics of DOC in the surface and subsurface flow during rainfall events, the molar absorptivity of DOC at 285 nm was measured in a 1 cm quartz window cuvette with a double beam Shimadzu UV-160 spectrophotometer (Chin *et al.*, 1994).

Iron and C concentrations in brownish-red precipitates of the subsoil solution were analyzed in 5 samples filtered through a Whatman GF/F filter (nominal pore size: 0.7 μm). Fe concentrations were measured with ICP-AES after dissolution in 10% HNO_3 . Carbon and N content of the precipitates on the filter and of soil samples were measured with a C/N analyzer (NA 1500, Carlo Erba Instr., Fisons, Italy).

4.3.6 Statistical analyses

Significance of the differences between depths, between acidified and unacidified soil solution samples, and the impact of N additions were estimated with a Wilcoxon matched pair test. Since N additions had effects neither on DOC nor on DON concentrations, it was possible to consider all plots for testing differences between mounds and depressions. The significance of this difference was estimated with a Mann-Whitney U-test, which does not require a normal distribution and allows the analysis of unbalanced groups. All statistical analyses were performed with STATISTICA (Version 5, Statsoft, Inc., Tulsa, OK).

4.4 Results and discussion

4.4.1 Redox conditions in the soil

The concentrations of inorganic constituents in the soil solution showed a vertical sequence of redox reactions confirmed by decreasing redox potentials (Fig. 4.3). In the depressions, Mn was dissolved at depths below 5 cm at an Eh lower than 250 mV and Fe below 10 cm depth at an Eh of 150 mV. Sulfate reduction as indicated by decreasing SO_4^{2-} concentrations occurred in the subsoil of the depressions below 50 cm depths at an Eh lower than 0 mV. The analogous decrease of dissolved Fe from 50 cm to 100 cm depth suggests the formation of $\text{Fe}_2\text{S}/\text{FeS}$. On the mounds, the reduction of all compounds occurred deeper in the profile than in the depressions, which is confirmed by a higher redox potential and a redder Bw horizon.

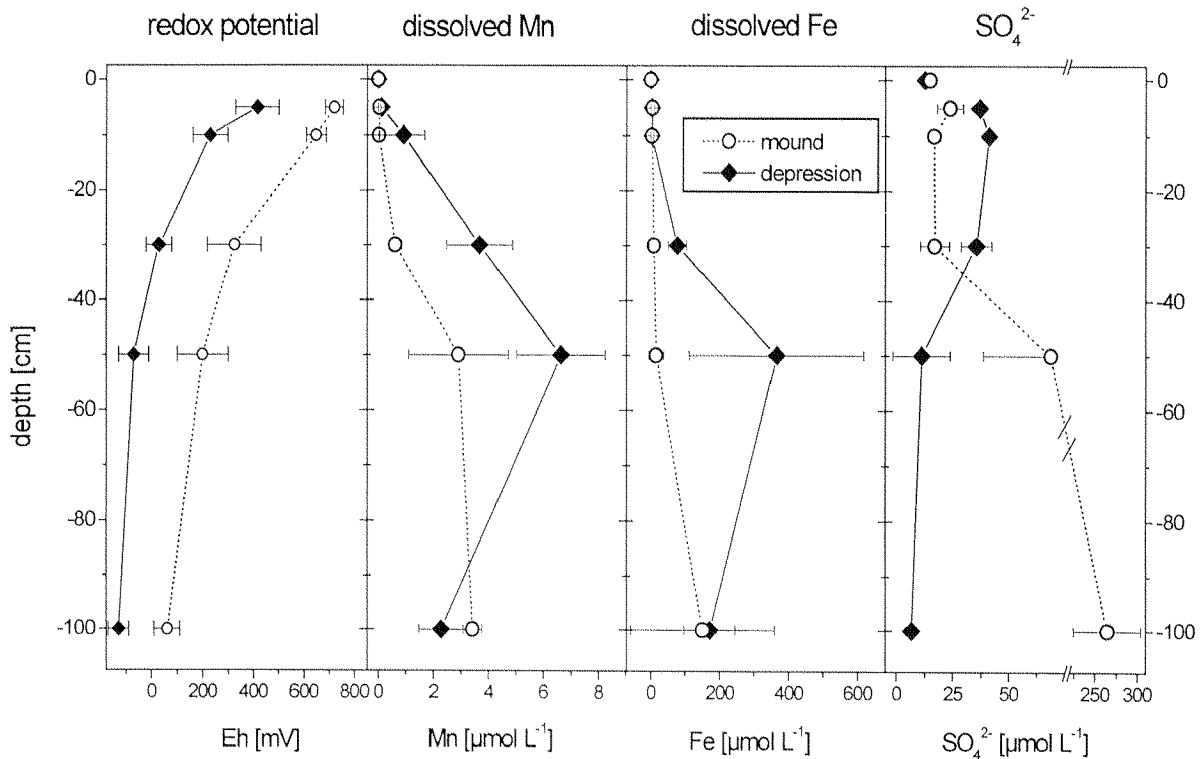


Figure 4.3: Redox potentials and concentrations of dissolved Fe, Mn, and SO_4^{2-} in throughfall and in soil solution from depressions ($n=9$) and from mounds ($n=3$). Means and spatial standard errors from May 1996 to January 1998 (sampling dates = 30).

There was a qualitative, but no direct quantitative relation between measured redox potentials and redox reactions. The critical redox potentials below which reduced elements appeared in the soil solution are consistent with published values (Patrick & Jugsujinda, 1992; Cogger *et al.*, 1992).

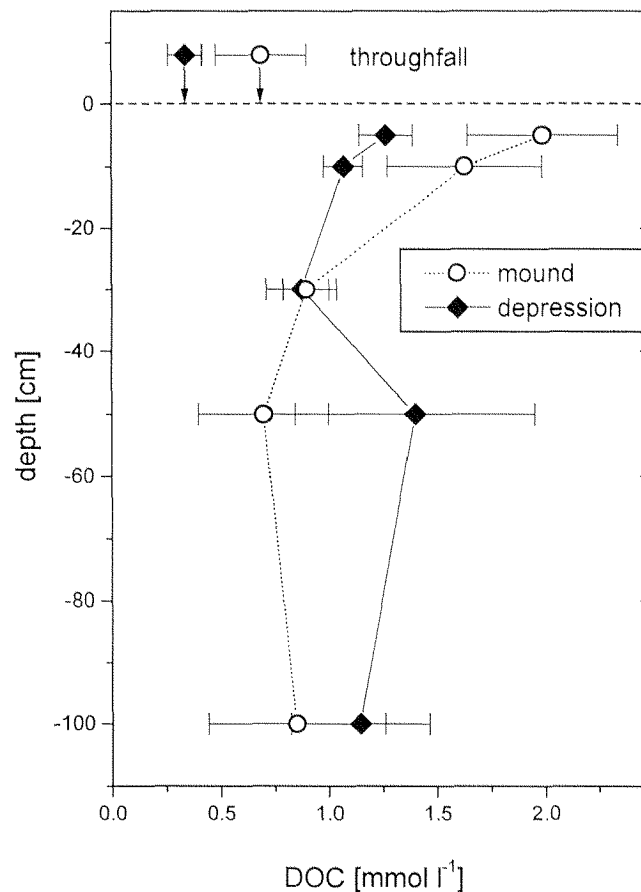


Figure 4.4: DOC concentrations in throughfall and in soil solution from depressions ($n=9$) and from mounds ($n=3$). Means and spatial standard errors from May 1996 to January 1998 (sampling dates $n = 30$).

4.4.2 Depth distribution of DOC and DON in the soil

Dissolved organic carbon concentrations in the upper soil were higher than in throughfall and decreased down to a depth of 30 cm (Fig. 4.4). The depth distribution of DOC concentrations differed considerably between mounds and depressions. At 5 and 10 cm depths DOC concentrations were significantly

higher on the mounds than in the depressions ($p=0.02$), probably due to the leaching of organic matter from the mor layer. The DOC concentrations of the mounds showed a significant larger decrease across the B horizon than those of the depressions ($p=0.01$). DOC concentrations in the depressions remained constant down to 100 cm depth.

In the soil solution at all depths, organic N was the dominant form of N (Fig. 4.5). On the mounds as well as in the depressions, the NH_4^+ and NO_3^- concentrations in the forest floor solution were low ($< 15 \mu\text{mol NH}_4^+ \text{ l}^{-1}$; $< 70 \mu\text{mol NO}_3^- \text{ l}^{-1}$) and decreased from throughfall to the Bg horizon, indicating N immobilisation and/or denitrification as measured by Mohn (1999). The proportion of the DON increased with depth. At depths below 30 cm, the TDN was completely organically bound. Our findings, that DON is the dominant N form in the topsoil, are in accordance with other studies (Sollins & McCorison, 1981; Qualls *et al.*, 1991). In turn, the increasing proportion of DON with depth contrasts with studies conducted in aerobic forest soils (Sollins & McCorison, 1981; Currie *et al.*, 1996). The reason for this is probably both the loss of NO_3^- through denitrification and the low retention of DON under reducing conditions as discussed below for DOC.

Three years of additional input of $30 \text{ kg N ha}^{-1} \text{ y}^{-1}$ had effects neither on DOC nor on DON concentrations. This is in agreement with the low impact of 7 years of high N additions (up to $150 \text{ kg ha}^{-1} \text{ y}^{-1}$) on DOC and DON concentrations in the Harvard forest (Currie *et al.*, 1996).

The C/N ratio was significantly higher in the dissolved than in the solid organic matter, which is consistent with findings in the Harvard forest (Currie *et al.*, 1996). Mounds had higher DOC/DON ratios than depressions ($p=0.01$), reflecting the greater soil C/N ratio of the mor type forest floor layer on mounds (Fig. 4.6).

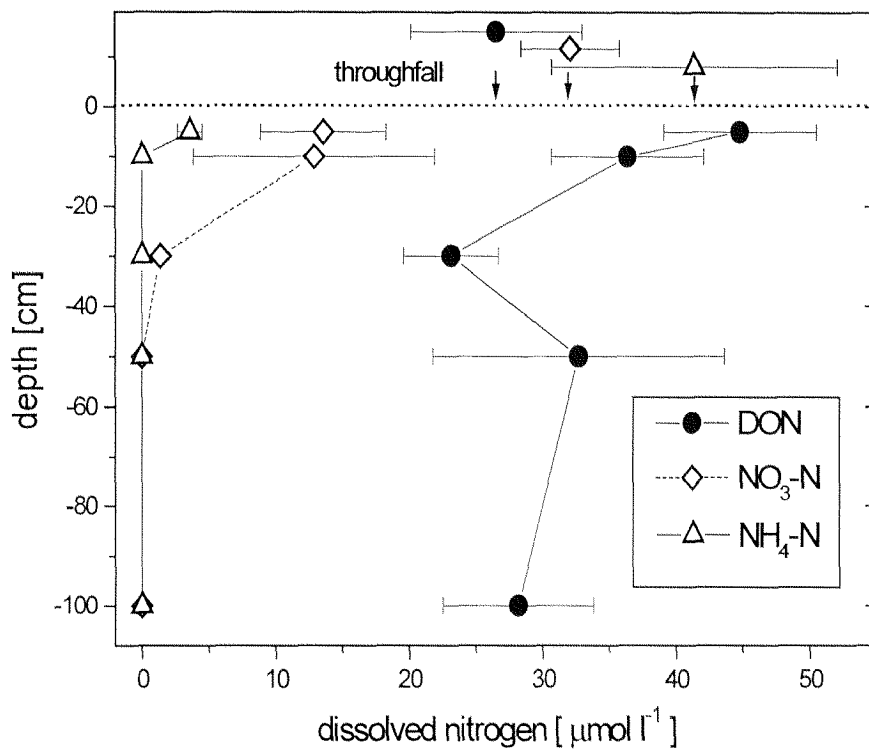


Figure 4.5: Forms of dissolved nitrogen in throughfall and in soil solution. Means and standard errors of 5 plots (4 depressions and 1 mound) without increased N inputs sampled from May 1996 to January 1998 (sampling dates = 30).

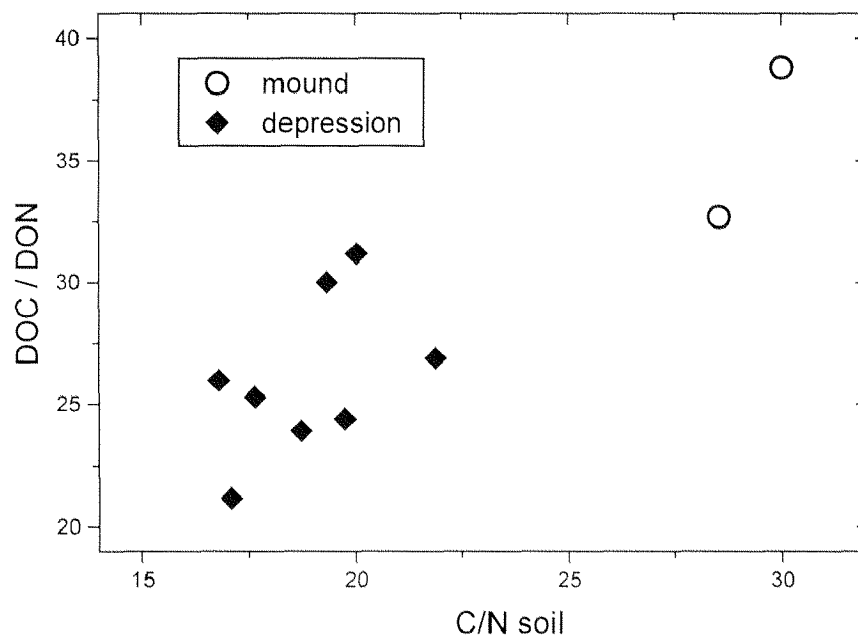


Figure 4.6: Relation between C/N ratio of the soil from 0 to 5 cm depth and DOC/DON ratio of the soil solution at 5 cm depth.

4.4.3 Mobility of DOC in the reduced mineral soil

The subsoil DOC concentrations, averaging 1.2 mmol l^{-1} and reaching up to 3.8 mmol l^{-1} in the depressions (Fig. 4.4), are high above the concentrations found in Spodosols or Inceptisols, in which DOC is effectively retained by the B horizon and where DOC concentrations usually are lower than 0.2 mmol l^{-1} (Guggenberger & Zech, 1993). Concentrations of DOC occurring in the subsoil were similar to those reported in peatlands (McKnight *et al.*, 1985; Moore, 1988), and in Bg horizons from wetlands (McLaughlin *et al.*, 1994).

The consistently high DOC concentrations in the subsoil were probably caused by a lack of strong sorption in the reduced mineral soil in contrast to soils with high Al and Fe oxide contents (Jardine *et al.*, 1989a; Moore *et al.*, 1992). Reducing conditions can decrease the sorptivity of DOC in the Bg horizon by: (i) a higher pH as a result of reduction, which leads to a decreased sorption by oxidic surfaces (Tipping, 1981; Jardine *et al.*, 1989a), and (ii) the depletion of Fe(III)-oxides through reductive dissolution and subsequent leaching of Fe^{2+} (Heyes & Moore, 1992). The pH of the mineral soil solutions were high (7.5-8.5), but were not significantly correlated with DOC concentrations (Table 4.2).

Table 4.2: Simple correlation coefficients between DOC and DON concentrations and inorganic constituents of the soil solution and soil variables. Correlations are based on means of 30 bi-weekly samples from 10 plots.

| | soil C | H ⁺ | Al | Fe | SO ₄ ²⁻ | redox potential |
|-----------------------|---------|----------------|--------|---------|-------------------------------|-----------------|
| 5, and 10 cm depths | | | | | | |
| DOC | 0.81*** | 0.60** | 0.60** | 0.07 | 0.00 | 0.49* |
| DON | 0.58** | 0.29 | 0.49* | 0.13 | 0.31 | 0.33 |
| 30, 50, 100 cm depths | | | | | | |
| DOC | n.d. | -0.12 | 0.15 | 0.91*** | -0.29 | 0.52* |
| DON | n.d. | 0.08 | 0.11 | 0.85*** | -0.25 | 0.46* |

*, **, *** r values significant at $p < 0.05$, $p < 0.01$, $p < 0.001$ respectively

n.d.: not determined in all plots at all depths

However, the solution became oxidized during the aerobic sampling, which probably changed the *in situ* pH. The high Fe concentrations in the subsoil solution suggests that Fe oxides were dissolved at an Eh lower than 150 mV (Fig. 4.3). Furthermore, dissolved Fe was significantly correlated with DOC in the subsoil (Table 4.2).

4.4.4 Hydrophilic and hydrophobic DOC

In order to verify our findings of a low retention of DOC under reducing conditions, DOC was fractionated into hydrophobic and hydrophilic compounds. Numerous studies have shown that the mineral soil acts as a chromatographic system with a strong retention of lignin-derived hydrophobic DOC (rich in carboxylic and phenolic acidity) and little retention of hydrophilic compounds (Jardine *et al.*, 1989; Guggenberger & Zech, 1993).

At 5 cm depth, the mean proportions of hydrophilic and hydrophobic DOC were 33 and 67% respectively (Table 4.3), which is typical for forest floor solutions (Cronan & Aiken, 1985; Guggenberger & Zech, 1993). However, the vertical variation of DOC fractions from the topsoil to the mineral Bg horizon was distinctly different from studies with Spodosols and Inceptisols. In the Fichtelgebirge (Germany), Guggenberger & Zech (1993) found a decline in the proportion of hydrophobic DOC from 65% in the forest floor to 40% in the mineral soil at a depth of 30 cm. In our study with Humaquepts, the proportions of DOC fractions remained almost constant over soil depths (Table 4.3) which shows that there was little preferential retention of hydrophobic DOC.

The retention of hydrophobic DOC from the topsoil to the mineral soil was closely related to the dissolved Fe concentrations of the B horizon (Fig. 4.7). The higher the Fe concentrations in the soil solution of the B horizon, the less hydrophobic DOC was sorbed between top and mineral soil. This again suggests that the reductive dissolution of Fe-oxides is the major reason for the high mobility of DOC under reducing conditions.

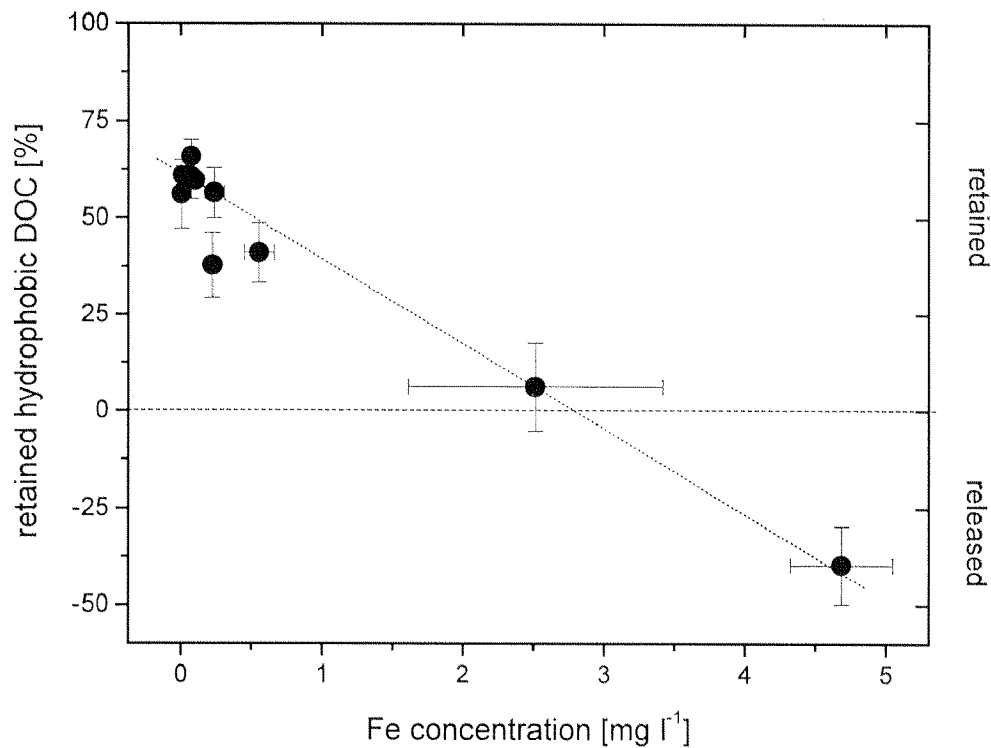


Figure 4.7: Relationship between hydrophobic dissolved organic carbon (DOC) retained between 5 and 30 cm depth and Fe concentration at 30 cm depth. Retained DOC (%) was estimated by the difference between the DOC concentrations at 5 and 30 cm divided by the DOC concentrations at 5 cm depth. Each point represents one circular plot ($n=10$), sampled from summer 1996 to spring 1997. Means and standard errors of 8 sampling dates.

4.4.5 DOC and Fe at the interface between aerobic and anaerobic soil

Soil water from the reduced mineral soil becomes aerobic when it enters the stream. Thus, processes occurring at the interface between anaerobic and aerobic soil are important for the contribution of DOC from the reduced mineral soil to the stream water.

We were not able to sample soil solution exactly at the anaerobic-aerobic interface. However, during the aerobic sampling of the soil solution from the Bg horizon, brownish-red material precipitated in the soil solution collecting devices. We suppose that analogous precipitate occur at the interface between anaerobic and aerobic soil. Acidification results in dissolution of these

precipitates. The comparison of soil solution samples with and without acidic dissolution of precipitated matter and the analysis of the precipitates itself therefore points to the process occurring at the anaerobic-aerobic interface.

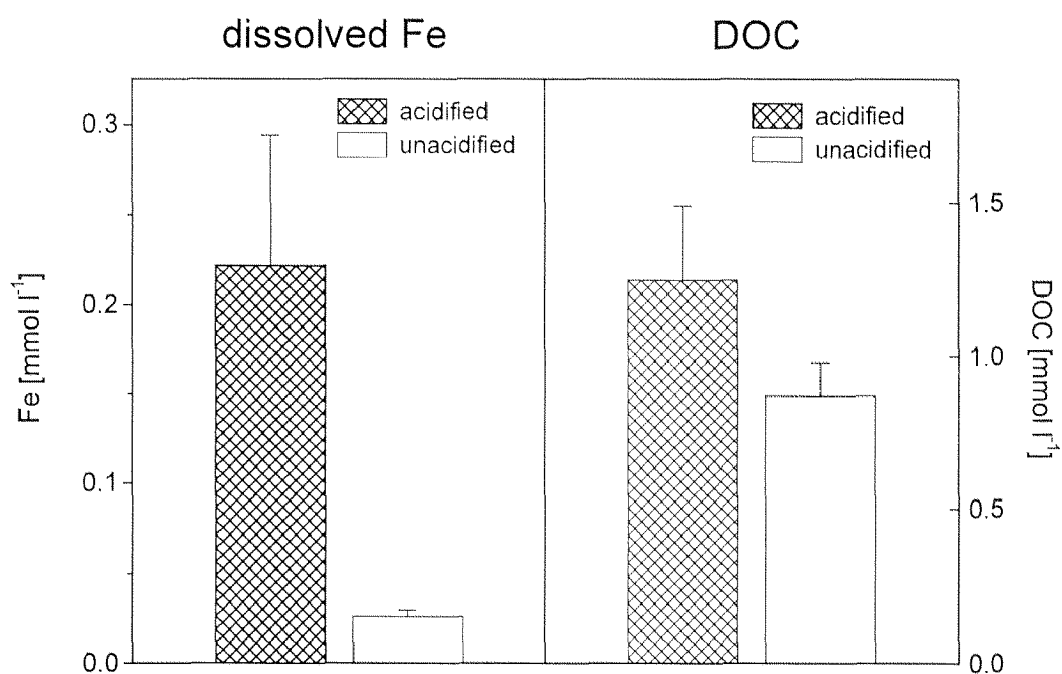


Figure 4.8: Effect of acidification on soil solution samples of 30, 50 and 100 cm depths from the Bg horizon. Acidification dissolved the brownish-red precipitates formed during the aerobic sampling of the soil solution from the reduced mineral soil. Means and standard errors of 24 samples.

As expected, the acidic dissolution of precipitates in the soil solution samples from the reduced B horizon increased Fe (+750%) and DOC (+40%) concentrations significantly (Fig. 4.8; $p < 0.01$). This indicates that precipitates contained significant amounts of Fe and C. Acidified samples had a DOC to Fe ratio of 0.7-4 : 1 while unacidified samples had values between 7:1 and 9:1. The comparison with published critical values of 6-8:1 (Moore, 1988) shows that DOC of the acidified soil solution was oversaturated with respect to Fe. Precipitates collected on glass microfibre filters contained between 30 to 40% Fe

and between 5 and 12% C. These findings suggest that DOC, mobile under reducing conditions, is co-precipitated with Fe(III) oxides at the interface between anaerobic and aerobic soil. Our results are consistent with experiments conducted in bottom sediments, which showed higher DOC and Fe concentrations in anaerobic than in aerobic pore waters, and co-precipitation of Fe and DOC at the interface between both pore waters (Hunchack-Kariouk & Suffet, 1994).

As a consequence of the formation of Fe-carbon precipitates, the input of DOC from the reduced mineral soil to stream water is probably lower than would be expected from the high DOC concentrations in the reduced mineral subsoil. This is supported by the low Fe and DOC concentrations in the stream water (Table 4.3).

4.4.6 DOC and DON in surface and subsurface flow

The clayey subsoil was well structured, had mouse burrows, and contained rotten wood and roots. As indicated by a very rapid response of the subsurface flow to rainfall events (Figure 4.9 and 4.11) and by tracer experiments, a large part of the infiltrating rainwater moved preferentially through the subsoil (Feyen, 1998). Since solute sampling by suction cups often fails to collect bypass flow (White, 1985), the surface and subsurface flow were sampled with sand-filled 'runoff gutters' from delineated plots (11.8 and 13.8 m²) and compared to the soil matrix water collected by suction devices.

The chemical composition of soil water differed considerably between matrix and subsurface flow. The subsurface flow of 30 to 60 cm depth had higher NO₃⁻ and lower Fe concentrations compared to the soil matrix water (Table 4.3). This indicates that either the residence time in the Bg horizon is too short for equilibrium and/or that preferential flow paths are more oxidized than the soil matrix. Based on the characteristics of DOM, preferential flow paths appear to have a more oxidizing environment (Table 4.3). Both the DOC/DON ratio and the proportion of hydrophobic DOC were lower in the subsurface flow than in

the soil matrix water. This points to an increased alteration of DOM along aerobic preferential flow paths compared to the reduced soil matrix. Hydrophobic compounds, having a lower nitrogen content than hydrophilic compounds (McKnight *et al.*, 1985; Qualls *et al.*, 1991), were probably preferentially sorbed along the aerobic flow paths, covered with Fe oxides, mainly lepidocrocite (Disserens, 1992).

Table 4.3: Characteristics of soil water sampled with suction plates (5 cm) and ceramic cups (30 cm), of surface (0-5 cm) and subsurface flow (5-30 cm, 30-60 cm) from the delineated plots (11.8 and 13.8 m²), and of stream water during 1996 and 1997. Coefficients of temporal variation (%) are given in parentheses.

| | Fe ^a μmol l ⁻¹ | NO ₃ ^{-a} μmol l ⁻¹ | DOC ^a mmol l ⁻¹ | DON ^a μmol l ⁻¹ | DOC/DON ^a mass ratio | HoDOC ^b % of DOC |
|-------------------------|---|---|--|--|------------------------------------|--------------------------------|
| mound (n=3) | | | | | | |
| 5 cm (O) | 4.6 (56) | 15.2 (150) | 1.99 (21) | 49.3 (36) | 36 (17) | 71 (13) |
| 30 cm (Bw) | 9.3 (44) | 2.4 (250) | 0.90 (30) | 26.4 (47) | 36 (28) | 60 (12) |
| runoff | | | | | | |
| 0-5 cm | 3.4 (22) | 229 (29) | 1.74 (8) | 46.4 (6) | 32 (12) | n.d. |
| 30-60 cm | 1.3 (76) | 48 (46) | 0.82 (18) | 29.3 (19) | 24 (24) | 57 (9) |
| depression (n=9) | | | | | | |
| 5 cm (O, A) | 3.1 (56) | 22.2 (126) | 1.27 (23) | 45.0 (38) | 26 (23) | 65 (11) |
| 30 cm (Bg) | 78.1 (74) | 1.6 (325) | 0.95 (22) | 32.1 (61) | 28 (46) | 60 (10) |
| runoff | | | | | | |
| 5-30 cm | 3.2 (22) | 51 (68) | 0.98 (23) | 45.7 (44) | 20 (22) | 57 (7) |
| 30-60 cm | 2.8 (9) | 66 (48) | 1.26 (28) | 44.3 (32) | 25 (35) | 59 (7) |
| stream water | 0.82 (53) | 17.0 (300) | 0.34 (33) | 20.7 (31) | 17 (29) | 55 (13) |

(n: sampling dates)

^a: soil solution, n = 30; runoff water, n = 20 to 27, stream water, n = 45

^b: soil solution, n = 8; macropore water, n = 6; stream water, n = 11

n.d.: not determined

HoDOC: hydrophobic DOC

4.4.7 Temporal DOC dynamics in the surface and subsurface flow

To identify the significance of flow processes for DOC transport through the soil, samples of the surface and subsurface flow from the delineated plots were taken with a high temporal resolution during simulated storm events.

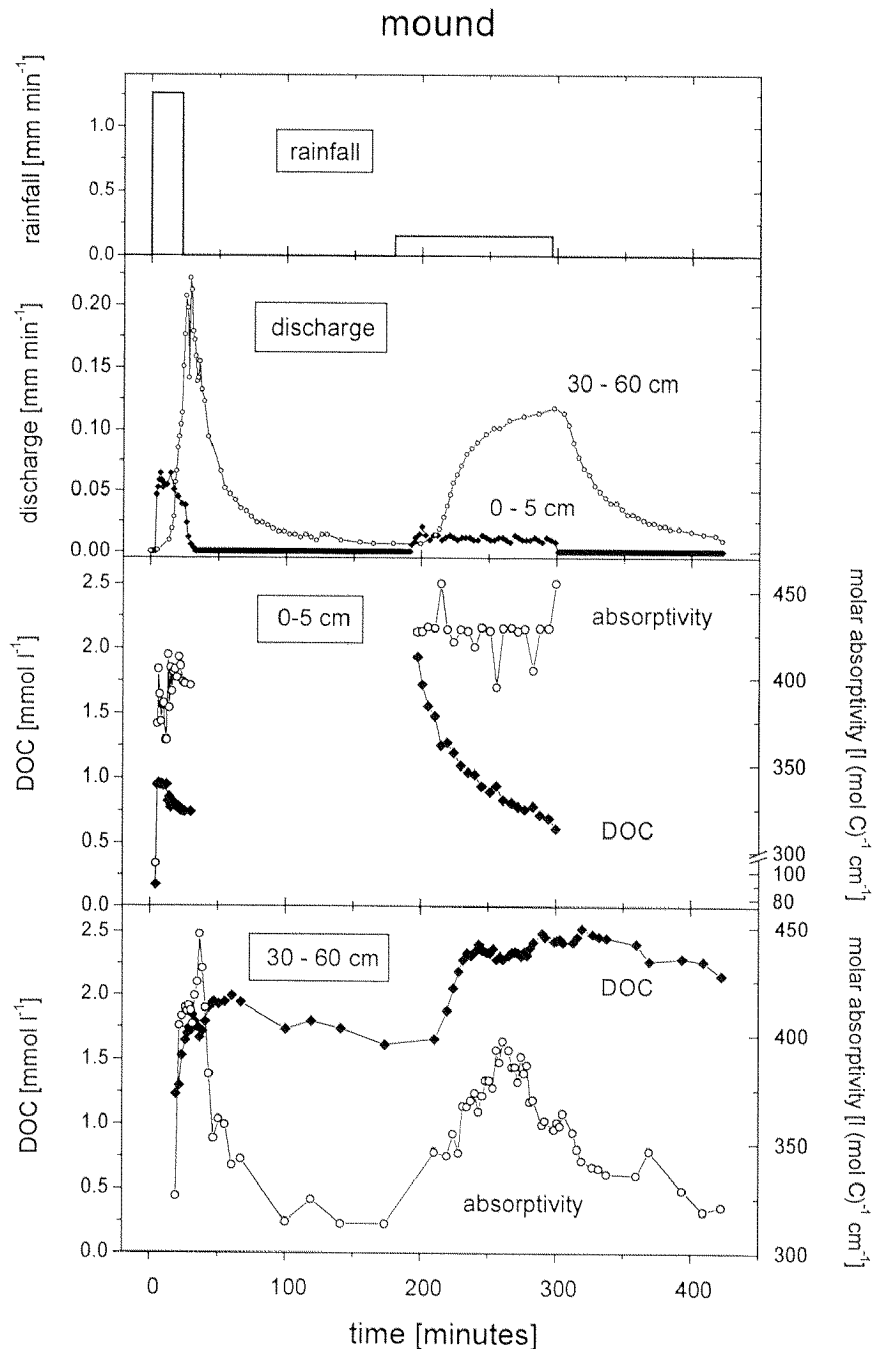


Figure 4.9: Discharge, concentrations and molar UV absorptivity of dissolved organic carbon (DOC) at 285 nm during the simulated rainfalls in the delineated mound plot.

The discharge responded rapidly to the irrigation (Fig. 4.9 and 4.11). Surface flow (0 to 5 cm depth) occurred only on the mound plot, probably promoted by the hydrophobic forest floor. In both delineated plots, the subsurface flows (30 to 60 cm depth) peaked 20 minutes after the start of the irrigation. Given the low permeability of the clayey soil matrix with a saturated conductivity lower than 5 cm d^{-1} , this rapid response of the subsurface flow is a strong indication of preferential water movement through the subsoil.

Dissolved organic carbon concentrations in the surface and subsurface flow increased rapidly with increasing discharge. Surface flow DOC showed a sharp rise immediately at the onset of the irrigation, followed by rapid exponential decline. In the subsurface flow (30 to 60 cm), concentrations of DOC were highest in the later stages of the simulated storm (Fig. 4.9 and 4.11). Comparable increases of DOC during storm events were observed for the larger sub-catchments (1500 m^2) and for the headwater catchment (0.7 km^2). Increasing DOC concentrations with increasing discharge are generally explained by (i) a change in water flow paths leading to a larger contribution of DOC-rich surface water to the runoff during peak flow as shown for large catchments (Tate & Meyer, 1983; Easthouse *et al.*, 1992), and/or (ii) a limited contact time between the soil solid phase and the soil solution caused by preferential flow and chemical nonequilibrium conditions (Jardine *et al.*, 1990; Weigand & Totsche, 1998). In our delineated plots, DOC concentrations of the subsurface flow at the discharge peak were twice as high as in the soil solution of corresponding depth. Since we sampled the subsurface flow at a distinct depth in the subsoil, this increase can only result from a vertical DOC transport from the topsoil.

The response of DOC differed between both rainfall events, indicating that the DOC-discharge relationship was nonlinear. This could be either due to changing initial soil conditions or to the dependency of flow paths on flow velocities. On the mound, the water table was -78 cm before the first, and -68 cm before the second event. Volumetric water content at 5 cm depth was 0.33 and 0.40 before the first and the second event, respectively.

The temporal pattern of the molar absorptivity of DOC at 285 nm shows that the characteristics of DOC varied considerably during storm events (Fig. 4.9 and 4.11). The molar UV absorptivity can be used as an easily measurable spectroscopic predictor of aromaticity and molecular weight (Chin *et al.*, 1994). In our study, the molar absorptivity of DOC at 285 nm was significantly correlated with the percentage of hydrophobic DOC ($r^2 = 0.56^{***}$, $n = 30$). Thus, the molar UV absorptivity of DOC showed a decrease with depth analogous to hydrophobic DOC, suggesting a preferential sorption of DOC with a high molar UV absorptivity (Fig. 4.10).

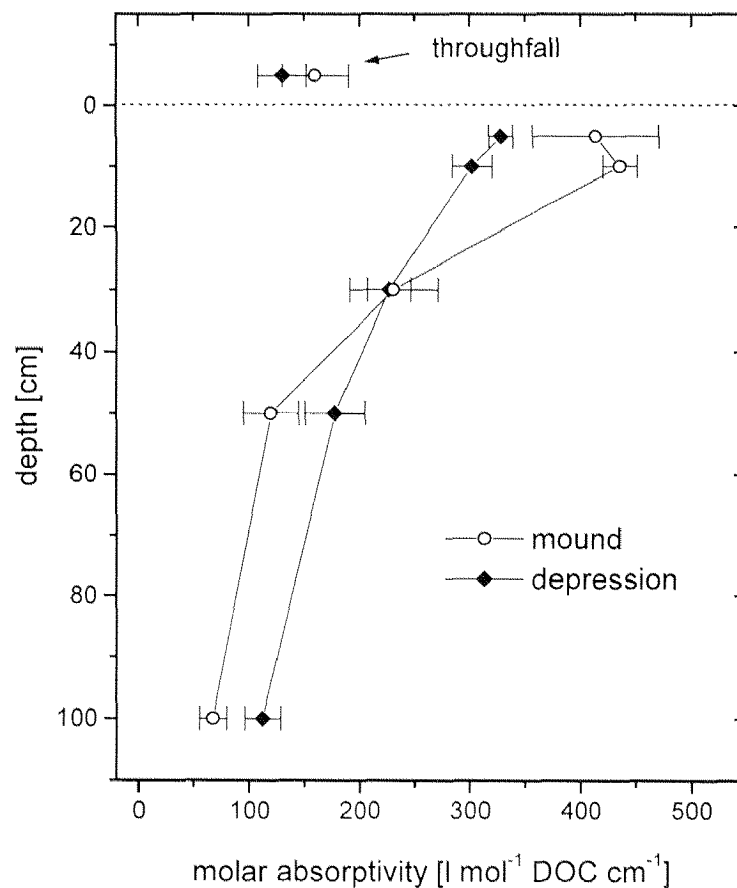


Figure 4.10: Vertical distribution of the molar UV absorptivity of DOC in the Humapuepts. Mean and standard errors of 9 plots in depressions and 3 plots on mounds.

In the subsurface flow, the molar UV absorptivity of DOC increased with increasing discharge (Fig. 4.9 and 4.11). At peak flow, the spectroscopic characteristics of DOC in the subsurface flow corresponded to that of the topsoil solution. This indicates that DOC is transported from the topsoil into the subsurface with no or little alteration due to a limited contact with the mineral soil matrix.

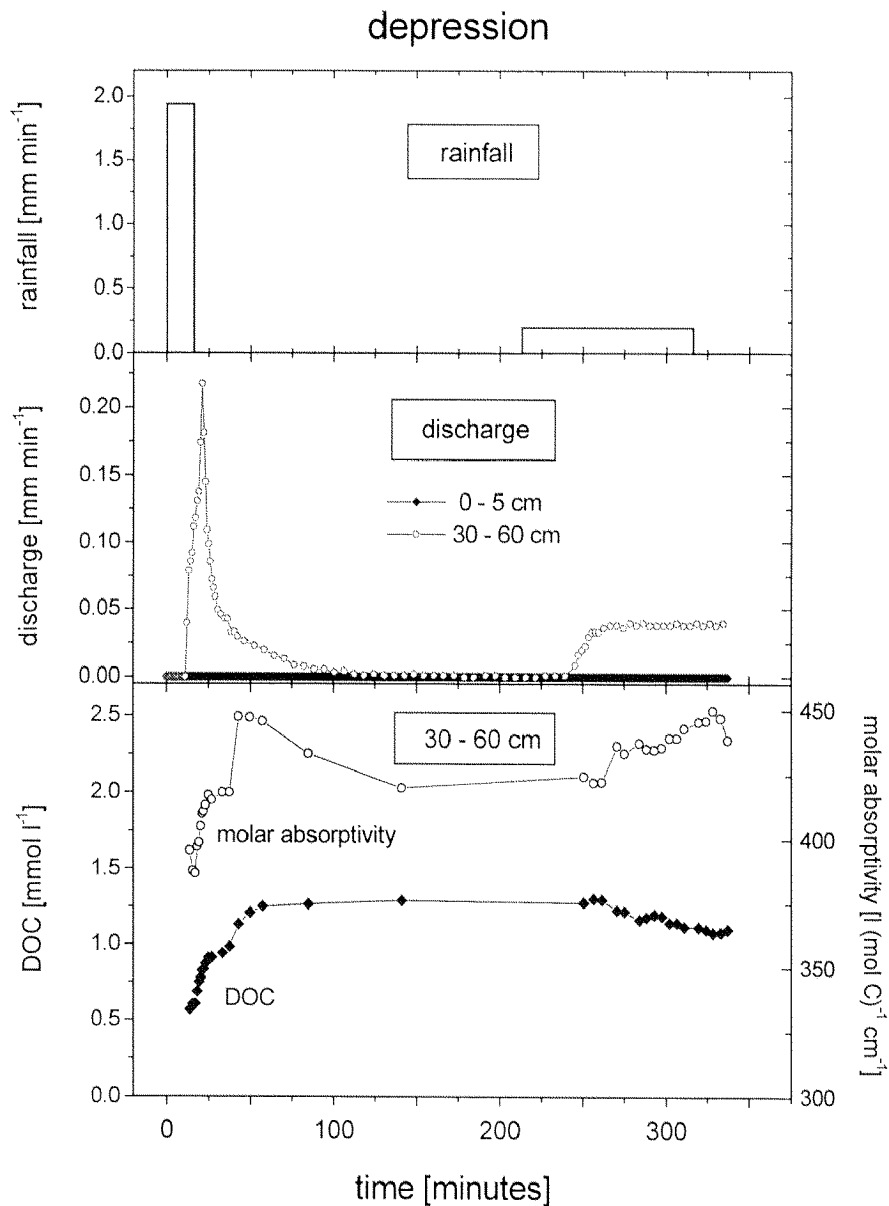


Figure 4.11: Discharge, concentrations and molar UV absorptivity of dissolved organic carbon (DOC) at 285 nm during the simulated rainfalls in the delineated depression plot.

The molar UV absorptivity of DOC had a greater linear correlation to discharge ($r^2 = 0.74^{***}$, mound plot; $r^2 = 0.48^{***}$, depression plot) than DOC concentrations, which exhibited a counterclockwise hysteresis with discharge. In comparison to DOC concentrations, the UV absorptivity of DOC decreased faster on the descending limb of the subsurface hydrograph. This suggests that the characteristics of DOC depend on flow velocity rather than absolute concentrations. At high flow velocities, the contact time between solutes and the soil solid phase was reduced and thus relatively more of the 'surface reactive' DOC compounds (= high UV absorptivity) were transported to the subsoil. At reduced flow velocities, the retention of these compounds increased strongly.

The sensitivity of DOC to flow variations was more pronounced in the delineated mound than in the depression plot (Fig. 4.9 and 4.11). This is probably related to the larger decrease with depth of DOC concentrations and molar UV absorptivity on the mounds than in the depressions (Fig. 4.4 and 4.10). Thus, on the mounds, DOC is affected to a greater extent by the transport of topsoil water to the subsurface than in the depressions. Another explanation for the greater temporal DOC variability on the mounds compared to the depressions could be the higher sensitivity of DOC transport to flow variations in a soil with a higher sorption capacity. This is supported by the column experiments of Weigand & Totsche (1998), which showed that DOC transport was only sensitive to flow velocities in a sorptive goethite-coated quartz sand but not in a pure quartz sand with little DOC sorption.

4.5 Summary and conclusions

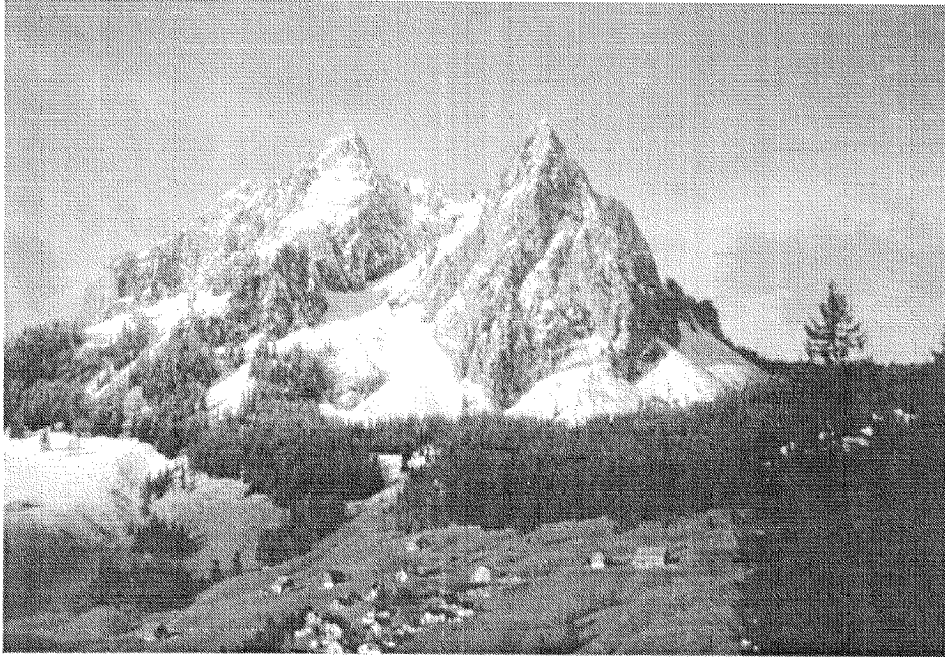
The mobility of DOC and DON in the studied Humaquepts was related to the redox environment. The vertical decrease of DOC and DON concentrations across the mineral soil was significantly higher in the oxidized horizons of the drier mounds than in the reduced mineral soil of waterlogged depressions. The low retention of DOC under reducing conditions, particularly of hydrophobic DOC, was probably caused by a lack of sorption of DOC. Possible mechanisms are a high pH due to reduction and/or the reductive dissolution of Fe-oxides. However, as indicated by the formation of precipitates during the aerobic sampling of soil solution from the Bg horizon, DOC co-precipitates with Fe at the interface between anaerobic and aerobic soil. Therefore, the DOC input from reduced mineral soils to aerobic stream water is probably lower than would be expected from the high DOC concentrations in the Bg horizon.

DON was the dominant form of dissolved N in the soil solution. In the reduced mineral soil, the dissolved N was completely organically bound. This was probably due to both immobilisation of inorganic N and low retention of DON under reducing conditions.

Runoff processes had a large impact on DOC mobility. Concentrations and spectroscopic characteristics of DOC in the subsurface flow changed within minutes with increasing discharge. At peak flow, the spectroscopic characteristics of DOC in the subsurface flow corresponded to that of the topsoil, indicating a decreased retention of 'reactive' DOC compounds. At reduced flow velocities, the retention of these compounds increased strongly. These findings suggest that DOC concentrations and properties are sensitive to flow velocities and that DOC is preferentially transported to the subsoil at high discharge.

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Chapter 5



Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments - the significance of water flow paths

with

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submitted to *Biogeochemistry*

5.1 Abstract

Dissolved organic carbon (DOC) and nitrogen (DON) are important components for nutrient and pollutant transport through catchments. In this study, we measured concentrations and properties of DOC and DON seasonally and during storms in the soil solution and in the runoff of three catchments: a forest and a grassland sub-catchment of 1500 m² delineated by trenches, and a headwater catchment of 0.7 km².

DOC and DON concentrations in weekly stream water samples were positively correlated with discharge. During individual storms, concentrations and properties of DOC and DON changed drastically. In all catchments, DOC concentrations increased by 6 to 7 mg DOC l⁻¹ compared to base flow, with the largest relative increase in the headwater catchment (+ 350%). Concentrations of DON, hydrolysable amino acids, and phenolics showed comparable increases, whereas the proportion of carbohydrates decreased at peak flow. To determine whether changes in hydrological pathways could explain the large temporal variations, we conducted an end-member mixing analysis (EMMA) using electrical conductivity, Ca²⁺, SO₄²⁻, and Cl⁻ concentrations to separate the runoff into three water flow paths. Prediction of DOC and DON concentrations on the basis of EMMA showed that changes in water flow paths largely explained the temporal variability.

DON was the major form of the dissolved N in soil and stream water. DON export from all catchments was approximately 6 kg N ha⁻¹ y⁻¹, which corresponds to 60% of the total N export and to 35% of the ambient N deposition. In contrast to NO₃⁻, DON concentrations showed only low seasonal variations and depended upon discharge in the catchment runoff. This suggests that the export of DON from the ecosystem is regulated by abiotic processes, such as changes in water flow paths, rather than by biotic processes.

5.2 Introduction

Dissolved organic carbon is an important component of solutions in terrestrial and aquatic ecosystems through its influence on acidity, nutrient and contaminant mobility (Eshleman & Hemond, 1985; Qualls *et al.*, 1991). DOC contains a range of organic compounds, from simple sugars to complex fulvic and humic acids (McKnight *et al.*, 1985; McDowell & Likens, 1988; Guggenberger & Zech, 1993). Concentrations and composition of DOC change as a result of both biotic and abiotic processes when it moves through the ecosystem (McDowell & Likens, 1988; Meyer, 1990; Guggenberger & Zech, 1993). Despite considerable information on various aspects of DOC cycling, little is known about the nitrogen fraction of DOC (Northup *et al.*, 1995; Creed & Band, 1998). However, DON is found to be the dominant vehicle of N leached from forest floors (Yavitt & Fahey, 1984; Qualls *et al.*, 1991), of N transported by subsurface runoff (Hill *et al.*, 1999), and of N exported from catchments (Hedin *et al.*, 1995; Arheimer *et al.*, 1996).

In catchments, DOC export during storms may account for a substantial proportion of the total DOC export (Sedell & Dahm, 1990; Hinton *et al.*, 1997). Easthouse *et al.*, (1992) and Hinton *et al.* (1998) showed that the large temporal variations of DOC concentrations and properties in streams were caused by changes in water flow paths contributing to the runoff. Other studies identified in-stream processes such as throughfall onto the stream, stream channel expansion at increasing discharge, and DOC production by algae as important regulators for variations in DOC concentrations (Kaplan & Bott, 1982; Tate & Meyer, 1983; Mulholland & Hill, 1997). To understand the regulating mechanisms of DOC export from catchments, there is a need for an interdisciplinary approach, which combines (1) the identification of water flow paths through the catchment with (2) the analysis of the composition of streams DOC as an indicator for the DOC origin (Cronan, 1990; Meyer, 1990; Kaplan & Newbold, 1993).

In this study, we measured concentrations and properties of DOC and DON in the soil solution, in the runoff of small sub-catchments of 1500 m², experimentally delineated by trenches, and in a stream draining a headwater catchment of 0.7 km². Water flow paths during storms were identified with an end-member mixing analysis based on inorganic chemistry (Christophersen *et al.*, 1990; Mulder *et al.*, 1995). This way we were able to track the fate of DOC and DON through the ecosystem and to separate effects of changing water flow paths and in-stream processes.

5.3 Materials and methods

5.3.1 Study site

The study area is located in the Alptal (47°03N, 8°43E), a south-north oriented valley in the Prealps of central Switzerland (Fig. 5.1). The mean air temperature is 6°C. The parent rock material is Flysch, consisting of alternating calcareous sandstones with argillite and bentonite shists. Major soil types are clayey Gleysols of low permeability with a water table close to the surface throughout the year.

Erlenbach headwater catchment: The Erlenbach headwater catchment covers 0.7 km², consisting of 40 % forest (mainly *Picea abies* (L.)) and 60% grassland (Fig. 5.1, Keller, 1990). The average slope is 20% with west aspect. At some locations open ditches drain waterlogged soils to improve slope stability. The stream channel is steep and narrow and does not have a riparian zone.

Runoff is measured with a large V-notch weir. The average annual water balance (1978-1993) shows that the total amount of precipitation of 2190 mm is partitioned into 1740 mm of runoff (80%) and 450 mm of evapotranspiration (20%) (Burch, 1994). The sampling of stream water was coupled to the permanent runoff measurements. Flow-proportional samples were automatically taken, bulked and collected weekly.

Experimental sub-catchments: At mid slope of the headwater catchment, three sub-catchments of 1500 m² were set up to study N cycling within the NITREX project (Schleppi *et al.*, 1998). One grassland and two forested areas were hydrologically delineated by 80 cm deep trenches. Since the clayey subsoils have a low permeability and water levels are high throughout the year (< 50 cm depth), it is assumed that deep seepage is small compared to surface and lateral subsurface runoff. This is supported by a closed water balance (Schleppi *et al.*, 1998).

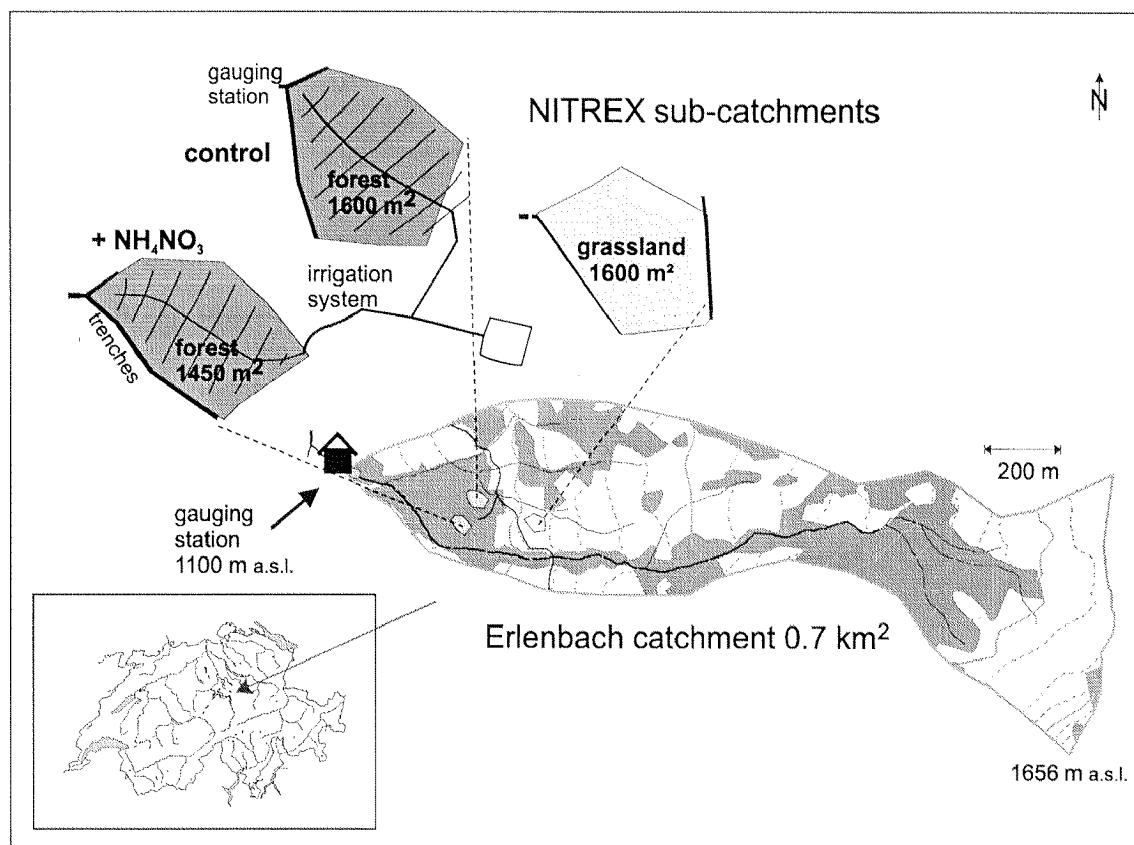


Figure 5.1: Location of the Erlenbach headwater catchment in Alptal, Switzerland, and experimental set-up of the forest and grassland sub-catchments.

In the forest sub-catchments, vegetation and soil form a mosaic pattern, which is closely related to the micro-topography. *Picea abies* (L.) and *Vaccinium* sp. grow on mounds where water tables are below 40 cm depth. The soil type is

an umbric Gleysol with an oxidised Bw horizon and a mor type humus layer. In depressions, the water table frequently reaches the surface. The mineral soil consists of a permanently reduced Bg horizon overlain by a muck humus (mollic Gleysol). The depressions are too wet for tree growth and the ground vegetation is dominated by *Caltha palustris*, *Petasites alba*, *Poa trivialis* and *Carex ferruginea* (Müller, 1997).

In contrast to the forest sub-catchments, the grassland sub-catchment shows no distinct micro-relief. The grassland is a fallow since 15 years and the vegetation consists mainly of *Poa trivialis* and *Carex ferruginea*. The soil is better drained than the depressions of the forest stand. A mollic epipedon is found on top of a thin Bw horizon and a permanently reduced Bg horizon.

Table 5.1: Selected properties of soil types.

| horizon (depth) | pH (CaCl ₂) | redox potential ^a [mV] | C content ^b [g kg ⁻¹] | N content ^b [g kg ⁻¹] | texture ^c % clay/silt/sand |
|-------------------|----------------------------|---|--|--|---|
| mound | | | | | |
| LF (0- 5 cm) | 3.3 | | 423 | 19 | |
| A (5-10 cm) | 4.6 | + 600 to + 800 | 70 | 4.1 | 47/47/6 |
| Bw1 (10-20 cm) | 5.2 | + 400 to + 700 | 27 | 1.8 | |
| Bw2 (20-50 cm) | 5.9 | + 200 to + 600 | 14 | 0.9 | 46/46/5 |
| depression | | | | | |
| LF (0- 2 cm) | | | 423 | 19 | |
| A (2-10 cm) | 5.4 | + 100 to + 600 | 156 | 8.5 | 51/45/4 |
| BA (10-20 cm) | 6.1 | 0 to + 400 | 86 | 4.8 | 44/44/11 |
| Bg (20-50 cm) | 6.9 | - 250 to + 100 | 16 | 0.8 | 43/42/15 |

^a measured with Pt electrodes (n = 20 per depth)

^b measured with a Carlo Erba C/N analyser

^c from Schleppe *et al.* (1998)

Soil properties and soil solution characteristics are strongly influenced by the carbonatic parent rock material and the depths of the water table (Tables 5.1 and 5.2). Redox potentials showed a vertical decrease, whereas soil pH, electrical conductivity (EC) and concentrations of base cations all increased with depths.

Water tables were recorded automatically every ten minutes by an ultrasonic device in both soil types, mounds and depressions. The discharge was permanently measured with V-notch weirs at the outlet of the sub-catchments. Samples of the runoff were taken proportionally to the measured discharge and collected weekly. As in the headwater catchment, this enabled us to estimate element exports by multiplying measured concentrations and discharge.

5.3.2 Monitoring of DOC and DON during storms

In all catchments, discharges was sampled with a high temporal resolution during four storms in the summer 1998. Flow proportional automatic sampling devices (ISCO 2900, Lincoln, NE, USA) were connected to the permanent discharge measurements in all catchments. The sampling rates were adjusted to collect one sample per 0.9 mm runoff.

5.3.3 Sampling of soil solution

Soil solution samples were collected in soil plots of 20 m² within the experimental site. Three plots were located on mounds, 6 plots in wet depression of the forest, and 3 plots in the better drained grassland. Five of the plots, one on a mound and four in depressions, received additional N inputs simultaneously added to rainfalls by sprinklers. Five control plots received the equivalent amount of additional non-amended rainwater, whereas 2 plots did not receive any additional inputs. Soil solution was sampled with horizontally installed porous glass filter plates (Ø 90 mm, max. pore radius <16 µm) 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.

The amount of rainfall was monitored in intervals of 10 minutes on a meteo tower above the forest and on open land close to the research site. Bulk deposition was sampled weekly on the grassland sub-catchment. Throughfall was collected on 10 plots in the forest with polyethylene (PE) funnels (\varnothing 15 cm). Sampling was conducted weekly and bulked bi-weekly.

5.3.4 Sample preparation and analyses

All solution samples were collected in acid-washed PE bottles, filtered (0.45 μm , Schleicher & Schuell ME25) within the next 48 h and stored at 4°C. For element analyses, sub-samples were acidified with concentrated HNO_3 to 2.5 % by volume. If time until analysis exceeded 1 month, samples were stored frozen. For the characterisation of DOC, water from the subsoil and from the stream was concentrated 3 to 5 times by freeze-drying to achieve accurate measurements.

All samples were analysed for major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe_{tot} , Al_{tot}) by induced-coupled plasma atomic emission spectrometry (Perkin Elmer ICPAES OPTIMA 3000), anions (Cl^- , NO_3^- , SO_4^{2-} , H_2PO_4^-) by ion chromatography (DIONEX DX-120), and NH_4^+ colorimetrically by automated flow injection analysis (Perkin Elmer FIAS-300).

Dissolved organic carbon (DOC) was measured with a Shimadzu TOC-500 analyser. Total dissolved nitrogen (TDN) was estimated by alkaline peroxodisulfate digestion converting all nitrogen to nitrate (Solorzano & Sharp, 1980; details see chapter 4). In contrast to the original procedure, the autoclavation bottles were tightly closed. This improved the reproducibility of the method considerably. Nitrate was then measured photometrically at 210 nm

with a Shimadzu UV-160 spectrophotometer. DON was obtained by subtracting the concentration of inorganic species from TDN. Recovery of the standards glycine, purine, pyridine and humic acid (Fluka) was found to be between 95 and 101 %. The coefficient of variation of the TDN measurements for a reference soil solution (n= 10) was found to be below 3 %. However, the detection limit for DON depends on the background of inorganic N. In bulk deposition and stream water during snowmelt, both typically with high inorganic N and low DON concentrations, the detection limit was about 0.1 mg I⁻¹. In the soil solutions of the subsoil, which contained no mineral N, DON measurements were reproducible even at concentrations of 0.05 mg N I⁻¹.

Dissolved organic matter characterisation. To characterise DOC, soil and stream water samples were fractionated into hydrophilic and hydrophobic DOC by the use of Amberlite XAD-8 adsorber columns (Aiken & Leenheer, 1993). The DOC adsorbing at pH 2 on XAD-8 resin, is operationally defined to be hydrophobic, while hydrophilic DOC passes through the columns. The molar UV absorbance of DOC at 285 nm was measured in 1 cm quartz window cuvettes with a double beam Shimadzu UV-160 spectrophotometer. Hydrolysable amino-acids were analysed according to a modified procedure of Allen (1981) (Michalzik, pers. comm.). 1.5 ml of sample were hydrolysed with 0.6 ml of 32% NaOH for 2 h. After neutralization, amino acids were measured colorimetrically at 570 nm using a ninhydrin reactive and cystein and glycin as standards. Phenol concentrations were measured according to Swaine & Hillis (1959) with Folin-Denis reactive. Hydrolysable carbohydrates content was determined by the phenol-sulfuric acid method (Chaplin, 1994), using a 5% phenol solution and glucose as standard.

5.3.5 End-member mixing analysis (EMMA)

To obtain information about the water flow paths in the catchments and their influence on DOC and DON in the runoff, an end-member mixing analysis (EMMA) (Christophersen *et al.*, 1990; Mulder *et al.*, 1995) was performed. The EMMA allows to identify the contribution of observed water sources or flow

paths (the so called end-members) to runoff based upon their water chemistry using a least-square regression technique. In order to be used successfully in EMMA, solutes must (1) differ significantly between end-members, and (2) mix conservatively. Potential end-members are those water sources which reproduce the concentrations of selected solutes in runoff water, when mixed in appropriate proportions under various hydrological conditions (Mulder *et al.*, 1995).

In our case, the variables used for EMMA were electrical conductivity (EC), Ca^{2+} , SO_4^{2-} , and Cl. The identified end-members were (1) precipitation, (2) topsoil, and (3) subsoil. The water chemistry is shown in table 5.2. The choice of precipitation as one end-member violates the assumption of EMMA that chemistry of end-members has to be constant in time (Christophersen *et al.*, 1990). Element concentrations in precipitation change drastically over time (Burch *et al.*, 1996), but solely precipitation explained the runoff chemistry at peak discharge with high Cl and low Ca^{2+} concentrations (Fig. 5.2). However, the storm was short compared to the subsequent runoff (Fig. 5.9), which allowed us to consider the precipitation as a short pulse with constant element concentrations. The subsoil end-member had to explain runoff chemistry at base flow. Since the headwater catchment had higher concentrations of base cations in the base flow than the sub-catchments (Fig. 5.2), we selected different subsoil end-members for the catchments: the Bg horizon in both sub-catchments and the Cv horizon in the headwater catchment.

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

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

$$f_1 + f_2 + f_3 = 1 \quad (2)$$

where c_i is the concentration of the variables $i = (\text{Ca}^{2+}, \text{Cl}^{-1}, \text{SO}_4^{2-}, \text{EC})$, 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.

The predicted DOC and DON concentrations $[\text{DOM}]_{\text{pred}}$ were determined by

$$[\text{DOM}]_{\text{pred}} = f_1 [\text{DOM}]_1 + f_2 [\text{DOM}]_2 + f_3 [\text{DOM}]_3 \quad (3)$$

where $[\text{DOM}]$ is both the DOC and DON concentration and f_j are the fractions of end-members estimated by EMMA.

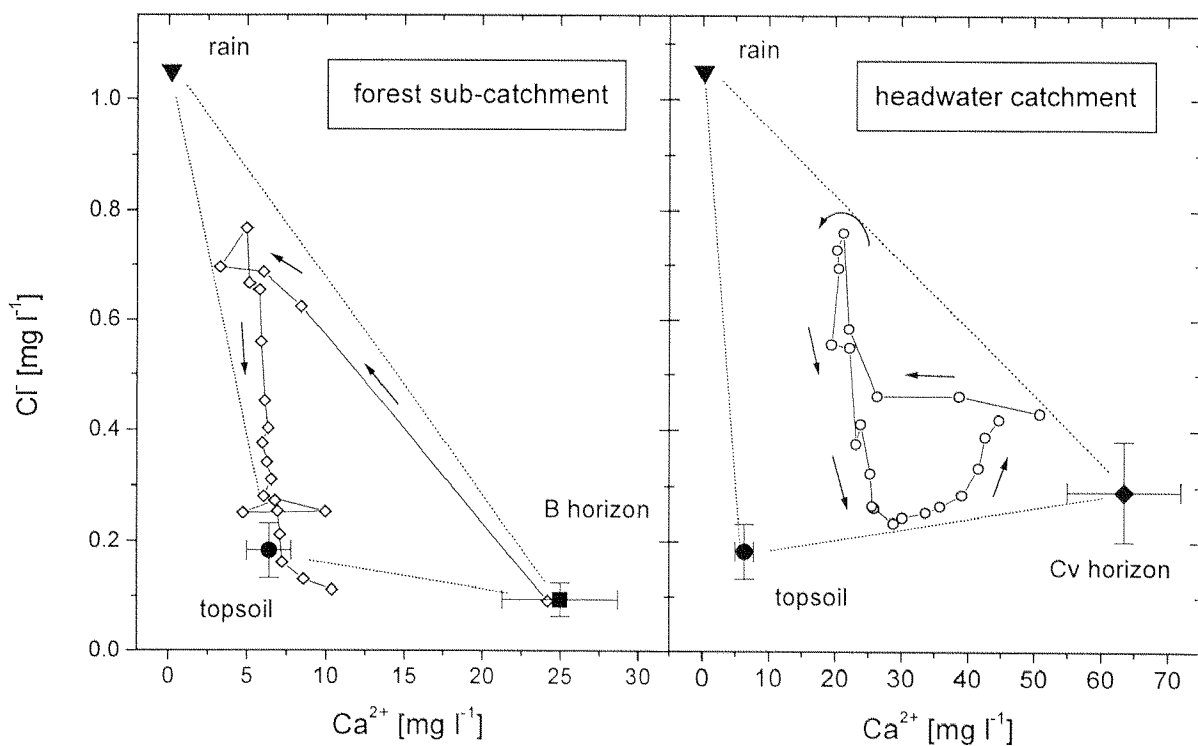


Figure 5.2: End-member mixing diagram for the forest and the headwater catchment showing concentrations of Ca^{2+} and Cl^- in the runoff and in the proposed water flow paths (water sources) contributing to the runoff. Error bars represent standard deviations. Arrows indicate the progression of time.

Table 5.2: Chemical composition of end-members. Means concentrations and standard deviations of 30 sampling dates.

| | Ca ²⁺ [mg l ⁻¹] | Cl ⁻ [mg l ⁻¹] | SO ₄ ²⁻ [mg l ⁻¹] | EC [μS cm ⁻¹] |
|-----------------------------|---|--|--|------------------------------|
| throughfall ^a | 0.165 | 1.06 | 2.52 | 12 |
| forest catchment | | | | |
| topsoil ^b (5 cm) | 6.4 (1.6) | 0.22 (0.05) | 2.13 (0.68) | 37 (9) |
| B horizon (30 cm) | 24.9 (2.8) | 0.09 (0.03) | 1.07 (0.43) | 118 (23) |
| grassland catchment | | | | |
| topsoil (5 cm) | 7.2 (2.1) | 0.22 (0.03) | 1.41 (0.64) | 42 (8.3) |
| B horizon (30 cm) | 30.8 (3.7) | 0.10 (0.03) | 1.70 (0.39) | 132 (18) |
| headwater catchment | | | | |
| topsoil ^c (5 cm) | 6.8 (1.9) | 0.22 (0.04) | 1.76 (0.64) | 39 (9) |
| Cv horizon (100 cm) | 64 (8.5) | 0.29 (0.09) | 12.5 (3.1) | 300 (41) |

^a concentrations of the storm; 13.07.1998.

^b mean of mound (n=3) and depression (n = 8).

^c mean of forest and grassland catchment topsoil.

5.4 Results and discussion

5.4.1 DOC and DON in throughfall and in the soil

The DOC and DON concentrations and characteristics showed a distinct vertical distribution (Table 5.3). In the precipitation, DOC and DON concentrations were low. They increased in the throughfall and in the topsoil, then decreased across the B horizon indicating retention in the mineral soil. DOC concentrations of the reduced mineral soil in the depressions, averaging 10 mg l⁻¹, were higher than concentrations found in Podzols or Cambisols which are usually lower than 2 mg l⁻¹ (Guggenberger & Zech, 1993). This suggests that the retention of DOC is low under reducing conditions.

Table 5.3: Concentrations and characteristics of DOC in precipitation, throughfall, and soil solution.

| horizon (depth) | DOC mg l ⁻¹ | carbo- hydrates %DOC | phenolics %DOC | HoDOC %DOC | mol.UV absorp. l cm ⁻¹ mol ⁻¹ | DON mg l ⁻¹ | amino acids % DON |
|---------------------------|---------------------------|----------------------------|-------------------|---------------|---|---------------------------|-------------------------|
| precipitation | 1.6 | <d.l. | <d.l. | n.d. | n.d. | <d.l. | n.d. |
| throughfall | 9.6 | 21 | 15.6 | n.d. | 120 | 0.44 | 83 |
| mound (n = 3) | | | | | | | |
| LF (5 cm) | 33.1 | 9.3 | 9.9 | 71 | 450 | 0.96 | 59 |
| Bw (30 cm) | 9.1 | 4.8 | 3.5 | 60 | 240 | 0.31 | 25 |
| depression (n = 8) | | | | | | | |
| A (5 cm) | 15.3 | 9.2 | 7.7 | 65 | 370 | 0.63 | 45 |
| Bg (30 cm) | 9.7 | 4.6 | 3.9 | 60 | 230 | 0.35 | 27 |
| Cv (100 cm) | 2.1 | 4.2 | 2.1 | n.d. | 90 | 0.10 | 20 |

d.l. : detection limit

n.d. : not determined

HoDOC: hydrophobic DOC

Sorption of DOC is low, either because of a high pH due to reduction or the reductive dissolution of Fe-oxides as indicated by high Fe concentrations in the subsoil (Kaiser & Zech, 1997b; Hagedorn *et al.*, 1999b; chapter 4). The pH of the mineral soil solution was high (7.5-8.5), but was not significantly correlated with DOC concentrations. In contrast, dissolved Fe showed a significant correlation with DOC and DON concentrations in the subsoil ($r^2 = 0.83^{***}$ for DOC and $r^2 = 0.72^{***}$ for DON, $n = 30$), suggesting that the reductive dissolution of Fe-oxides largely explains the low sorption of DOC and DON in the mineral soil.

The fractions of total DOC present as carbohydrates and phenolics were highest in the throughfall (Table 5.3). The proportions of hydrophobic DOC and the molar UV absorptivity at 285 nm showed their maximum in the soil solution at 5 cm depth. The molar UV absorptivity was used as an easily

measurable spectroscopic indicator for aromaticity and molecular weight (Chin *et al.*, 1994; McKnight *et al.*, 1997). All four fractions decreased across the mineral soil, indicating their preferential retention in the mineral soil.

DON was the dominant form of the total dissolved N (TDN) (Fig. 5.3 and 5.4). Concentrations of NH_4^+ and NO_3^- in the forest floor soil solution were low ($< 0.2 \text{ mg NH}_4^+-\text{N l}^{-1}$; and $< 1 \text{ mg NO}_3^--\text{N l}^{-1}$) and decreased from throughfall to the Bg horizon, indicating denitrification as measured by Mohn (1999), or N-immobilisation. The DON proportion of TDN increased with depth. Below 30 cm depth, all of the TDN was found in the organic form. A large fraction of the DON consisted of hydrolysable amino acids. Their proportion at DON decreased from 80% in the throughfall to 20% in the subsoil, indicating a substantial alteration of DON across the soil.

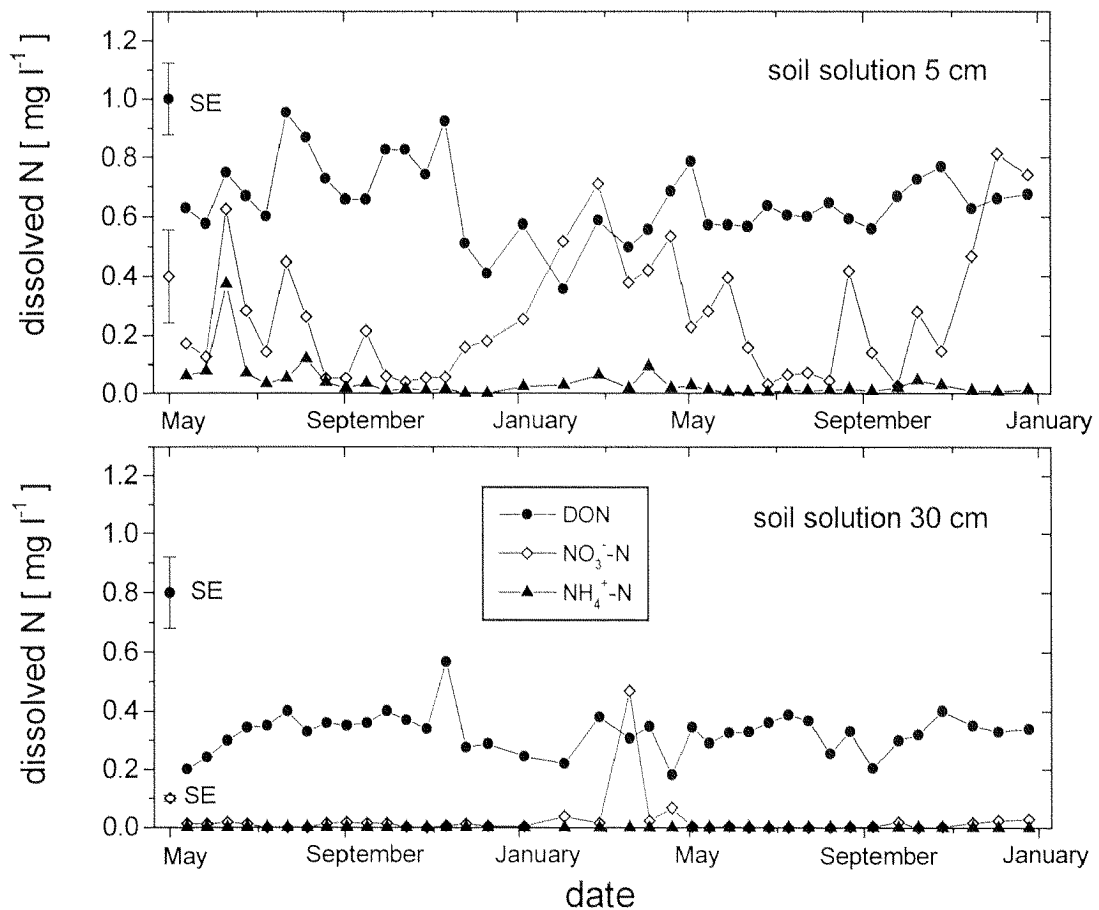


Figure 5.3: Concentrations of DON, NO_3^- , and NH_4^+ in the soil solution at 5 and 30 cm depth in 1996 and 1997. Means and standard errors of 5 plots.

The micro-topography of the forest influenced DOC and DON significantly. Mounds with mor layers had higher DOC and DON concentrations, a higher proportion of phenolics, of hydrophobic DOC, and of hydrolysable amino acids, and a higher molar UV absorptivity at 5 and 10 cm depth than the depressions with muck topsoils (Table 5.3). However, the decrease of the concentrations and fractions of DOC and DON across the B horizon were smaller in the reduced subsoil of the depressions than in the oxidised subsoil of the mounds. This again suggests that the sorption of DOC is impeded under reducing conditions.

5.4.2 DOC and DON export from catchments

Concentrations and properties of DOC in the runoff were similar to those of the soil solution. Highest DOC concentrations occurred in the runoff from the forest catchment followed by the grassland and the headwater catchment (Fig. 5.6). The runoff from the forested catchment also had the highest phenol concentrations, the largest DOC/DON ratio and the highest molar UV-absorptivity, all of which reflects the properties of DOC mobilised in the throughfall and the forest floor.

The average annual DOC export from the sub-catchments was 185 kg DOC ha⁻¹ y⁻¹ for the forest, 108 kg DOC ha⁻¹ y⁻¹ for the grassland and 84 kg DOC ha⁻¹ y⁻¹ for the headwater catchment (Table 5.4), indicating DOC removal between the sub-catchments and the headwater catchment. This could be either due to sorption along pathways from the sub-catchments to the stream, to different water flow paths contributing to the runoff or to in-stream processes as discussed later. Annual DOC export of catchments are higher than those from upland ecosystems (4.3 to 25 kg DOC ha⁻¹ y⁻¹; Tate & Meyer, 1983) and within the range of exports measured in peatland ecosystems (80 to 400 kg ha⁻¹ y⁻¹, McKnight *et al.*, 1985, Urban *et al.*, 1989). However, DOC concentrations in the runoff of the headwater catchment were lower than those in streams draining these peatlands, suggesting that the high export from our catchments is partly

due to the large discharge (1700 mm) as a consequence of 2000 mm annual rainfall.

DON was the major component of N exported from the catchments (Table 5.4). The annual DON export was similar for all catchments. It sums up to 6 kg DON ha⁻¹ y⁻¹, which is approximately 30% of the ambient N deposition (wet + dry deposition) and 60 % of the TDN export. As observed for DOC, the DON export from the catchments is similar to that of peatland dominated catchments (Urban & Eisenreich , 1988, Adamson *et al.*, 1998). The DOC/DON ratio decreased from the soil solution to the runoff of the sub-catchment and finally to the headwater catchment, suggesting that the ecosystem is less retentive for DON than for DOC. This was probably due to the preferential sorption of hydrophobic DOC (Table 5.3) and of high molecular and aromatic DOC as indicated by a decrease of the molar UV absorptivity. These DOC fractions have lower nitrogen contents than hydrophilic and low molecular DOC (McKnight *et al.*, 1985; Qualls *et al.*, 1991).

Table 5.4: Annual fluxes of water, NH₄⁺, NO₃⁻, DON, and DOC in 1997.

| | water [mm y ⁻¹] | NH ₄ ⁺ -N ----- kg ha ⁻¹ y ⁻¹ ----- | NO ₃ ⁻ -N | DON | DOC |
|---------------------|--------------------------------|--|---------------------------------|-----|-----|
| bulk deposition | 2036 | 5.6 | 5.3 | < 1 | 20 |
| throughfall | 1726 | 8.1 | 8.6 | 3.6 | 71 |
| forest catchment | 1440 | 0.1 | 2.8 | 5.7 | 185 |
| grassland catchment | 1487 | 0.2 | 2.7 | 6.2 | 108 |
| headwater catchment | 1740 | 0.05 | 3.8 | 5.5 | 84 |

5.4.3 Regulating factors for DON export

In order to investigate regulating factors for the DON export, DON concentrations were monitored for 2 years in the soil solution and in the catchments runoff and compared to NO_3^- concentrations, the major inorganic N compound in our catchment (Fig. 5.3 and 5.4).

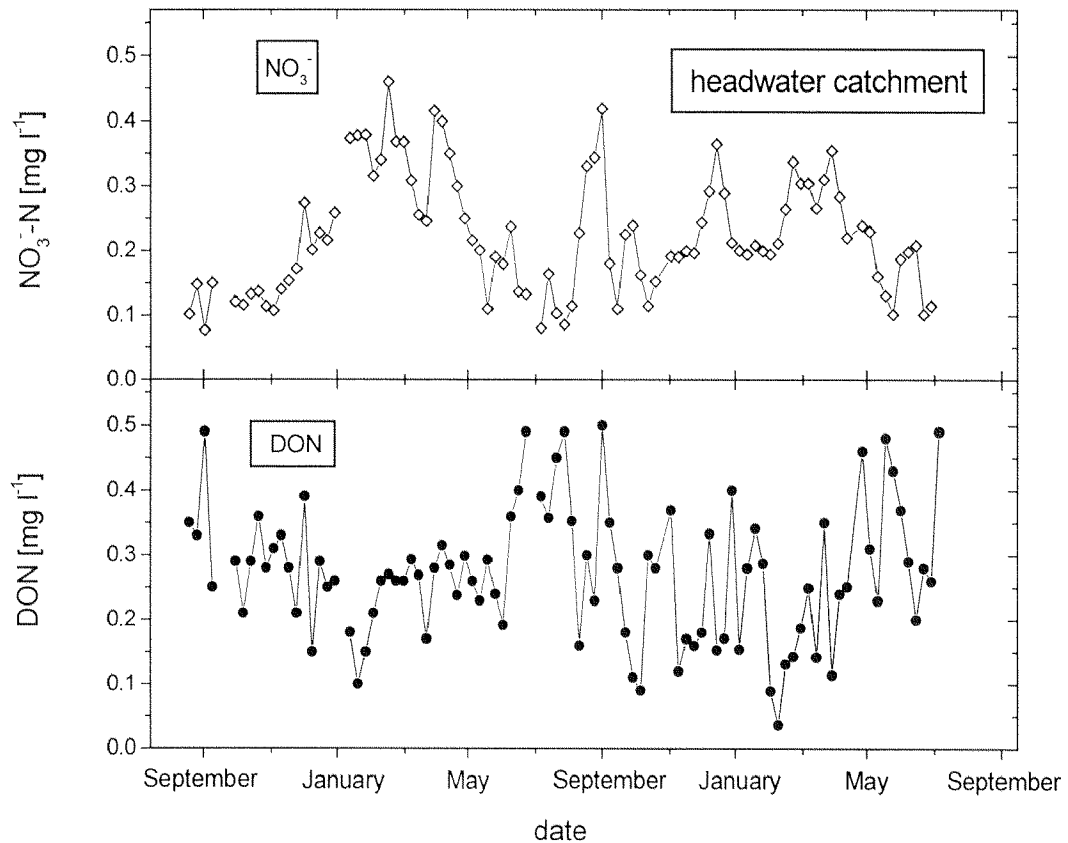


Figure 5.4: Nitrate and DON concentrations in the stream draining the headwater catchment from August 1996 to August 1998. Samples were taken proportionally to runoff and collected weekly.

Concentrations of NO_3^- showed distinct seasonal variations with highest concentrations in the late winter, particularly at snowmelt and during dry periods in the summer. In contrast to NO_3^- , the seasonal variations of DON were low. DON concentrations of the headwater catchment runoff were significantly

and positively correlated with discharge (Fig. 5.5). This again contrasts to NO_3^- , which suggests that the export of DON and NO_3^- from the ecosystem are

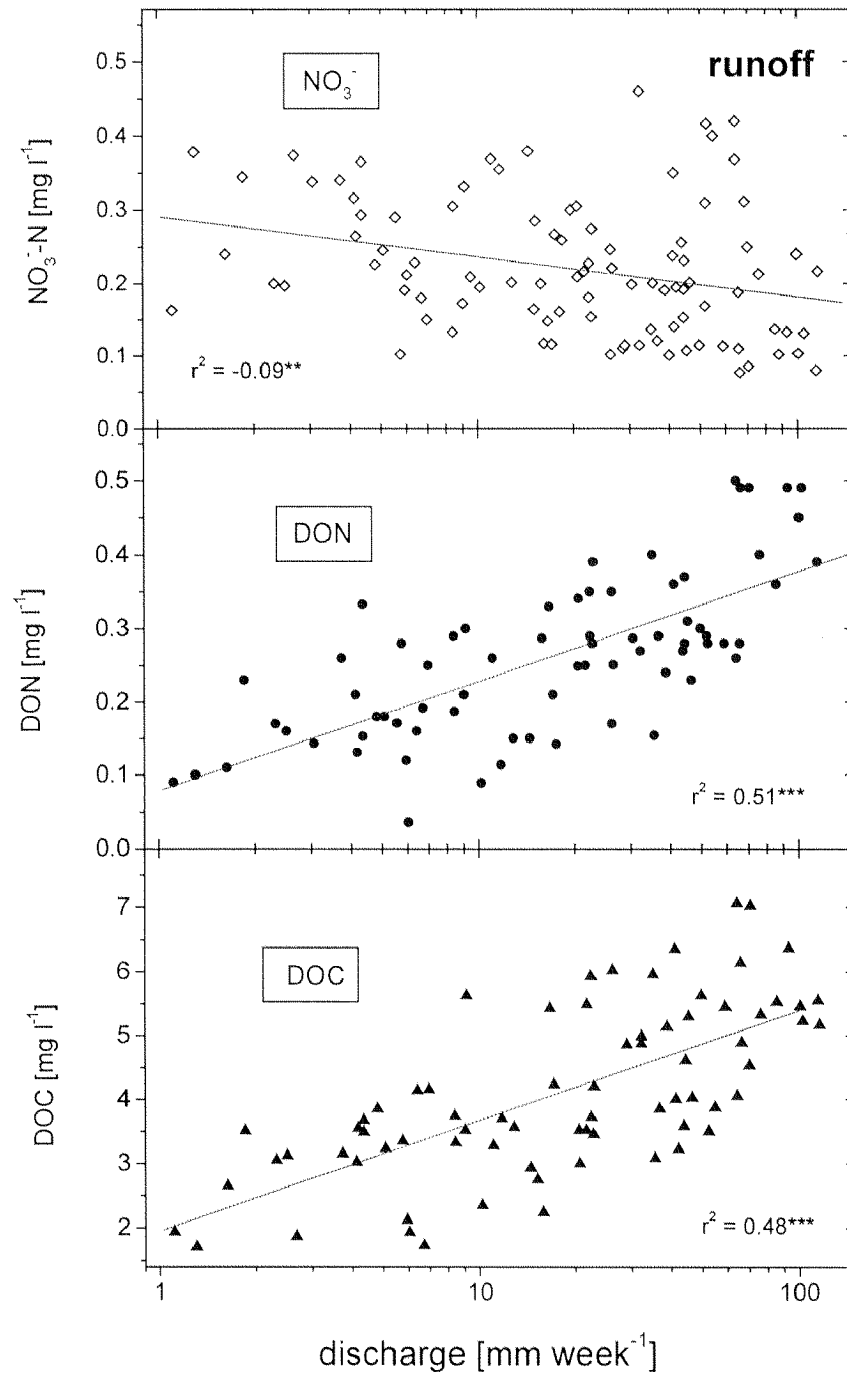


Figure 5.5: Relation between weekly discharge of the headwater catchment and concentrations of NO_3^- , DON, and DOC. Samples were taken proportionally to runoff.

controlled by different factors. Nitrate as a major nutrient for microorganisms and plants is driven by biotic processes leading to a pronounced seasonality. DON was found to be mobilised by leaching from organic matter while passing the forest canopy and the upper soil horizons. However, the export of DON from the catchment and thus the DON retention in the ecosystem appears to be rather regulated by abiotic mechanisms such as sorption on soil surfaces and runoff processes. This agrees with findings of Qualls & Hains (1992) and Northup *et al.* (1995), which show that DON leached from organic matter is not readily available to most soil organisms and plants and cannot easily be converted into inorganic forms.

5.4.4 DOC and DON during storms

In weekly stream water samples, DOC and DON concentrations were positively correlated with discharge (Fig. 5.5). To gain insight into the effects of runoff dynamics on DOC and DON, samples were taken with a high temporal resolution during storm events.

In all catchments, DOC concentrations increased during all of the 4 monitored runoff events compared to base flow. This increase reached 6 mg DOC l⁻¹ (+ 80%) in the grassland, 6.5 mg DOC l⁻¹ (+ 50%) in the forest, and up to 7 mg DOC l⁻¹ (+ 350%) in the headwater catchment (Fig. 5.6). Concentrations of DOC displayed counterclockwise hysteresis with rising and falling discharge (Fig. 5.8), indicating that highest DOC concentrations occurred on the descending limb of the hydrograph.

As concentrations, the properties of DOC varied considerably during runoff events (Fig. 5.6). The molar absorptivity at 285 nm as an indicator for aromaticity and molecular weight first decreased. Then, the absorptivity increased and reached its highest values on the descending limb. The percentage of hydrolysable carbohydrates at DOC was relatively constant in time during high flow (Fig. 5.6). In the headwater catchment, however, carbohydrates increased substantially when discharge dropped back to base flow.

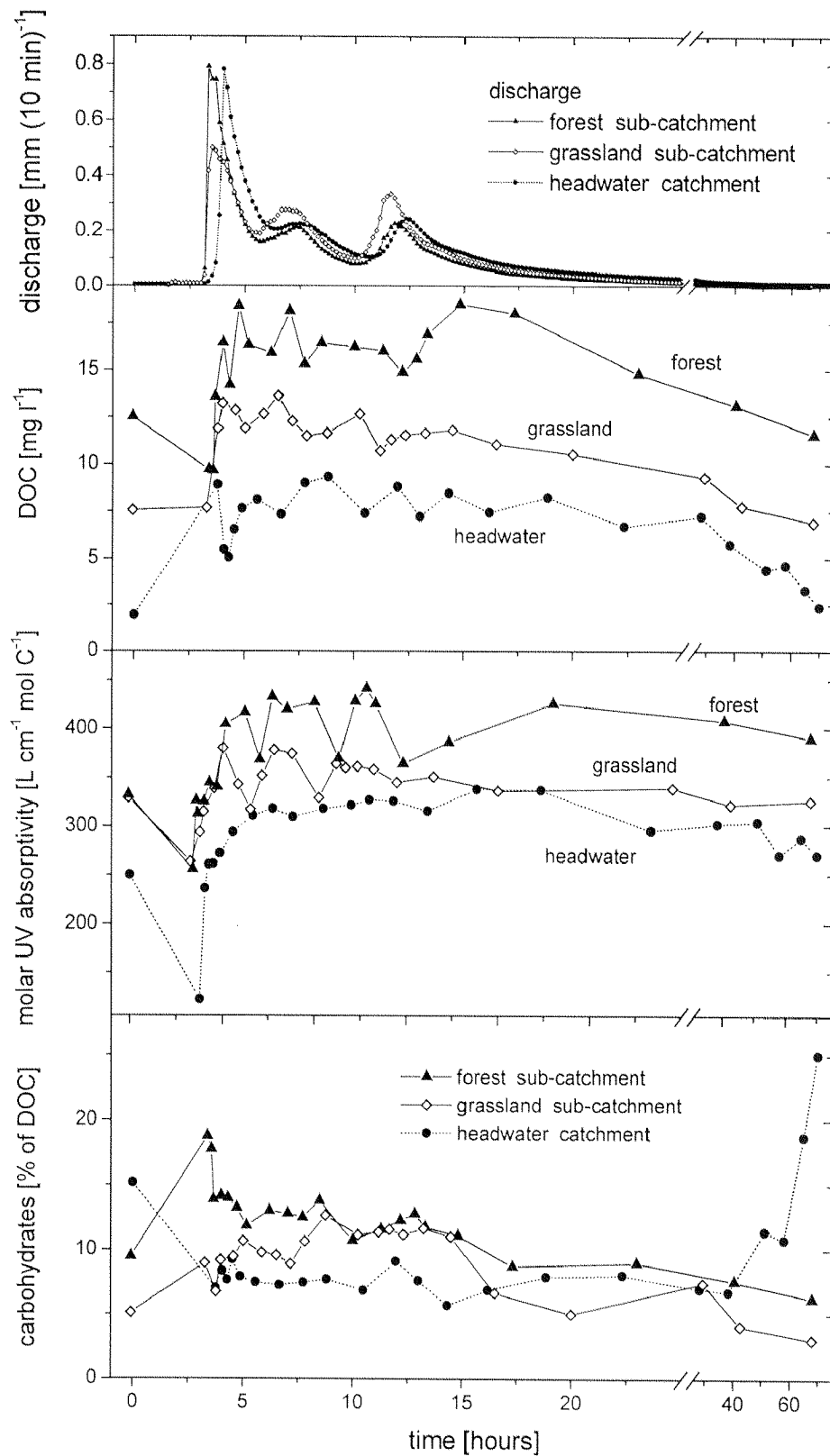


Figure 5.6: Discharge, DOC concentrations, molar UV absorptivity, and proportions of carbohydrates in the runoff from all catchments during the storm of July 13 – 16, 1998. Samples were taken proportional to the runoff.

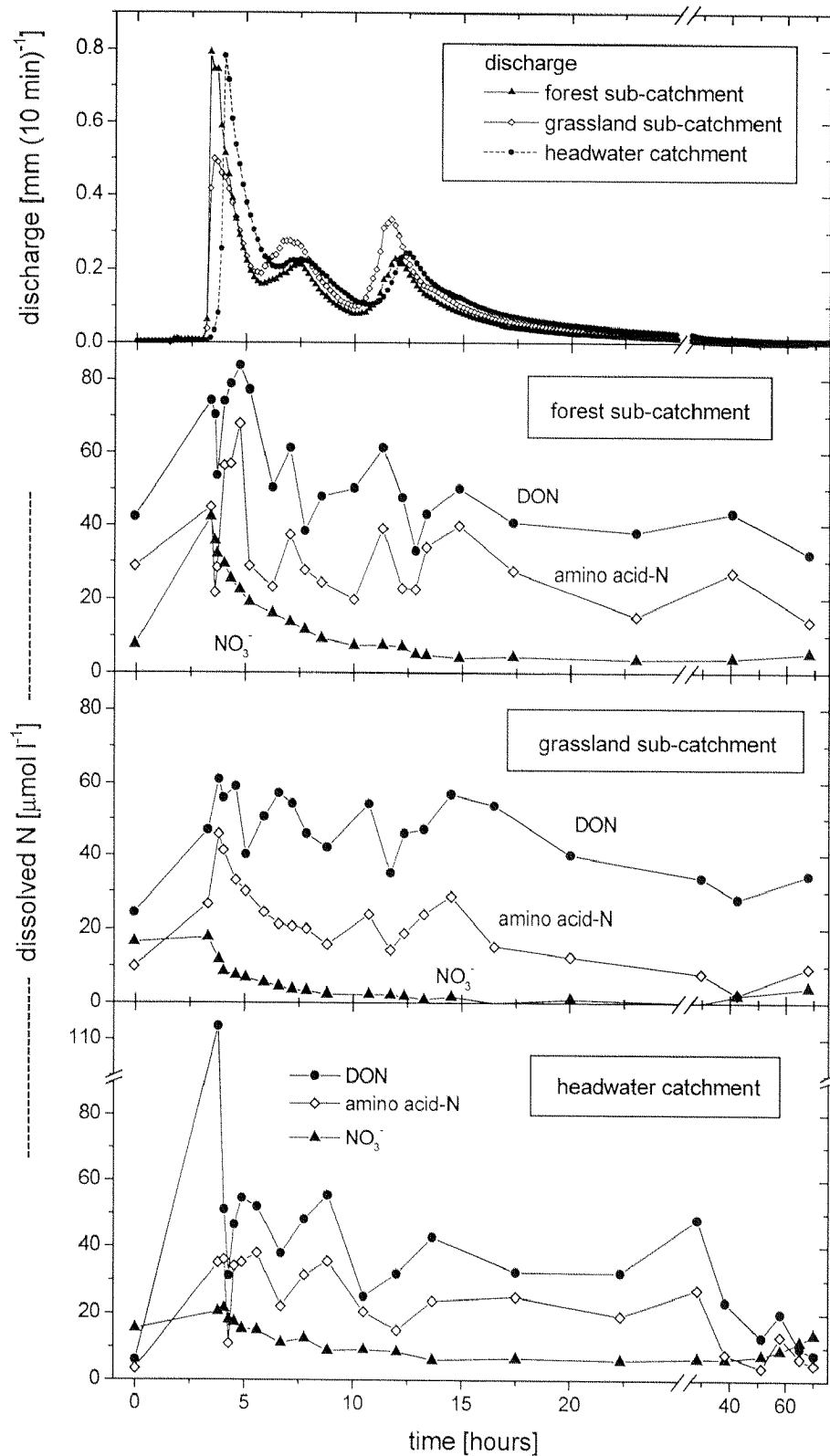


Figure 5.7: Discharge, and concentrations of DON, hydrolysable amino acid-N, and NO_3^- in the runoff from all catchments during the storm of July 13 – 16, 1998. Samples were taken proportional to the runoff.

DON concentrations were also considerably higher at high than at low flow (Fig. 5.7). Compared to base flow, DON concentrations increased by 0.52 mg DON l⁻¹ (+ 250%) in the grassland, by 0.58 mg DON l⁻¹ (+ 250%) in the forest, and by 1.4 mg DON l⁻¹ (+ 1000%) in the headwater catchment. The DOC/DON was highest in the later stages of the event. Alkaline hydrolysable amino acids followed the temporal variations of DON (Fig. 5.7). During storms, however, the proportion of hydrolysable amino acids at DON increased from approximately 60% at base flow up to 80%.

NO₃⁻ concentrations showed a sharp rise immediately at the onset of the event, followed by rapid exponential decline. The first stream water samples after the rain had 5 to 10 time higher NO₃⁻ concentrations than in the soil solution at 5 cm depth, suggesting a large contribution of rainfall with the highest NO₃⁻ concentrations in the ecosystem. This temporal pattern is characteristic for 'NO₃⁻ flushing', where the water table rises to the soil surface with subsequent mobilisation of NO₃⁻ stored near or at the soil surface to streams (Creed & Band, 1998).

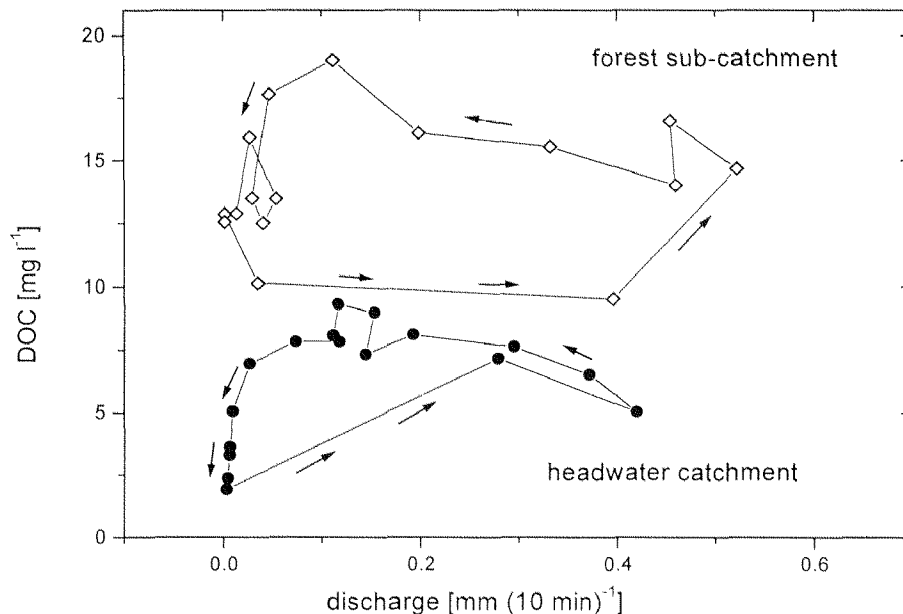


Figure 5.8: Hysteresis of DOC concentrations with discharge in the forest and the headwater catchment during the storm of July 6 – 9, 1998. Arrows indicate the progression of time.

There are several mechanisms which have been postulated to explain increases of DOC during storms: (a) changes in water flow paths contributing to the runoff, (b) input of throughfall directly entering the stream, and (c) channel flushing and elongation, thereby leaching DOC from particulate organic matter deposited in the previous dry period and flushing of DOC from isolated pools (Tate & Meyer, 1983; Sedell & Dahm, 1990).

The hysteresis of DOC with discharge (Fig. 5.8) and the hysteresis of Ca^{2+} with Cl^- during the storm (Fig. 5.2) suggest that the water sources contributing to the catchment runoff change in time. Moreover, concentration-discharge hysteresis indicate that the runoff consists of at least three components (Evans & Davies, 1998).

5.4.5 End-member mixing analysis

To determine whether temporal variations in runoff components (called water flow paths) could explain the variations of DOC and DON during storms, an end-member mixing analysis (EMMA) was performed using EC, Ca^{2+} , SO_4^{2-} , and Cl^- concentrations as input parameters. This way we were able to separate the runoff into three components (end-members), precipitation, topsoil, and subsoil. In all catchments, the discharge responded within minutes to storm events (Fig. 5.9), which points to a rapid water movement through the soil system and/or surface runoff. EMMA indicated that precipitation contributed substantially to the runoff. The proportions of rain water at peak discharge were approximately 61% in the forest sub-catchment, 57% headwater catchment, and 42% in the grassland sub-catchment (Fig. 5.10). These proportions agree with the maximum discharge of the catchments: 0.79, 0.78, and $0.42 \text{ mm (10 min)}^{-1}$, respectively. Both the lower contribution of rain water and the lower discharge peak in the grassland were possibly caused by the absence of waterlogged depressions. Waterlogged depressions are probably the main source for the rapid runoff generation in the catchments as suggested by the sharp rise of the measured water table in a depression and the low increase of the water table on a mound (Fig. 5.10). This is confirmed by runoff

experiments and time series analysis, which showed that the initial discharge peak originates mainly from waterlogged depressions (Feyen, 1999).

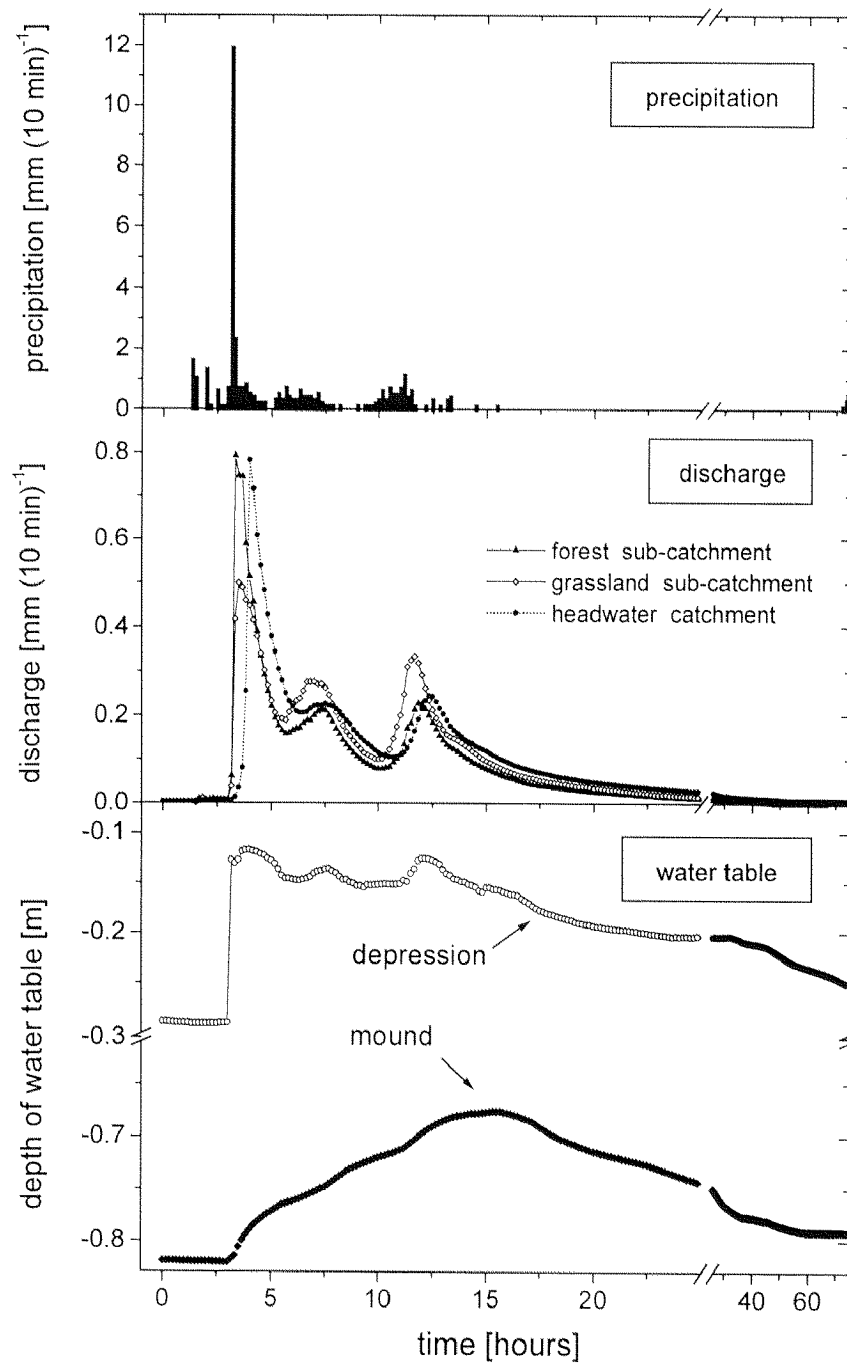


Figure 5.9: Response of discharge and water tables to the storm event of July 13 – 16, 1998.

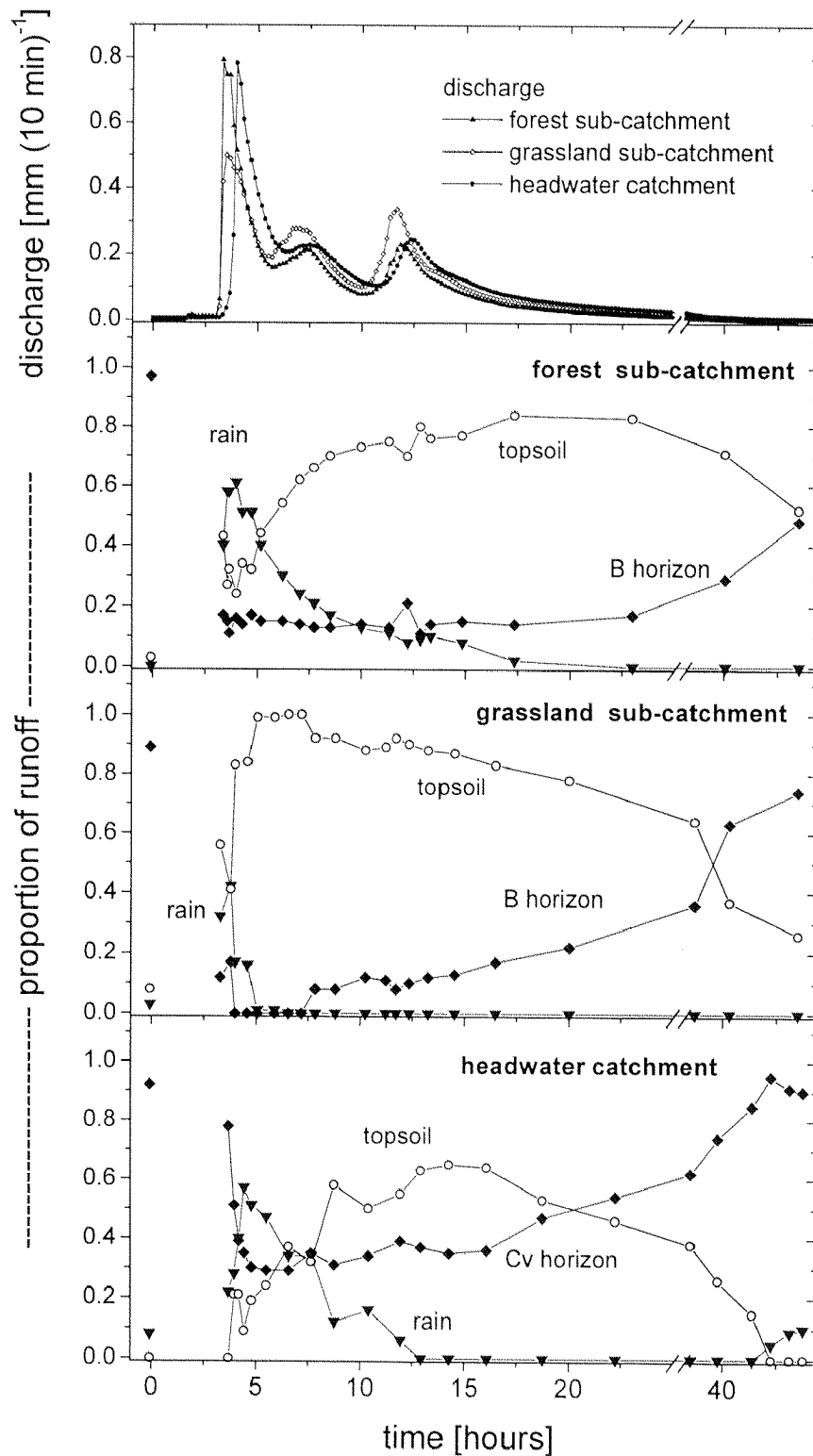


Figure 5.10: Estimated contribution of water flow paths (end-members) to the catchments runoff during the storm of July 13 – 16, 1998

In the headwater catchment, the estimated proportion of rain water peaked with a time lag of about 30 minutes compared to the sub-catchment, which is in accordance to the retardation of the runoff peak. The equally high contribution of rain water in all catchments contrasts to the findings of Sklash *et al.* (1986), that the fraction of 'new' water contributing to storm runoff declined with increasing catchment size. This is probably due to a network of drainage trenches in our headwater catchment which rapidly routes the runoff from waterlogged areas to the stream.

The largest average contribution of all end-members came from the topsoil water, particularly at later stages of the event. Water from the subsoil contributed substantially only to base flow. As expected, the highest contribution of subsoil water was found in the headwater catchment.

To check the EMMA predictions against independent information, estimated subsoil contributions were compared with measured water tables. They were all significantly negatively correlated ($r^2 = -0.88^{***}$, $r^2 = -0.82^{***}$, $r^2 = -0.72^{***}$ for the grassland, headwater, and forest catchment, respectively). This strongly supports the findings of EMMA. Finally, to evaluate if uncertainty in the inorganic composition of the end-members causes errors in the estimates of flow path contributions, we performed another EMMA based on variation in the measurements (\pm standard deviation). The contributions of end-members changed by less than 10%. Thus, the results of our mixing analyses appear to be robust.

5.4.6 Changes in runoff components – an explanation for DOC variations?

DOC and DON concentrations were predicted solely on the basis of the estimated contribution of the three end-members. In the grassland and the headwater catchment, predicted and observed concentrations of dissolved organic compounds were closely correlated (Table 5.5), suggesting that changes of water flow paths are important determinants for catchments DOC and DON concentrations and properties. For instance, EMMA indicated that the contribution of the DOC and DON-rich topsoil peaked in the later stages of the

storm, which explains well the highest DOC and DON concentrations and the highest molar UV absorptivity as the hydrograph receded. Furthermore, the subsoil end-member of the headwater catchment (Cv horizon) had lower DOC and DON concentration than that of the sub-catchment (B horizon). Thus, the end-members contributing to the runoff in the headwater catchment covered a broader range in DOC and DON concentrations, which lead to the larger increase of DOC and DON concentrations during storms compared to the sub-catchments.

Table 5.5: Prediction of nutrient, DOC, and DON concentrations based on estimated changes in water flow paths. Coefficients of determination (r^2) of measured and predicted concentrations ($n=22$).

| | forest sub-catchment | grassland sub-catchment | headwater catchment ^b |
|--|-------------------------|----------------------------|-------------------------------------|
| ^a Ca ²⁺ | 0.91 | 0.95 | 0.95 |
| ^a Cl ⁻ | 1.00 | 0.91 | 0.95 |
| ^a SO ₄ ²⁻ | 1.00 | 0.85 | 0.90 |
| ^a EC | 0.93 | 0.95 | 0.97 |
| DOC | 0.32 | 0.75 | 0.74 |
| phenolics | 0.29 | 0.74 | 0.85 |
| UV absorptivity | 0.56 | 0.56 | 0.65 |
| DON | n.s. | 0.65 | 0.58 |
| NO ₃ ⁻ | 0.83 | 0.62 | 0.52 |

^a variables used for the EMMA, ^b without the first sample after the rainfall

In the forest catchment, maximum DOC and phenol concentrations (Fig. 5.11) were well predicted (differences within 7 %), but temporal variations of predicted and observed concentrations showed discrepancies (Table 5.5). This was probably due to the inadequate description of the runoff as a mixture of 3

components. For EMMA, we assumed that the forest topsoil consisted of a constant mixture of both soil types, 50% mor humus (mounds) and 50% muck topsoil (depressions). Due to the large differences between DOC concentrations and properties of the mor and the muck topsoil, minor variations in their contributions would cause large effects in the runoff DOC. To evaluate whether the contribution of both topsoil types changed in time, we recalculated the EMMA with both topsoils and thus with 4 end-members: precipitation, mor, muck, and subsoil. Here, we had to include DOC concentrations to achieve reproducible results. The mixing analysis of 4 components showed that the contributions of mor and muck topsoil were variable in time in the forest catchment, whereas in the grassland and the headwater catchment, the contribution from the mor layer was negligible.

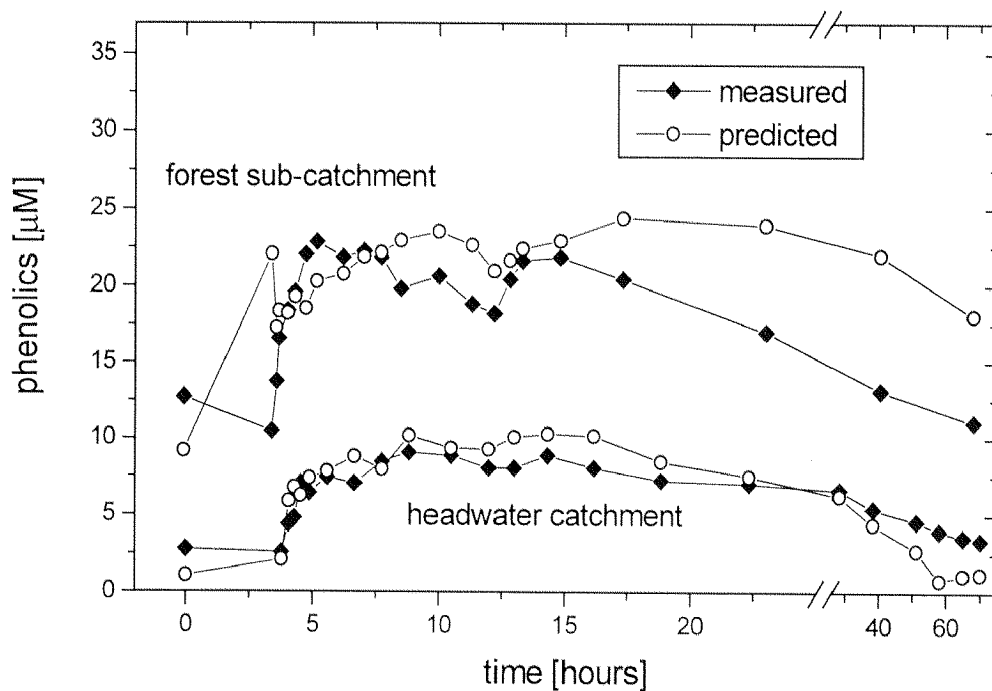


Figure 5.11: Prediction of phenol concentrations based on estimated water flow paths. Comparison with measured concentrations in the forest and the headwater catchment.

Ratios of measured DOC concentrations and properties to those predicted based on EMMA provides an estimate of how much of the variation in runoff concentration can be explained by variations in the water flow paths. Observed/predicted concentration ratios near 1.0 suggest that changes of water flow paths largely explained runoff chemistry, whereas ratios substantially different from 1.0 suggested that other processes were important determinants.

The temporal variations of the observed/predicted ratio were low for DOC and DON concentrations and the molar UV absorptivity, except for the first sample of the headwater catchment (Fig. 5.12). In contrast, the observed/predicted ratios for carbohydrates, amino acids and NO_3^- showed a distinct temporal pattern. Ratios were generally more variable and above 1.0 in the initial phase of the storm (up to 5 for carbohydrates; Fig. 5.12). In the later stages of the storm, the ratios dropped below 1.0 and increased again at base flow, particularly in the headwater catchment. These temporal variations are an indication that other mechanisms than changes in runoff components, such as in-stream processes, played important roles.

Experiments investigating the effects of drying and wetting showed that DOC accumulates in the soil solution during dry periods (Christ & Davis, 1996; Guggenberger *et al.*, 1998). In the subsequent rainfall, this DOC can be rapidly leached, followed by a slower release of DOC (Boyer *et al.*, 1996; Reemtsma *et al.*, 1999). Drying and wetting increase specifically the release of hydrophilic DOC (Christ & David, 1996; Guggenberger *et al.*, 1998). In a leaching experiment, Reemtsma *et al.* (1999) observed that the characteristic of leached DOC changes in time. DOC, leached in the initial phase, was found to have the lowest molar UV absorptivity. This might explain the immediate drop of the molar UV absorptivity (Fig. 5.6) and of its observed/predicted ratio (Fig. 5.12) at the onset of the storm.

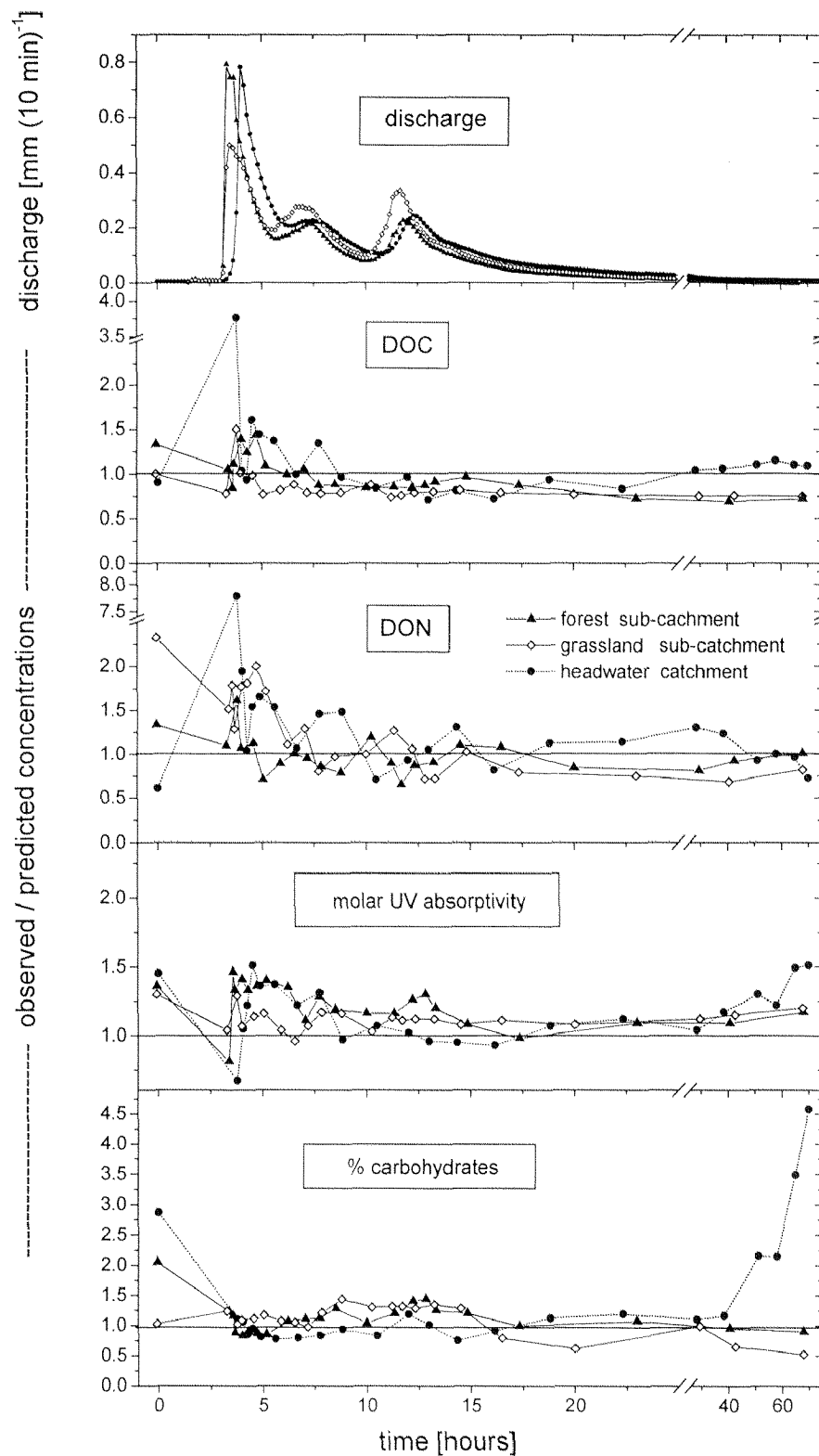


Figure 5.12: Ratios of observed and predicted concentrations of DOC and DON, of the molar UV absorptivity, and the proportion of carbohydrates during the storm of July 13 – 16, 1998. Predictions were performed on the basis of estimated contributions of the individual water flow paths.

The occurrence of in-stream processes are supported by the comparison of the headwater catchment with the sub-catchments, which have no streambed. In the headwater catchment, DOC and DON concentrations showed two peaks, one directly after the rainfall and one on the descending limb of the hydrograph (Fig. 5.6 and 5.7). The sub-catchments DOC and DON concentrations did not have the initial DOC and DON peak. Moreover, the first runoff sample after the rainfall showed a much larger discrepancy between observed and predicted concentrations in the headwater than in the sub-catchments (Fig. 5.12). This suggests that the first DOC and DON peak was rather caused by in-stream processes than by changes in water flow paths.

In-stream processes that might lead to an initial DOC peak could be both an input of throughfall onto the stream or channel flushing as a result of the stream expansion during increasing discharge. The initially exported DOC had a lower proportion of carbohydrates (7%), a lower percentage of phenolics (2%) and a narrower DOC/DON ratio (= 6) than usually found in throughfall (21% carbohydrates-C/DOC; 16% phenol-C/DOC; DOC/DON = 22). Thus, the initial DOC peak appears to result from the expansion of the stream during increasing discharge, leading to DOC transport from previously isolated sections of the streambed (Tate & Meyer, 1983; Meyer, 1990). Another DOC source could be the flushing from the saturated zone below the stream bottom, the hyporheic zone. Schindler & Krabbenhoft (1998) identified the hyporheic zone as an important source for DOC of low molecular weight, which is in accordance with the particular low molar UV absorptivity of the initially exported DOC (Fig. 5.6).

After the storm, when discharge returned back to base flow, the concentrations and the proportions of carbohydrates at DOC increased in the headwater catchment, but not in the sub-catchments (Fig. 5.6). As indicated by the large observed/predicted ratio, changes in water flow paths cannot account for this increase (Fig. 5.12), since the contribution of the subsoil with low carbohydrate concentrations was largest at base flow. This again suggests that in-stream processes such as production of DOC (Kaplan & Bott, 1982; Meyer,

1990) are important determinants of stream water DOC at base flow. Our results are consistent with the observations of Mulholland & Hill (1997), based upon weekly stream water samples, that at low flow in-stream processes primarily control stream water DOC, whereas water flow path effects dominate at high flow.

5.5 Conclusions

DOC and DON concentrations in weekly stream water samples were positively correlated with discharge. During storms, DOC and DON concentrations increased with increasing discharge, reaching their maximum concentrations on the descending limb of the hydrograph. End-member mixing analysis based upon inorganic chemical composition of runoff water showed that water flow paths changed substantially during storms. The prediction of DOC and DON concentrations and properties by the estimated contributions of water flow paths indicated that a large part of the variation in DOC and DON was explained by changes in hydrologic pathways. Discrepancies between observed and predicted concentrations occurred at base flow and in the initial phase of storms, suggesting that other mechanisms such as in-stream processes or a time-variant release of DOC played an important role.

The occurrence of in-stream processes was supported by the comparison of the headwater catchment with the sub-catchments, which are experimentally delineated by trenches and have no streambed. Only the headwater catchment showed a DOC and DON peaked immediately after the rainfall. The properties of the initially exported DOC (low proportion of carbohydrates and phenols, and a low DOC/DON ratio) contrasts to that of throughfall, suggesting that this DOC derives primarily from the expansion of the stream at high flow. After the storm, when discharge dropped back to base flow, the percentage of carbohydrates at DOC increased in the headwater catchment, but not in the

sub-catchments. This is another indication for in-stream processes, in this case, the within-stream production of carbohydrates.

DON was the dominant form of dissolved N in the soil water and the major N component exported from the catchments. In contrast to NO_3^- , DON concentrations showed only low seasonal variations and depended upon discharge in the catchment runoffs. This points to a low biologic control on DON retention in the catchment. DON export appears to be rather regulated by abiotic processes such as sorption or changes in water flow paths.

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Chapter 6

Synthesis

This thesis studies the effects of elevated N deposition on N transformation and transport in a forested catchment with Gleysols in Central Switzerland. Elevated N deposition was experimentally increased by applying 30 kg $\text{NH}_4\text{NO}_3\text{-N ha}^{-1} \text{y}^{-1}$ to a spruce forest stand simultaneously and proportionally to rainfall. The response of N transformation and NO_3^- leaching to the increased N inputs was studied at different spatial scales, ranging from the micro scale of mm^2 to the plot scale of 20 m^2 up to the catchment scale of 1500 m^2 and 0.7 km^2 . To gain insight into the role of DON for the soil's N cycle and for the N export, DON concentrations were monitored seasonally and during storms in the soil solution and in catchment runoffs.

6.1 Increased NO_3^- leaching - caused by N saturation or hydrologically driven?

The definitions of N saturation focus on the inability of a forest ecosystem to retain increased N inputs (Aber *et al.* 1989; Stoddard, 1994). Elevated NO_3^- leaching is usually regarded as the main symptom of N saturation. Aber *et al.* (1989) hypothesised that before NO_3^- leaching increases, nitrification has to be accelerated and inorganic N has to exceed total plant N demand.

In the NITREX project in Alptal, three years of N additions had effects neither on vegetation (Schleppi *et al.*, 1999b) nor on N-pools in the soil such as bulk soil N, microbial N, and K_2SO_4 -extractable N. However, N losses from the ecosystem through denitrification and NO_3^- leaching increased significantly. This is consistent with findings of other NITREX experiments, which have shown that NO_3^- leaching responded within the first year of manipulating N

inputs, whereas responses in vegetation and soil are delayed (Gundersen *et al.*, 1998). There are several indications that the rapid change in NO_3^- leaching is mainly hydrologically driven. The discharge and NO_3^- concentrations of the sub-catchment responded to rainfall within minutes. The water chemistry of the sub-catchment runoff showed that during storms a large part of the runoff derives directly from precipitation and from water which had interacted only with the topsoil. This suggests the occurrence of preferential flow through near-surface or subsoil pathways. As a consequence, the contact time of the water with the soil matrix is insufficient for a complete retention of NO_3^- . Thus, the increased NO_3^- leaching is due to the bypassing of the soil and the root system rather than to 'N saturation'.

6.2 Preferential flow paths – locations of preferred N transformation ?

Preferential flow is a common phenomenon in soils (Flury *et al.*, 1994). Analogous to the heterogeneous nature of solute movement, microbial activity is usually heterogeneously distributed in the soil (Parkin, 1993). In chapter 3, I investigated the role of rapid flow paths for N transformation using 50 micro-suction cups, each having a surface area of only 12 mm².

The response of the micro suction cups to dye tracer, SO_4^{2-} , and Cl^- applications showed that a large portion of the soil volume does not come into direct contact with the infiltrating rainwater. Based on the response to the applied dye tracer, the micro suction cups were divided into two groups, flow paths and soil matrix. With respect to N transformation, locations within reach of flow paths were more active than those in the soil matrix. Highest NO_3^- concentrations were found along flow paths at depths below 2 cm under temporarily reducing conditions. Along flow paths, the temporal variation of the $\text{NO}_3^-/\text{Cl}^-$ ratio was larger than in the soil matrix. The $\text{NO}_3^-/\text{Cl}^-$ ratio decreased faster after a rainfall event and increased first in the subsequent dry period in the flow paths. This indicates that net nitrification started earlier at locations in or near flow paths than in the soil matrix. The results of this case study suggest that flow paths are microhabitats with an increased N

transformation compared to the soil matrix. This is probably caused by a better nutrient supply and aeration along flow paths.

The observed variability of NO_3^- concentrations in space and time at the microscale may be important in interpreting the effects of N deposition at larger scales. Here, losses from the ecosystem via NO_3^- leaching and denitrification were increased despite unchanged N pools in the soil. At the microscale, it was shown that a large portion of the soil does not come into direct contact with the NO_3^- in the infiltrating rainwater. This is consistent with the bypassing of the soil at the catchment scale, where a large fraction of the runoff resulted from preferential flow through near-surface or subsoil pathways. The consequence of this bypassing is an incomplete retention of NO_3^- in the soil.

6.3 Retention of DON – regulated by biotic or abiotic factors ?

Recently, DON was identified as a dominant vehicle for N leaching from forest floors (Currie *et al.*, 1996), and for N export from catchments (Arheimer *et al.*, 1996). Little is known about the regulating factors of the DON dynamic in the soil and of the DON export from catchments (Creed & Band, 1998).

The results in chapter 4 and 5 demonstrate that DON is the dominant form of dissolved N in the soil water and the major N component exported from the sub and the headwater catchments. An important fraction of the DON consisted of hydrolysable amino acids. Their proportion decreased from 80% in the throughfall to 20% in the subsoil, indicating a substantial alteration of DON in the soil profile. DON was mobilised by leaching from organic matter while passing through the forest canopy and the upper soil horizons. In the mineral soil, the retention of DON appears to be controlled by sorption to soil surfaces, as suggested by the DON concentrations which were higher under reducing than under oxidising conditions and the close correlation of DON with Fe concentrations. In contrast to NO_3^- , which is a major nutrient for microorganisms and plants, the seasonal variations of DON concentrations in soil and stream water were small. Stream water DON concentrations were regulated largely by runoff processes. In the headwater catchment, DON

concentrations were significantly and positively correlated with stream discharge. During individual storms, DON concentrations increased substantially in the runoff from all catchments compared to base flow. These results suggest that DON retention and thus the DON export from the ecosystem is regulated by abiotic mechanisms such as sorption to soil surfaces and runoff processes rather than by biotic processes.

6.4 DOC and DON mobility - increased under reducing conditions ?

In forest ecosystems, fluxes of organic solutes play prominent roles in pollutant and nutrient transport (Qualls *et al.*, 1991). Field studies, conducted in aerobic soils, have shown that the output of DOC from the mineral soil is low due to sorption by sesquioxides in the subsoil (Guggenberger & Zech, 1993; Moore *et al.*, 1992). However, under reducing conditions, Fe(III)-oxides dissolve to Fe²⁺, which may decrease the sorption of DOC. In chapter 4, I studied the DOC and DON dynamics in a Gleysol where reducing conditions were prevalent.

The redox environment had a pronounced impact on DOC and DON mobility. Concentrations of DOC and DON in the soil solution of the mineral soil were higher under reducing than under oxidising conditions. In the reduced mineral soil, DOC and DON concentrations remained constant over depths, which contrast to the findings of studies in aerobic soil such as Podzols or Cambisols (Jardine *et al.*, 1989a, Moore *et al.*, 1992). The apparently low retention of DOC under reducing conditions can be caused either by an increased high pH or by the reductive dissolution of Fe-oxides, as indicated by high Fe concentrations in the subsoil. Concentrations of DOC and DON were significantly correlated with dissolved Fe concentrations, but not with pH. This suggests that the reductive dissolution of Fe-oxides was the main reason for the low sorption of DOC in the reduced mineral soil.

However, as indicated by the formation of precipitates during the aerobic sampling of soil solution from the Bg horizon, DOC co-precipitates with Fe at the interface between anaerobic and aerobic soil. Therefore, the DOC input

from reduced mineral soils to stream water is probably lower than would be expected considering the high DOC concentrations in the Bg horizon.

6.5 DOC and DON export – controlled by runoff processes ?

Runoff processes may affect DOC and DON transport by changes in water flow paths contributing to streams (Easthouse *et al.*, 1992) or by a limited contact time between the soil solid phase and the soil solution caused by preferential flow (Jardine *et al.*, 1989b).

I monitored the concentrations and properties of DOC and DON in the subsurface flow of two small soil plots (15 m²) during controlled rainfall events (chapter 4) and in the runoff from the forest, grassland and headwater catchments during storms (chapter 5).

Runoff processes had a large impact on DOC and DON mobility. During storms, concentrations and properties of DOC and DON changed drastically in both subsurface flow and catchment runoff.

In the subsurface flow at 30 to 60 cm depth, DOC concentrations increased within minutes with increasing runoff. Concentrations of DOC at high flow were doubled compared to base flow. At peak flow, the molar UV absorptivity at 280 nm in the subsurface flow, which is used as an indicator for aromaticity and molecular weight of DOC, increased up to values similar to those of the forest floor water. This indicates a decreased retention of 'reactive' DOC compounds. At reduced flow velocities, the retention of these compounds increased greatly. These findings suggest that DOC concentrations and properties are sensitive to flow velocities in the subsurface flow and that DOC is preferentially transported to the subsoil at high discharge.

In the runoff from all catchments, DOC concentrations increased during storms by 6 to 7 mg DOC l⁻¹ compared to base flow, with the largest relative increase in the headwater catchment (+ 350%). Concentrations of DON, hydrolysable amino acids, and phenolics showed comparable increases, whereas the proportion of carbohydrates decreased at peak flow. To determine whether changes in hydrological pathways could explain the large temporal

variations, I conducted an end-member mixing analysis (EMMA) using electrical conductivity, Ca^{2+} , SO_4^{2-} , and Cl^- concentrations to separate the runoff into three water flow paths: (1) precipitation, (2) topsoil, and (3) subsoil. Prediction of DOC and DON concentrations solely on the basis of EMMA showed that changes in water flow paths largely explained the temporal variability. EMMA indicated that the highest concentrations of DOC and DON and the highest molar UV absorptivity, which all occurred on the descending limb of the hydrograph, were caused by the largest contribution of DOC- and DON-rich topsoil water.

6.6 Implications

The results of this thesis show that elevated N inputs caused increased NO_3^- leaching despite unchanged N pools in the soil and vegetation at the study site. Rapid transport through the Gleysol was identified as the primary reason for these findings. Nitrate in the infiltrating rainwater bypassed a large portion of the soil and root system. Therefore, I anticipate that increasing or lowering N inputs leads to a rapid increase or reduction in NO_3^- leaching.

The runoff processes and NO_3^- concentrations in the runoff of the larger headwater catchment were comparable to those of the experimental sub-catchments. At both scales, a large fraction of the runoff originated from the precipitation and from the topsoil water. Thus, I expect that elevated N inputs would have similar effects in the headwater catchment as those found in the manipulation experiment. Nitrate concentrations in the stream water will rapidly increase due to elevated N deposition.

This study shows that DOC is mobile in the Gleysol-dominated catchment. Retention of DOC in the mineral soil is low under reducing conditions. Preferential flow causes a substantial vertical DOC transport. The large contribution of topsoil water at high flow leads to increased DOC concentrations in the stream water during storms. Since DOC is a transport-facilitating agent for contaminants such as heavy metals and organic pollutants, these compounds will be highly mobile in Gleysols. Thus, Gleysols at the

interface between terrestrial and aquatic ecosystems represent a potential pathway for contaminants to ground and surface waters.

6.7 Future research

Despite numerous studies on N cycling in forest soil and on the effects of N deposition in forest ecosystems, the mechanism of N retention in the soil is poorly understood. Manipulation experiments indicate that 70 to 85% of the added N are retained in the soil (Aber *et al.*, 1998; Schleppi *et al.*, 1999). Soil organic matter is identified as the final sink, but mechanisms accounting for the N incorporation are largely unknown. Possible processes could be (i) the immobilisation by microbes through biomass production, (ii) the abiotic incorporation into existing soil organic matter, or (iii) the conversion to organic N by mycorrhizae. A promising approach would be the application of ^{15}N , followed by the analysis of N-pools with a high temporal resolution and the characterisation of soil organic matter by ^{15}N -NMR spectroscopy.

The case study with micro suction cups demonstrates that preferential flow paths play an important role for microbial processes. The results suggest that flow paths are locations with a better nutrient supply and aeration than locations in the soil matrix. It would be an interesting objective to clarify whether these findings can be extrapolated to other soils, to other conditions, and to other processes.

My results show that DON is the dominant form of dissolved N in the soil water and the major N component exported from the catchment. This is consistent with other studies (Qualls *et al.*, 1991; Arheimer *et al.*, 1996). However, we do not know much about the structure and the bioavailability of DON. Useful information could derive from the natural ^{15}N abundance of DON in comparison to that of the solid organic matter. An approach to estimate the availability of DON for biota would be the extraction of DON from ^{15}N enriched litter and its subsequent incubation in the soil or in stream water.

The estimation of water flow paths through the catchment by the end-member mixing analysis shows that hydrochemical data can be used to identify the origin of the runoff. This additional information on runoff generation may improve and validate physically based runoff models. The coupling of both hydrochemical and physically based runoff models would enhance our understanding of runoff processes in catchments.

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