Doctoral Thesis

Nitrogen dynamics and leaching from humus-rich and tile-drained agricultural soil

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Nitrogen Dynamics and Leaching
from Humus-Rich and Tile-Drained Agricultural Soil

Dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZÜRICH
for the degree of
DOCTOR OF NATURAL SCIENCES

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2001
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Summary

The wetland soils in the basin of the Furttal valley, north of Zürich, Switzerland, were reclaimed in 1920’s and brought under cultivation. The humus-rich soils of the valley have since been under intensive arable production and vegetable gardening, and hence, suspected of being a major source of N input to the Furtbach creek, especially during the growing season. The aim of the current research study was to test the hypotheses that the mineralisation of the organic matter in the drained humus-rich soils is the major source of nitrogen export and that the mineralised nitrogen is transported rapidly through the preferential flow paths and via the subsurface drainage system to the Furtbach creek. Thus, substantial N export through the drainage system may occur during periods of low groundwater table and high temperatures.

The most important results of the current research are summarised as follows:

**Field studies of N fluxes**

Field studies showed that during the growing season of 1996 the net mineralised nitrogen in two tile drained fields with different crops were about 150 and 300 kg N ha⁻¹ in the main root horizon from 0-40 cm depth. Contrary to the expectations, *ex situ* mineralisation studies using undisturbed soil cores indicated that net N mineralisation from the “fossil” organic matter in the subsoil was of minor importance. This is because the soil investigated is in transition from a wetland to a mineral soil and only few places exist where the humus rich layer still reaches to about 100 cm in thickness. It was estimated that about 8 kg N ha⁻¹ y⁻¹ was released from the 40-70 cm subsoil layer.

Monitoring the outflow of different drainage subsystems showed that annual N exports via drain varied between 12 and 31 kg N ha⁻¹ y⁻¹ of which a substantial portion (20-60%) was leached during the 6-month period from May through October. Since mineral N in these soils mainly accumulated in the spring before plant uptake became effective, the risk of N leaching was very high at the beginning of the vegetation period.

Although subject to a high degree of uncertainty in estimation, net N mineralisation and plant N uptake were found to be the most important N fluxes. In comparison, N losses via drain were small, that is after a 17-month monitoring period, about 5-7% of plant N uptake and 3-10% of net N mineralisation. However, they were not negligible for the water quality of the Furtbach.
Summary

Modelling mineral N dynamics in the field

It was possible to successfully describe the water and mineral N dynamics of the investigated field soil by using inverse modelling to identify the model parameters. Addressing the inherent modelling uncertainties, the concept of ‘conditioned parameter distributions’ was introduced as a more appropriate alternative to ‘best-fit’ parameters. In this study measured pressure heads and nitrate concentrations were used to estimate 12 hydraulic parameters and up to 14 nitrogen turnover related parameters. Most of the measurements in three soil layers fell within the 95% confidence interval of the Bayesian distribution. Some observed pressure heads corresponding to intense rainfall events and periods of soil freezing were exceptions, as well as some high nitrate concentrations in the subsoil between 40 and 70 cm depth. The discrepancies were attributed to processes that were not addressed by the simulation model, such as freezing and short-circuiting due to macropore flow.

The results suggest that this approach may be a promising tool not only for modelling well-controlled lab experiments, but also for field ecosystems.

Modelling net N mineralisation

Using net N mineralisation rates determined in ex situ incubation experiments of undisturbed subsoil cores in combination with an empirical moisture and temperature response function provided a good description of the observed fluctuations of mineral N in the field. To describe the net N mineralisation below the plough layer (20-40 cm depth), it was sufficient to assume a single “humus” pool. For the topsoil (0-20 cm) it was necessary to account for an additional “litter” pool with a higher turnover rate. The two-pool model resulted in a fair description of the overall net N mineralisation in 0-40 cm depth, but did not honour the observed dynamics in the topsoil, dominated by litter turnover. This may due to the upward movement of capillary water evaporating at the soil surface leading to nitrate accumulation and, thus, to an overestimation of measured NNMin the uppermost layer. However, the mineralisation model applied did not account for N transport. In addition, it may be needed to include greater differentiation of fast decomposing organic matter pools and factors affecting decomposition rates in the surface layer, such as short-time wetting-drying processes.

The calibrated two-pool model estimated that about 340 kg N ha\(^{-1}\) were mineralised during the experimental year in the upper 40 cm of the soil, of which about 50% derived from the fast decomposing material.
Transport characteristics of solutes depending on initial moisture and application mode

The hypothesis was tested that the leaching characteristics may strongly depend on the way solutes are applied to the soil, in particular if the soil is dry at the beginning of infiltration. Two leaching experiments were conducted with undisturbed soil monoliths taken from the study site. One monolith was initially wet, the other dry, when infiltration started and three mobile tracers (deuterium (D), bromide (Br) and chloride (Cl)) were applied, each in a different way, that is by the infiltrating water (D), placed on the soil surface (Br), and injected in the soil matrix at 5 cm depth (Cl). Elution curves were almost identical for Br and Cl under initially wet conditions, whereas the displacement of Br was faster than that of Cl in the initially dry column. Apparently, a large fraction of Cl had been bypassed in the initial phase of infiltration in the initially dry column, indicating a higher degree of flow through preferential paths. An important practical implication of these findings to a field situation for the application of nitrate fertilisers is that if the fertiliser is applied shortly before a rainfall event to dry soils, then there is a higher risk of leaching than if the fertiliser is placed within the soil or applied to a wet soil. This assumption also holds for mineral N released from organic matter decomposing at the soil surface.

Application of the steady-state transport models using the CXTFIT code led to reasonable descriptions of the observed elution curves under initially moist conditions, which were not far from steady-state equilibrium of the infiltration. For the initial dry column, neither a equilibrium nor a non-equilibrium model assuming steady-state flow could adequately described the experimentally observed leaching characteristics of chloride. To some degree, this was probably due to the inadequate description of the initial distribution of resident solutes, since the simulation codes used in this study automatically assume equilibrium between mobile and immobile regions as conditions for solutes initially present in the columns. Even a model allowing for transient and macropore flow and, thus, also for more flexibility with respect to the initial conditions, was not able to fully cope with the change of transport conditions in the initially dry column at the beginning of the infiltration.
Zusammenfassung


Die wichtigsten Ergebnisse dieser Studie lassen sich wie folgt zusammenfassen:

**Stickstoffdynamik im Feld**

Im Hauptwurzelaum (0-40 cm Tiefe) von zwei unterschiedlich bewirtschafteten Parzellen wurden während der Vegetationsperiode 1996 netto rund 150 bzw. 300 kg N ha⁻¹ mineralisiert. Die N-Nettomineralisation aus dem 'fossilen' Material des Unterbodens war hingegen gering. Letzteres ist vor allem darauf zurückzuführen, dass die ehemaligen Ried- und Moorböden des Untersuchungsgebiets sich im Übergangsstadium zu mineralischen Böden befinden, und die humusreichen Schichten sich nur noch an einigen wenigen Stellen bis in tiefere Bodenschichten erstrecken. Aufgrund von *ex situ* Mineralisationsstudien mit ungestörten Bodenproben wurde für die Tiefe von 40-70 cm eine jährliche Stickstofffreisetzung von rund 8 kg N ha⁻¹ berechnet.

Die Überwachung des Abflusses verschiedener Dränabteile zeigte, dass die mittleren mineralischen N Exporte im Bereich von 12 und 31 kg N pro ha⁻¹ a⁻¹ lagen. Davon wurde ein beträchtlicher Anteil (20-60%) während des Sommerhalbjahres von Mai bis Oktober beobachtet. Da der mineralische Stickstoff (Nmin) im Boden vor allem im Frühjahr bis zum Einsetzen einer effizienten Pflanzenaufnahme akkumuliert, war sein Auswaschungsrisiko zu Beginn der Vegetationsperiode besonders gross.

Trotz des hohen Unsicherheitsbereichs der geschätzten Flussgrössen waren die N-Netto-
mineralisation und die N-Aufnahme der Kulturen die dominierenden Bilanzgrössen. Im
Vergleich dazu fielen die N-Verluste via Dräne gering aus: Nach einer 17-monatigen Überwachungsperiode betrugen diese nur 5-7% der Pflanzenaufnahme und 3-10% der N-Nettomineralisation. Trotzdem stellten sie für den Furtbach eine relevante Beeinträchtigung der Wasserqualität dar.

**Modellierung der Dynamik des mineralischen Bodenstickstoffs im Feld**


Aufgrund der Ergebnisse empfiehlt sich der hier verwendete Ansatz als vielversprechendes Vorgehen nicht nur bei der Modellierung von gut kontrollierten Laborexperimenten, sondern auch im Falle von Agrarökosystemen.

**Modellierung der Stickstoffnettomineralisation**

Auf der Grundlage von *ex situ* bestimmten Raten der Stickstoffnettomineralisation (NNM) und ihrer Feuchtigkeits- und Temperaturabhängigkeit wurden die über drei Tiefen beobachteten Veränderungen des \( N_{\min} \)-Gehaltes *in situ* gut beschrieben. Zur Beschreibung der NNM unterhalb der Pflugsohle (20-40 cm Tiefe) genügte es, einen einzigen „Humuspool“ anzunehmen. Für den Oberboden (0-20 cm Tiefe) musste hingegen ein zusätzlicher Pool an organischer Substanz mit einer höheren Abbaurate („Streupool“) eingeführt werden.

Dieses Zwei-Pool-Modell konnte die N Mineralisation für den Hauptwurzelraum insgesamt (0-40 cm Tiefe) gut widergeben, nicht jedoch die durch den Streuabbau dominierte Dynamik im Oberboden. Letzteres kann unter anderem damit erklärt werden, dass der mineralische Stickstoff im Feld in Form von Nitrat mit dem aufsteigenden Kapillarwasser nach oben transportiert wurde und aufgrund der Evaporation an der Bodenoberfläche akkumulierte. Dieses Phenomen würde die Diskrepanz zwischen Messung und Modellierung erklären, da es zur Überschätzung der NNM in der obersten
Zusammenfassung


Aufgrund des kalibrierten Zwei-Pool-Modells wurde die jährliche NNM in den oberen 40 cm des Untersuchungsstandortes auf rund 340 kg N ha⁻¹ geschätzt. Rund 50% davon stammte aus dem schnell abbaubaren Pool.

Charakteristik des Stofftransports in Abhängigkeit der Bodenfeuchte und der Stoffapplikation

Die Hypothese wurde getestet, dass der Stofftransport stark von der Ausbringungsart der Stoffe abhängt, insbesondere bei trockenen Anfangsbedingungen. Dazu wurden Auswaschungsexperimente mit zwei Bodenmonolithen aus dem Untersuchungsgebiet durchgeführt. Drei mobile Tracer (Deuterium (D), Bromid (Br) und Chlorid (Cl)) wurden auf verschiedene Weise ausgebracht, nämlich im Beregnungswasser (D), salzformig auf die Bodenoberfläche gestreut (Br) und gelöst in 5 cm Tiefe eingespritzt (Cl). Zu Beginn der Beregnung unterschieden sich die beiden Monolithen zudem in ihrer Bodenfeuchtigkeit (nass/trocken). Die Austragskurven im anfänglich nassen Monolithen waren für Br und Cl nahezu identisch, während Br in der anfänglich trockenen Bodensäule rascher als Cl verlagert wurde. In der Anfangsphase wurde offenbar ein grosser Anteil des Chlorides im trockenen Boden umflossen, was darauf hindeutet, dass das infiltrierende Wasser vermehrt über präferentielle Fliesswege in die Tiefe gelangte. Für die Praxis bedeutet dieses Resultat, dass Mineraldünger, der kurz vor einem Niederschlag auf trockene Böden appliziert wird einem höheren Auswaschungsrisiko unterliegt als wenn er in oder auf einen nassen Boden ausgebracht wird. Dies gilt auch für Nitrat, das aus der Mineralisation von organischem Material an der Bodenoberfläche stammt.

Im Falle der anfänglich nassen Bodensäule konnte mit Hilfe eines steady-state Transportmodels (CXTFIT Code) eine zufriedenstellende Übereinstimmung zwischen simulierten und gemessenen Tracerkonzentrationen im Abflusswasser erzielt werden. Offenbar beinflusste die anfängliche Zustandsänderung der Bodenfeuchtigkeit den Transportprozess wenig, was auf einen annähernd stationären Zustand schliessen lässt. Dasselbe Model konnte die Austragskurven im anfänglich trockenen Bodenmonolithen hingegen nicht beschreiben, weder unter der Bedingung eines chemisch-physikalischen Gleichgewichts noch mit Hilfe eines Zwei-Regionen-Modells. Möglicherweise ist das teilweise auf die mangelhafte Beschreibung der Anfangsverteilung der Stoffe im Boden...
Zusammenfassung

zurückzuführen, da das verwendete Simulationsmodell automatisch Gleichgewicht zwischen der mobilen und der immobilen Region annimt. Jedoch konnte auch ein Modell, das transiente Bedingungen und Makroporenfluss und demzufolge mehr Flexibilität bezüglich der Anfangsbedingungen zulässt, die sich verändernden Transportbedingungen in der anfänglich trockenen Bodensäule nicht zufriedenstellend beschreiben.
Intensification of agriculture has led to an increased input of nitrogen (N) into agricultural ecosystems as well as to a faster N-turnover within the system. The increased crop production is accompanied by increased N losses to the environment. Besides gaseous losses to the atmosphere, waterways are important pathways by which nitrogen is carried from their sources to the larger world, leading eventually to eutrophication of aquatic systems, such as freshwater lakes and streams or coastal environments, and pollution of groundwater resources at various scales. The mineral nitrogen species ammonium and nitrate are of particular concern because ammonium is fish toxic already at low concentrations, and nitrate is very mobile and thus easily leached from soil into water.

Riverine nitrogen inputs from the North Sea regions into the North Atlantic Ocean, for instance, have increased by some 11-fold due to human activity (Howarth, 1998). About 65% of the Swiss riverine water drains via the Rhine. To reduce its high annual N discharge into the North Sea Switzerland has agreed by international agreements to reduce its nitrogen loads (IKSR, 1987, 1989). Braun et al. (1991) estimated that 1986 about 80'000 t of nitrogen left Switzerland by the Rhine. New data show improvement, but still reveal a gap between actual and target reduction of N input into Swiss resource waters (BUWAL, 1996, 1998; AWEL, 1998; IKSR, 1998). Compared with the improvements of point sources, such as wastewater treatment plants the control of non-point sources proved to be a far more difficult task (IKSR, 1992; Braun et al., 1994).

In agricultural systems the soil mineral N pool, consisting mainly of ammonium and nitrate, is fed by fertilisation and mineralisation of N fixed in the soil organic matter and plant residues. Both sources contribute to N losses from the soil-plant system particularly when the amount of N released into the system does not coincide with plant uptake. Since mineralisation depends on a wide variety of factors, such as climate, cultivation management, and soil properties, it is difficult for farmers to optimise the N supply to the crops and to minimise the mineral N pool at the same time. This conflict between agricultural land use and the protection of water resources is particularly accentuated in drained wetland soils in which the humus-rich soil layers represent a
large pool of mobilisable nitrogen. According to Braun et al. (1991) non-point sources from agriculture, forest or atmospheric deposition contributed with 21'000 t to the annual N load of 80'000 t of nitrogen in the Rhine, whereof 9% were attributed to artificially drained soils.

In such soils, low groundwater tables and high temperature, especially in summer, promote soil aeration and decomposition of the “fossile” soil organic matter also in greater soil depths. Additionally, desiccation stimulates the development of macroporosity by formation of cracks and biopores, such as root and earthworm burrows, providing channels for preferential water flow and solute transport through the root zone. In recent years it has become evident that preferential flow and transport of solute is rather the role than the exception under field conditions (e.g. Luxmoore et al., 1990; Flury et al., 1994; Stagnitti et al., 1995). It may occur not only in winter, when soils are highly saturated with water, but also in dry summer periods, when rainfall intensities of summer storms exceed the infiltration capacity of the soil matrix (Edwards et al., 1993).

This can be a problem of particular concern in fields with artificial drainage (Smettem et al., 1983; Richard and Steenhuis, 1988; Coles and Turdill, 1985; Everts and Kanwar, 1990; Milburn et al., 1990; Magesan et al., 1995; Kumar et al., 1997). Drainage may accelerate desiccation and, thus, the formation of preferential flow channels. In addition, the drainpipes may act as artificial macropores connecting the preferential pathways of the soil to surface water by-passing the filter capacity of the soil matrix. As a consequence, artificial drainage and cultivation of these soils produces a particular high risk of nitrate leaching from the fields to surface water bodies (e.g. Stamm et al., 1998; Kamra et al., 1999; Addiscott et al., 2000; Gentry et al., 2000).

These questions were addressed in a case study in the Swiss Furttal valley north of Zürich. In the basin of the Furttal valley about 250 ha are drained humic soils, which are under intensive, arable or vegetable production. The area is a former wetland, which was reclaimed and brought under cultivation between 1920 and 1930. Today, the organic matter content of the humic rich layers varies between 10-17%. Monitoring the water quality of the Furtbach creek, the main drainage of the valley, showed that nitrate and ammonium concentrations regularly exceeded Swiss quality standards1 (Kupper, 1991). About 45% of the annual N load had to be attributed to non-point-sources, such as the outflow from drainage systems. Since in a preliminary study substantial mineral

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nitrogen losses were found not only during the non-growing season, but also during the growing season, the following hypotheses were formulated:

1. In humus-rich soils mineralisation of organic matter may be a major source of nitrogen export.
2. Large parts of nitrogen losses by leaching may occur during the growing season.
3. Preferential flow is a dominant mechanism of N leaching in drained soils.
4. Transport by preferential flow contributed substantially to nitrogen export by the drainage system, in particular during summer.

The hypotheses were tested in the framework of the research project “Risk Assessment for the Input of Nitrogen into Surface Waters from Artificially Drained Agricultural Land with Humus-Rich Soils” on experimental plot areas in the Furttal, divided into two sub-projects. One of these focused on the N dynamics in humus-rich arable soils, the second on water flow and solute transport in a drainage system. These investigations included field as well as laboratory and modelling work. The scope of these studies was to improve our understanding of the mechanisms involved in the N export from such systems and to evaluate the relevant risk factors as a basis for better control.

The thesis presented here is based on the results obtained in the sub-project on N dynamics. The hydrological investigations are subject of the PhD thesis of Kohler (in preparation). For more details concerning the field studies we refer to the final project report titled “Nitrataustrag aus einem humusreichen, landwirtschaftlich genutzten und dränierten Boden” (Schmied et al., 2000) summarised by Kätterer et al. (2000) for a broader readership.

The dissertation is written so that each chapter stands on its own. Some elements are repeated for clarity where we found it appropriate. A general introduction into the fundamentals of nitrogen dynamics in the soil-plant system is given in Chapter 2.

The experimental part and the most important results of the field study investigating the importance of N export during the growing season and the role of microbial N turnover associated with N losses are presented in Chapter 3. To estimate field parameters, inverse modelling offers sometimes the only viable choice because of time, expenses, practical limitations and inadequacy of laboratory methods. Chapter 4 investigates inverse estimation of parameters of a soil-plant model used to analyse the complex dynamics of the nitrogen pools in the field.

Chapter 5 presents ex-situ mineralisation studies in humus-rich subsoil monoliths and undisturbed soil cores and compares the result with the in-situ measured mineralisation in the main root zone. The aim of this study was to determine to what extent ”old”
stabilised soil organic matter, originating mainly from the former peat layers, and "new" labile organic matter, such as recently incorporated plant residue, contribute to net N mineralisation in the growing season. Additionally, the hypothesis was tested that N mineralisation rates and their dependence on soil moisture as estimated in small undisturbed soil cores in the laboratory also apply to undisturbed monoliths of much bigger size and to the field below the plough layer, where the soil is less disturbed by cultivation or climatic influences.

Finally, using a multiple tracer experiment under controlled lab conditions, we studied the influence of solute exposure to infiltrating water (that is in the infiltrating solution, spread at the surface and injected in 5-cm depth) and initial soil moisture on the travel time distribution of the solutes. Experimental set-up and results are presented in Chapter 6. Whereas Chapter 7 deals with single- and dual-porosity modelling of the tracer experiments, performed in collaboration with Dr. Thomas Kätterer from the Department of Soil Sciences of the Swedish Agricultural University (SLU) in Uppsala.

The main conclusions of this research are summarised in Chapter 8.

References


Fundamentals of Nitrogen Dynamics

Based on a literature review this chapter gives a general introduction into nitrogen dynamics focusing on the main scientific aspects related to the study work. First a description of the nature of soil organic matter and the microbial processes related to soil nitrogen turnover is given. Thereafter, the term “net N mineralisation” used in this thesis is introduced together with a method for quantifying N fluxes in situ, that is net N mineralisation, plant N uptake, and net N leaching. Since soil processes may extremely vary in space and time some insights into the current discussion of soil heterogeneity are given in addition. Finally, concepts of nitrogen turnover in soils and bases of numerical modelling are presented, followed by a summary of the most important conclusions related to nitrogen transport by preferential flow.

2.1 Soil organic matter

Only a small fraction, in average about 15%, of the organic matter in soil is living matter (biomass). This fraction mainly consists of microorganisms (bacteria, fungi, actinomycetes, algae), plant roots and to a lesser degree also of soil fauna, in particular protozoa, nematodes, earthworms, and arthropods. The term “soil organic matter” (SOM) in its strict sense refers to the dead organic matter (necromass) consisting of residues and deposits from animal, plant and microorganisms. According to Oades (1988) SOM may be divided into macro-morphological identifiable substances and humus, the transformed organic matter pool with its humic and non-humic fraction (see Figure 2-1).

The non-humic fraction mainly consists of polymers and metabolites directly originating from organisms. Quantitatively most important are carbohydrates (e.g. cellulose, hemicellulose and mucopolysaccharide), aromatic polymers (e.g. lignin and tannin), proteins and extra-cellular enzymes as well as aliphatic macromolecules (e.g. lipids, suberin and cutin). In SOM only few monomers (e.g. carbon and amino acids, phenols or sugars) were present, since they are quickly decomposed by microbial activity. The humic organic matter fraction covers chemical different substances classified by their solubility into humins, humic and fulvic acids.
Chapter 2

Organic Matter in Soil

Biomass Necromasse (Soil Organic Matter - SOM)

Macroorganic Substances Humus

Non-Humic Fraction Humic Fraction

Polymers Monomers Humin Humic Acids Fulvic Acids

Carbohydrates, Carbon Acids

Proteins, Aliphatic Amino Acids

Molecules Phenols, Sugars

Figure 2-1. Characterisation of organic matter in soils (after Oades 1988).

About 95% of the nitrogen typically found in soils are organic (N_{org}). The three major biological forms of N_{org} are proteins, microbial cell wall constituents, such as chitin and peptidoglycans, and nucleic acids.

2.2 Soil nitrogen dynamics

The N turnover in soil is part of the earth’s overall N cycle. The annual rate of N removal from the atmosphere by fixation and its incorporation into soils is approximately balanced by an equal amount of N returned to the atmosphere by denitrification. Thus, over time, a quasi-equilibrium exists between the amount of N in the atmosphere and the amount of N in soils on a global scale (Foth and Ellis, 1997). The circulation of N through the soil is mediated by a series of microbial reactions that shuttle N back and forth at the discretion of the microorganisms (Figure 2-2).

Biological N\textsubscript{2} fixation (BNF) occurs in symbiotic systems, where the host plant supplies the N-fixing organisms with fixed carbon (C), and benefits from the nitrogen fixed by the microorganisms. Most important is the genus *Rhizobium*, which lives in the root nodules of leguminous plants. The nonsymbiotic N\textsubscript{2} fixation is due to several kinds of bacteria, which are of minor importance in agricultural soils. Inputs of nitrogen to the soil from BNF vary widely from one ecosystem to another. While free living microorganisms may fix up to 30 kg N ha\textsuperscript{-1} y\textsuperscript{-1}, symbiotic BNF yields up to 300-600 kg
N ha⁻¹ y⁻¹ (Gisi et al. 1990). It is estimated that over half of the BNF is due to leguminous symbioses in agricultural production (Foth and Ellis, 1997).

**Industrial N₂ fixation (INF)** is due to the Haber-Bosch-Synthesis, in which N₂ is dissociated and synthesised to inorganic N, i.e. for fertiliser production. This process requires temperature of about 500 °C and 200 bar pressure.

**Atmospheric deposition (AD) of N** is largely a consequence of human activities, e.g. by combustion processes in which N₂ is oxidised to NOₓ or by volatilisation (VOL) of ammonia (NH₃) from manure. Deposition can be dry, i.e. in gaseous form or sorbed to sedimenting particles, or wet, i.e. dissolved in rainwater.

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![Figure 2-2. Schematic N cycle: Most important processes of N transformation. BNF biological N fixation, INF industrial N fixation, AD atmospheric deposition, VOL volatilisation.](image)

The four main processes of N turnover in soils are mineralisation (ammonification), nitrification, immobilisation and denitrification. **Mineralisation** refers to the soil processes by which organic nitrogen is converted into mineral nitrogen. Since ammonia (NH₃) is the first mineral form produced, mineralisation of N is also called ammonification. Under aerobic conditions ammonification is followed immediately by nitrification, i.e. the transformation of ammonium (NH₄⁺) into nitrate (NO₃⁻). This condition is predominant in arable soils (Myers, 1975). Therefore the term mineralisation is also used to embrace both transformation processes leading to the mineral N forms NH₄⁺ and NO₃⁻ (Runge, 1983). **Immobilisation** is the opposite of mineralisation, that is the conversion of soil mineral nitrogen into organic forms by
incorporation into living matter. Usually the term is restricted to the uptake of mineral N, mainly ammonium, into the microbial biomass of the soil. Denitrification is a process also performed by microorganism leading to N losses from the soil in the form of molecular $N_2$ mainly, or to a lesser extent as $N_2O$. This process is the counterpart of N fixation and the only natural process by which $N_2$ is returned to the atmosphere. Thus it closes the biogeochemical N cycle. While it represents a loss of N fertiliser and may add to the “greenhouse” problem of the global climate if nitrogen oxide reduction does not proceed further than $N_2O$, denitrification reduces the risk of N leaching into water resources by depleting the pool of mobile mineral N.

Soil microorganisms have a unique role in N transformation. They may be regarded as a catalyst of SOM decomposition, as materials are taken up, converted into new products, and subsequently released actively or passively. In addition, microbial biomass by itself is an important pool. Although microbial N represents only approximately 5% of total nitrogen it is a major source for mineralised N in soil and its high turnover rate may determine short-term N dynamics (Smith and Paul, 1990).

In the following these N turnover processes are described in more detail. For further reading we refer to the literature, e.g. Killham (1994), Coleman and Crossley (1995), Paul and Clark (1996), and Foth and Ellis (1997).

### 2.2.1 Ammonification

The first steps of soil microbial decomposition of biopolymers occur by extracellular enzymes (exo-enzymes), e.g. extra-cellular proteases in the case of protein degradation. The ammonification, i.e. hydrolytic deamination of low molecular organics (R-NH$_2$), such as free amino acids, nucleotides or amino-polysaccharides, to NH$_3$ is accomplished by a large group of physiologically different microorganisms and - with the exception of urea hydrolysis - linked to cell-bound processes of living cells (Alef, 1991):

$$R\text{-}NH_2 + H_2O \rightarrow NH_3 + R\text{-}OH \quad (\text{Eq. 2-1})$$

NH$_3$ is strongly polar and readily combines with a proton to form NH$_4^+$:

$$NH_3 + H^+ \leftrightarrow NH_4^+ \quad (\text{Eq. 2-2})$$

Generally, in arable soils accumulation of NH$_4^+$ is rare because ammonium is converted rapidly along various pathways keeping pool sizes small: Volatilisation with increasing pH respectively high partial pressure; immobilisation by plant and microbial uptake, the latter preferring ammonium to nitrate as N source; humification such as forming of quinon-NH$_2$ complexes; and nitrification. In addition, as a cation, ammonium is much
more retained by the soil matrix through cation exchange processes than the anionic form of nitrate and nitrite and consequently much less mobile.

The size of organic nitrogen pools in the root layer of mineral soils ranges between 3-50 t N per hectare, depending on soil type, management and depth (Stadelmann, 1988). Per year approximately 1-3% of the SOM are mineralised. Assuming an average N content of 10 t per hectare for mineral soils about 100-300 kg N of mineralised N may be expected. On calcareous drained organic soils ammonification may yield up to 1000 kg N ha$^{-1}$ y$^{-1}$ (Furrer and Stauffer, 1986).

### 2.2.2 Nitrification

Nitrification occurs under aerobic conditions by oxidation of NH$_4^+$ via nitrite (NO$_2^-$) to nitrate (NO$_3^-$). Nitrifiers are usually chemolithoautotrophic as they use this reaction to reduce and assimilate carbon dioxide. The two most important nitrifying genera are the obligate aerobic bacteria *Nitrosomonas*, oxidising ammonium to nitrite, i.e.

\[
\text{NH}_4^+ + 1.5\text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + 2\text{H} \\
\text{(Eq. 2-3)}
\]

and *Nitrobacter*, oxidising nitrite to nitrate, i.e.

\[
\text{NO}_2^- + 0.5\text{O}_2 \rightarrow \text{NO}_3^- \\
\text{(Eq. 2-4)}
\]

Since the two operate in close association and because the second reaction is faster than the first, nitrite is hardly detectable in soils. Within the soil-plant-system nitrate follows two main pathways, i.e., immobilisation and denitrification. A third, very important pathway is the nitrate export from the system: Since the charge of matrix surface sites is predominantly negative and complex-formation is negligible, nitrate is highly mobile and easily leached from soils with seepage or runoff water.

### 2.2.3 Environmental factors affecting mineralisation

Temperature, water content, oxygen availability, pH and nutrient supply are generally considered to be the most important factors affecting ammonification as well as nitrification.

In general, ammonification is accelerated by a factor of two to three if temperature increases 10-degree (Figure 2-11, left). This response is valid below the temperature optimum, i.e. within the range of about 5-50 °C. Optimal temperature depends on, e.g. the composition of soil microbial population. In composts, for instance, ammonification appears to have optimal conditions at temperatures exceeding 65 °C due to the activity of thermophilic bacteria. Stadelmann (1981) found a non-linear increase of ammonifi-
cation with several optima at 10-15 °C, 40-50 °C and >65 °C.

In dry soils ammonification is limited by lack of water. As soil becomes wetter, turnover increases to a maximum and then decreases again as oxygen-diffusion becomes limiting with increasing water-saturation (Figure 2-11, right). According to Foth and Ellis (1997) moisture conditions are optimal when soils are slightly wetter than field capacity, i.e. between -100 and -300 hPa water tension and with 80-90% of the air space filled with water. Wetting of dry soils appears to stimulate biological activities by producing a flush in N availability (e.g. Stadelmann, 1978; Van Veen et al., 1984; Foth and Ellis, 1997). This effect, which is not completely understood, increases with the length of the previous drought.

A wide variety of organisms participate in ammonification resulting in low sensitivity of ammonification to soil pH over a wide range of soil reaction. Under strongly acid conditions, however, organic matter accumulates at the soil surface, because of a lack of decomposition or ammonification.

Nitrification is more sensitive to soil conditions than ammonification (Beck, 1983; Paul and Clark, 1996; Ellis and Foth, 1997). Little nitrification occurs in wet and cold soils. Since all nitrifiers need oxygen, nitrification ceases in its absence. Therefore, nitrification is affected by soil structure and water content. On the other extreme, lack of water may retard bacterial proliferation. However, usually nitrification proceeds readily at water tensions between \(-10^3\) and \(-10^4\) hPa. Optimum water content varies with soil type. In most soils, it is at 50-70% of the water-holding capacity. Nitrification is very sensitive to temperature and occurs mainly in the range of 5-40 °C. Values for temperature optima given in the literature vary between 20-25 °C (Gisi et al., 1990), 25-30 °C (Stadelmann, 1988), and 30-35 °C (Paul and Clark, 1996; Ellis and Foth, 1997). Nitrifiers are also sensitive to \(H^+\). Their activity is reduced below pH 6.0 and becomes negligible below pH 5.0-4.0. The optimum soil reaction is at pH 6.6-8.0. High pH values inhibit transformation from nitrite to nitrate (Paul and Clark, 1996).

### 2.2.4 Immobilisation

Immobilisation refers to the uptake of mineral N and its conversion to organic N by microorganisms. The amount of immobilised N thus depends on the soil microbial biomass and its C/N ratio. The carbon/nitrogen (C/N) ratio of microorganisms varies between species. Fungi can have wide C/N ratios, ranging from 4.5 to 15, while the C/N ratios of bacteria usually are in the range 3 to 5.

Microbial assimilation of inorganic N varies largely depending on the C/N ratio of the decomposed organic substrates in relationship to the C/N ratio of newly produced
microbial biomass. If the C/N ratio of the decomposed substrate is larger than that of the produced biomass, e.g. in the case of straw residues with a C/N ratio between 100 and 150, extra mineral N will be required to process the straw and net N immobilisation will occur. If organic matter with a lower C/N ratio decomposes, excess is released into the mineral N pool.

Thus, immobilisation is closely coupled with the turnover of SOM and does not only depend on the availability of inorganic N in the soil. Generally, for arable soils a C/N ratio of about 20 is regarded as the approximate threshold between mineralisation and immobilisation (Killham, 1994). Then the net effect of both processes is zero, although they may occur at significant rates.

Despite of the simplicity of the basic principles it is not easy to predict whether at a given moment N release or N immobilisation will prevail, because substances of differing C/N ratios are usually decomposed simultaneously, and selective decomposition changes the nitrogen content of decomposing residues over time.

2.2.5 Denitrification

Denitrification is the sequential reduction of nitrate to nitrite, nitric oxide (NO), nitrous oxide (N₂O), and consequentially to dinitrogen (N₂)

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]  

(Eq. 2-5)

where, the last three products are highly volatile and thus easily escape as gases into the atmosphere. Denitrifying microorganisms are mostly heterotrophic, facultative anaerobes using nitrate as electron acceptor under conditions of oxygen lack. But also aerobic denitrification was reported (e.g. Robertson and Kuenen, 1984; Lloyd, 1993; Mona et al., 1995; Wilson et al., 1997; Bergwall and Bengtsson, 1999) often observed together with heterotrophic nitrification (e.g. Robertson et al., 1988; 1989; Van Niel et al, 1992). Davidson and Oremland (1993), for instance, found that the aerobic process of chemoautotrophnic denitrification predominated when the water filled pore space was smaller than field capacity, whereas at higher water saturation anaerobic process became more pronounced.

However, overall denitrification rates decrease as oxygen availability increases (Lloyd, 1993). Since anaerobic microenvironments arise where soils are at or near water saturation, denitrification is closely linked to the water regime of a soil. Because oxygen supply by diffusion in the aqueous phase is very limited, soil structure plays an important role, allowing for at times, extreme spatial heterogeneity even on the microscale. Nitrification may occur in the outer part of soil aggregates and
denitrification at the same time in the interior. The growth of plant roots may inhibit
denitrification depleting nitrate pools and drying out the soil. On the other hand, roots
exudate organic C and consume oxygen. Significant amount of gaseous N losses may
occur even in well-drained arable soils after tillage (Flessa and Beese, 1995) or mulch
tillage (Aulakh et al., 1991). Since nitrate is produced under aerobic conditions, while
denitrification depends on anaerobic conditions, rapid fluctuation between saturated and
unsaturated conditions is particularly favourable for denitrification as are transition
zones between unsaturated topsoil and saturated subsoil in wetlands.

Denitrification depends on the presence of nitrate and substrate availability as N, C and
energy source as well as on the composition of microbial population. Optimal are a
warm climate, high nitrate concentrations and easily degradable organic C. Under such
conditions a daily loss of about 1 kg N ha\(^{-1}\) may occur by denitrification (Killham,
1994). Estimations for denitrification losses from Swiss agriculture vary widely
between 1 and 20 kg N ha\(^{-1}\) y\(^{-1}\) for arable fields and between 25 and 220 kg N ha\(^{-1}\) y\(^{-1}\)
for grassland (Stadelmann, 1988; Gupta, 1988; Braun et al., 1994).

Acidity affects both the rate of denitrification and the type of gas produced. Above pH
6.0 the dominant gas released is N\(_2\), whereas in more acid environments N\(_2\)O production
becomes prevailing. Furthermore, an increasing ratio of nitrate to organic C as well as
increasing oxygen availability are favouring N\(_2\)O as end product and are restricting
complete reduction to N\(_2\) (Firestone and Davidson, 1989).
2.3 Net N mineralisation (NNM)

2.3.1 Definition

The amount of mineral soil nitrogen (Nmin) largely depends on the difference between mineralisation and microbial immobilisation rates. Jansson (1958) and Zöttl (1958) define the combination of these processes as net N mineralisation (NNM).

In this thesis, we use the term NNM differently, because standard methods of NNM determination in situ (see below) do not allow to separate denitrification from mineralisation and microbial immobilisation. Therefore, we define NNM as the net effect of mineralisation, immobilisation and denitrification (Figure 2-3). N fixation is not considered here because it played a minor role in our study. Using this definition NNM leads to a mineral N pool available to plant uptake and leaching.

\[ A \quad \text{Ammonification} \]
\[ N \quad \text{Nitrification} \]
\[ I \quad \text{Immobilisation} \]
\[ D \quad \text{Denitrification} \]

![Diagram of the processes determining NNM as defined in this thesis.](image)

Figure 2-3. Scheme of the processes determining NNM as defined in this thesis.

2.3.2 Methods for quantifying N mineralisation in situ

Methods for quantifying (net) mineralisation in soils can be divided into laboratory and field methods. A variety of laboratory methods have been proposed, including aerobic incubations where soils are either leached (Standford and Smith, 1972) or incubated in closed containers (Keeney, 1982) and anaerobic incubations (Waring and Bremner, 1964). To get reliable results with these methods, homogenised, dried and sieved soil
samples have to be used. Laboratory methods are useful to study mineralisation kinetics and to analyse the release from individual organic matter fractions (Paustian and Bonde, 1987), as well as to rank the mineralisation potential of different soils. Since laboratory methods apply conditions, which are far from the environmental influences in situ, they are of little value in quantifying field N fluxes.

Incubation methods using undisturbed soil cores in the laboratory (e.g. Stenger, 1994; Stockdale et al., 1994) are closer to field situations as soil structure and micro-scale heterogeneity is not destroyed. Still they do not account for the very transient field situation governed by climate conditions, farm managing factors or changing influences of growing plants.

Since N turnover is strongly affected by micro-environmental conditions, in situ methods give more reliable results for N mineralisation in the field than laboratory methods (e.g. Adams and Attiwill, 1986; Binkley and Hart, 1989). Because of the importance of soil N availability in regulating the productivity of ecosystems considerable efforts have been made to develop methods for the measurement of NNM in the field. They rely on the accumulation of mineral nitrogen in the absence of actively growing roots, which typically involves in situ incubation of soil cores or samples in sealed containers. The problem of this approach is the soil disturbance involved. Depending on the experimental set-up, the physical structure of the soil may be disturbed considerably and the moisture regime altered artificially. If soil cores in plastic or metal cylinders are used, decomposition of cut-off plant roots will affect soil N turnover. In addition, rhizosphere microbial processes will not take place, which may affect mineralisation. Field techniques are very laborious and require extensive analytical and measuring procedures, taking into account the heterogeneous nature of the soil and the uncertainties of measured values. Currently, the determination of N fluxes in managed and natural ecosystems is still restricted by the lack of easy, fast and reliable methods. Although recent publications indicate that in situ 15N techniques leading to separate estimates of both gross N mineralisation and immobilisation may be an promising alternative approach (Mary and Recous, 1994; Mary et al., 1998; Recous et al., 1999).

In this study, we used the sequential in situ coring technique (Adams and Attiwill, 1986; 1989; Raison et al., 1987) developed for measuring net N mineralisation as well as leaching and plant uptake. To prevent N uptake by roots, steel cylinders were inserted into the soil. Some of the cylinders were covered to prevent water infiltration and thus leaching of nitrogen. To minimise soil disturbance we used larger cylinders (25 cm in diameter and 40 cm in length) than proposed by the above authors (Figure 2-4).

Mineral N was determined in the soil samples taken in the bulk soil at the beginning of
each incubation period. After approximately six weeks the soil from the cylinders and, again, unconfined soil was sampled for mineral N analysis. Net mineralisation (NNM) was then calculated as the difference between the mineral N measured in the bulk soil at the beginning and inside the covered cylinders at the end of each incubation period. Net N leaching (NNL) was assumed to be the difference between the covered and uncovered cylinders, and plant N uptake (PNU) was estimated as difference between the mineral N content inside the covered cylinders and the unconfined soil at the end of each incubation period. Sequential implementing of this set-up on different test plots (split-plot-design) allowed to measure N fluxes over the season.2

This technique has been used to study N fluxes in forest soils (Adams and Attiwill, 1986; Raison et al. 1987, 1990; Whynot and Weetman, 1991), grassland soils (Hatch et al., 1990, 1991; Debosz 1994), peat soil (Williams and Wheatly, 1992) and fertilised agricultural soils (Debosz and Vinther, 1989; Boone, 1990; Vinther 1994; Stenger et al. 1995, 1996).

Figure 2-4. Set-up of the in situ incubation designed for this thesis (3 replications), here shown for spring 1996 in a field cropped with sugar beet. One steel tubes (L: 40 cm, D: 25 cm) is covered by a plastic roof to prevent N leaching.

2 For a more detailed description of the sequential in situ coring technique we refer to Chapter 3.2.2 of this thesis.
2.4 Spatial heterogeneity

Soil properties and processes may extremely vary in space and time. In recent years many studies focused on the spatial distribution of soil properties, such as texture, bulk density, soil moisture, hydraulic conductivity, soil pH or organic matter content (e.g. Beckett and Webster, 1971; Conyers and Davey, 1990; Buchter et al., 1991; Strong et al., 1997, 1998; Bruckner et al., 1999; Bednorz et al., 2000) meso- and micronutrients (e.g. Singh et al., 1985; Paz et al., 1996) or enzyme activity (von Steiger et al., 1996).

Spatial and temporal variability of N turnover processes may be even more extreme. With respect to mineral N concentrations in arable soils, generally, most of the variability can be found within short distances (Biggar, 1978; Meisinger 1985, Van Mervenne et al., 1990; Schmidhalter et al., 1992; Gross et al., 1995; Stenger et al., 1998). Bonde and Rosswall (1987) related seasonal variations of potentially mineralisable nitrogen within management systems, which occurred throughout the year, to variations in organic matter inputs over the seasons. Additionally, variation in microbial populations leads to different mineralisation patterns in different soils. Zak et al. (1994), for example, emphasised the functional diversity of microbial communities in soils. Various authors have presented evidence that mineralisation varies with structural, textural and physico-chemical soil properties (e.g. van Veen and Kuikman, 1990; Verbene et al. 1990; Gregorich et al. 1991; Amato and Ladd, 1992; van Gestel et al. 1993; Hassink, 1992, Hassink et al. 1993a, 1993b; Ladd et al. 1990, 1993; van Golchin et al. 1994; Strong et al. 1997, 1998).

To describe the heterogeneous nature of soil properties and the uncertainties that arise from this variability in sampling spatial statistics has been employed in recent studies, including nested sampling plans. In nested sampling, observation points are spatially grouped according to a hierarchical scheme, with increasing distances between groups as the hierarchical level increases. The spatial structures in the observed parameters may then be identified by nested variance analysis (Webster and Oliver, 1990) or geostatistics (Burrough, 1993). This information can be used to optimise and to select sampling scales that reflect the spatial variation of the properties under consideration.

Von Steiger et al. (1996), for instance, used nested sampling and analysis of variation to identify appropriate sampling scales for urease activity and organic C content. Paz et al. (1996) sampled the topsoil according to a nested pattern to describe the spatial dependency of nutrients and other soil properties (pH, organic carbon, CEC) and the two texture fractions sand and silt content using geostatistics.
Figure 2-5. Sampling scheme and example for sample point configuration at a grid point. Distances from grid point were fixed directions chosen at random. (Schmied et al., 1997)

Figure 2-6. Accumulated variance of the nitrate contents in two fields cropped with grassland and winter wheat in spring 1995 in the Furttal by order of distance classes including analytical variance of about 0.12 mg N per kg dry soil (dotted line). Dashed lines refer to the overall sample variance. (Schmied et al., 1997)
Figure 2-5 shows the nested sampling scheme, which was used in the present study at two test sites, a grassland and a winter wheat field, in the Furttal to determine spatial variability of mineral N in spring 1995.

The partitioning of the variances showed that on both fields soil nitrogen concentrations varied little over distances up to 3 m as compared with the variation of the entire field (Figure 2-6). On the grassland, a minimum spacing of 10 m between samples was found to be necessary to cover whole-field variation, whereas on the winter wheat field minimum spacing was more than 30 m (Schmied et al., 1997).

2.5 Modelling nitrogen dynamics

2.5.1 Introduction

Modelling nitrogen turnover in a soil-plant system has become common practice in agricultural and environmental research. Originally, models had been primarily designed as tools to improve understanding of the system, i.e. mechanisms and processes governing the fate of N in soil. Today, models are used more and more as management tools, although their prediction capabilities are still limited.

Models differ considerably with respect to scope and target variables, the way processes are represented, the degree of detail and complexity, spatial and temporal scales and resolution as well as numerical technique. Comparing earlier (Frissel and Van Veen, 1981) and more recent (e.g. Groot et al., 1991; Thomasson et al., 1991; Diekkrüger et al., 1995; Hansen et al., 1995) approaches reveals that although numerical models in general have become more comprehensive, limitations still exist due to incomplete and inadequate representation of the governing processes of water fluxes, soil N turnover or plant N uptake. Additional difficulties arise in the assessment of the required input parameters, in particular with respect to the biological processes, and in the availability of measurements for model validation. However, modelling proved to be useful dealing with problems in soil management on the short-term scale in small field plots. Since the exact determination of boundary conditions for long-term forecasts are essential long-term application of a model calibrated on a short period may fail.

Although N demand of crops is most important for controlling soil mineral N we do not further discuss the different ways in which plant growth may be simulated because in our study plant N uptake was treated as boundary condition in monitoring soil N turnover. For details of the different model approaches the reader is referred to the literature, e.g. Johnsson et al. (1987), Schröder et al. (1995), Smith et al. (1996), and Brisson et al. (1998), among others.
Current research suggests that knowledge of bulk soil properties such as pH, soil water, temperature, and substrate quality is not sufficient to adequately account for the influence of soil on N turnover. Interrelations of soil properties (Strong, 1998) and spatial and temporal patterns of heterogeneity (Addiscott, 1996; Huwe and Totsche, 1995; Abbaspour et al., 1998), for instance, are per se important and often decision factors in modelling the N regime of a soil.

2.5.2 Concepts of N turnover in soils

In the literature modelling of soil carbon and nitrogen turnover is dominated by two main concepts. One, represented by the diagram in Figure 2-7, conceptualises soil nitrogen cycling from the viewpoint of soil fauna and flora in terms of food webs (e.g. De Ruiter et al., 1993; Andrén et al. 1990; Hunt et al., 1987; Hendrix et al., 1986). The other concept, schematically shown by Figure 2-8, considers N cycling as an exchange of N between pools of different chemical and biochemical forms, and sometimes also physical properties linked to SOM turnover (e.g. Johnsson et al., 1987, van Veen et al., 1984).

Figure 2-7. Example of a food web diagram (after Hunt et al., 1987).
Food web models are based on the well-established notion that soil microbial activity and, thus, C and N mineralisation strongly depend on the activity of the soil fauna, especially protozoa and nematodes. Basically, food web models describe the nutrients cycling between the different groups of organisms involved by calculating their consumption, biomass production and excretion of organic and inorganic, that is mineralised, material. De Ruiter et al. (1993), for instance, successfully simulated N mineralisation rates with the food web model of Hunt et al. (1987) for seven ecological systems, such as a shortgrass prairie and arable farming systems with different management practices.

Figure 2-8. Scheme of the N mineralisation-immobilisation model after Van Veen et al., 1984.
In the basically physical-biochemical concepts, soil microorganisms play the role of biological catalysts. Thus, they are typically represented only in terms of turnover rate coefficients. Transport models including N turnover generally define different fractions of organic material, each with a specific substrate quality and its respective turnover rate. High turnover rates are attributed to small pools of recent inputs of biological deposits or residues; slower turnover rates characterise pools of greater size and higher transformation status. Van Veen et al., 1984 proposed a model with several organic matter pools, including living microbial biomass and the availability of the soil organic matter as a substrate for microbial growth (Figure 2-8). The latter was implemented by dividing both SOM and living biomass into a physically protected and a physically non-protected fraction.

The more detailed a model tries to describe the processes involved, the more complex it becomes, the more difficult it is to use, and the more sensitive it is likely to depend on the choice of its parameter values. More parameterisation means that more data are needed for calibration, which are often difficult, expensive and time-consuming to obtain. Thus, the art in modelling is to reduce complexity and required data input to a minimum, which still gives the desired results.

In soil N modelling biotic factors are particularly difficult to determine experimentally. Therefore, efforts are usually made to account for their influence indirectly, relating them to parameters, which are available more easily. In particular, microbial biomass is often included in the litter pool or a certain kinetically or biochemically defined fraction of SOM.

By similar reasons, the partitioning of SOM is usually restricted to very few pools. These pools are often only conceptually defined in the context of a specific model to increase its capability to fit observable target variables, but otherwise often have no clear model-independent physical meaning. The program LEACHM (Hutson and Wagenet, 1991), for instance, assumes N mineralisation to follow the rate of SOM decomposition classified in three organic matter pools, i.e., litter, easily degradable manure and relatively stable humus, and their average C/N ratios (Figure 2-9).³

³ See Chapter 4.
Figure 2-9. Scheme of C and N turnover in the LEACHM model (Hutson and Wagenet, 1991) after Johnsson et al. (1987). Abbreviations refer to the mineralisation rates of litter ($k_{li}$), humus ($k_{hum}$), and manure ($k_{man}$), and to the reaction rates of nitrification ($k_{nit}$), urea hydrolysis ($k_{hyd}$), denitrification ($k_{den}$), and volatilisation ($k_{vol}$). $K_d$ represents the distribution coefficient of ammonium adsorption / dissolution.
2.5.3 Nitrogen turnover and transport modelling

Mineralisation kinetics

As a result of decomposition, carbon compounds are converted into cellular and extracellular material, CO₂ or waste products. In general, organic matter decomposition processes are described by first-order kinetics of the following form:

$$\frac{dC_i}{dt} = k_i e_0 e_T C_i$$  \hspace{1cm} \text{(Eq. 2-6)}

where \( k_i \) (T⁻¹) is the constant basic reaction rate for the organic carbon pool \( C_i \) (M), \( e_0 \) and \( e_T \) are two correction functions accounting for the influence of soil moisture and temperature, respectively. The use of first-order kinetics means that the decomposition of plant residues is proportional to the plant residue content \( C_i \), whereas the specific rate constant \( k_i \) is independent of \( C_i \) and characteristic for the decomposed plant residue. The use of first-order kinetics implies also that the microbial inoculation potential is not limiting the decomposition rate.

An example for a first-order decomposition model is shown in Figure 2-10, while Table 2-1 lists the respective parameters, i.e. pool sizes, decomposition rates and efficiency of microbial production, accounting for the decomposition of 1000 µg C of straw per gram dry soil by such a model (Paul and Clark, 1996).

Table 2-1. Pool size and efficiency of microbial production used in a carbon-nitrogen turnover model for the decomposition of 1000 µg C g⁻¹ of straw in soil. C1, C2, and C3 refer to the decomposition curves in Figure 2-10 (after Paul and Clark, 1996).

<table>
<thead>
<tr>
<th>Pool</th>
<th>Residue carbon [µg g⁻¹]</th>
<th>Decomposition rate [day⁻¹]</th>
<th>Utilisation efficiency [%]</th>
<th>Residue nitrogen [µg g⁻¹]</th>
<th>C/N ratio [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Easily decomposable (C1)</td>
<td>150</td>
<td>0.2</td>
<td>60</td>
<td>25</td>
<td>6</td>
</tr>
<tr>
<td>Slowly (C2)</td>
<td>650</td>
<td>0.08</td>
<td>40</td>
<td>23</td>
<td>54</td>
</tr>
<tr>
<td>Lignin and associated nitrogen (C3)</td>
<td>200</td>
<td>0.01</td>
<td>10</td>
<td>3</td>
<td>67</td>
</tr>
<tr>
<td>Decomposable microbial products †</td>
<td>6</td>
<td>0.8</td>
<td>40</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Active protected soil organic matter</td>
<td>5000</td>
<td>0.0003</td>
<td>20</td>
<td>555</td>
<td>9</td>
</tr>
<tr>
<td>Old soil organic matter</td>
<td>7000</td>
<td>0.0008</td>
<td>20</td>
<td>700</td>
<td>10</td>
</tr>
<tr>
<td>Recalcitrant microbial and plant material †</td>
<td>4</td>
<td>0.3</td>
<td>25</td>
<td>0.2</td>
<td>20</td>
</tr>
</tbody>
</table>

† The sizes of these pools are much larger. The values shown refer to amount produced from the added substrate.
Figure 2-10. Decomposition of straw carbon (C) in the laboratory, plotted as a series of first-order reactions after correction for microbial production. Curves refer to the actual plant carbon-C remaining as proteins and solubles (C1), cellulose and hemicellulose (C2), and lignin (C3) as well as CO2 evolution and microbial production (after Paul and Clark, 1996).

Based on thermodynamics, the effect of soil temperature on mineralisation is commonly taken into account by an exponential equation of the type

\[ e_T = Q_{10} \left( \frac{(T - T_{ref})}{10} \right)^{T_{ref}} \]  

(Eq. 2-7)

where \( Q_{10} \) is the factor by which the reaction rate increases if the temperature increases by 10 Kelvin, \( T \) is soil temperature and \( T_{ref} \) is the reference temperature at which \( e_T \) is equal to unity. Alternatively, a quadratic response function has been proposed by Ratkowsky et al. (1982):

\[ r(T) = \frac{(T - T_{min})^2}{(T_{ref} - T_{min})^2} \quad ; \quad T > T_{min} \]  

(Eq. 2-8)

where, \( T_{min} \) is the minimum temperature below which microbial activity is assumed to be zero.

The effects of soil moisture on mineralisation are generally described by equations of the following form:
where \( h \) is the soil water tension, \( h_{\text{max}} \) is the tension at which \( k \) was highest and \( a \) and \( b \) are fitting parameters.
Examples of the preceding temperature and water response functions are shown in Figure 2-11. According to the concept of Linn and Doran (1984) the relative reaction rates of ammonification and respiration, nitrification or denitrification are affected differently by soil moisture as shown in Figure 2-12. In modelling N turnover the same response functions are usually assumed to hold simultaneous for all microbial transformation processes, of which only the moisture response of denitrification is modelled differently.

**Preferential flow**

It is well documented that solute transport through soils deviates from descriptions given by the classical convection-dispersion equation (e.g. Beven and Germann, 1982; Van Genuchten et al., 1990; Jury and Flühler, 1992; Stamm et al., 1998).

In structured soils short-circuiting of infiltration water through macro-structures such as root and earthworm channels or cracks and fissures can result in a rapid preferential displacement of solutes and suspended particles by-passing the soil matrix between these structures (e.g. Ehlers, 1975; Beven and Germann, 1982; Edwards et al., 1993; Flury et al., 1994; Hagedorn, 1999). As a consequence travel time of solutes is much shorter than in uniformly distributed flow (Stamm et al., 1998). Even in unstructured soils such phenomena may be observed where the infiltration fronts lead to ‘fingering’ (Hillel, 1980). In recent years it has become evident that preferential flow and transport of solute is rather the rule than the exception under field conditions (e.g. Luxmoore et al., 1990; Flury et al., 1994; Stagnitti et al., 1995).

Preferential flow leads to relatively large amounts of water flow through a small proportion of the whole soil volume, with only a small proportion of the reactive sites within the soil getting in contact with percolating water. In addition to higher flow velocities, transport with preferential flow is also less affected by interactions with the soil matrix because preferential flow channels are in general exposed to much lesser surface area in relation to the cross-section of these pathways. Therefore, even strongly sorbing solutes may be only weakly retarded in preferential flow (Flury et. al, 1995). Figure 2-13 shows preferential flow pathways at the study site visualised by an irrigation experiment with blue dye dissolved in infiltrating water (Schmied et al., 2000).

Displacement of nutrients or pesticides into ground or surface water may occur through preferential flow paths in very differently textured and structured soils under various climatic conditions (Flury et. al, 1995; Ritsema, 1999). This can be a problem of particular concern in fields with artificial drainage (Smettem et al., 1983; Richard and Steenhuis, 1988; Coles and Turdgill, 1985; Everts and Kanwar, 1990; Milburn et al.,
There the drain pipes may act as artificial macropores connecting preferential pathways of the soil to surface water. Preferential flow phenomena have been observed in winter, when soil matrix were highly saturated with water as well as in dry summer periods, when rainfall intensities of summer storms exceeded the infiltration capacity of the bulk soil. Triggering of preferential flow depends on many factors such as soil surface properties and moisture status, rain intensities, and time interval between rain events (e.g. Magesan et al., 1995; Bouma, 1990; Coles and Turdgill, 1985; Bronswijk et al., 1995).

![Figure 2-13. Preferential flow pathways in the humus-rich Fluvisol at the study site (Schmied et al., 2000).](image)

**Nitrogen transport**

Whether preferential flow leads to preferential displacement of solutes also depends on their distribution within the soil profile. Thus, the effect of preferential flow on the displacement of chemicals may be very different for surface-applied substances (i.e., solute pools dissolved in the rainwater or surface-applied fertilisers) and chemicals residing within the matrix (i.e., soil-born solutes such as mineralised nitrate, or heavy metals resulting from weathering) because of their different exposure to preferential flow.

To study the role of preferential flow in solute transport, tracer experiments are a valuable method *in situ* as well as *ex situ*. Tracer studies can be used to investigate
preferential pathways through undisturbed field soils (Gupta et al., 1999; Wojick et al., 1998), across layer boundaries and pans (Chen et al., 1999; Kamra et al., 1999; Wilkinson and Blevins, 1999), and macropores (Ghodrati et al., 1999; Iqbal, 1999). Tracer experiment were also performed to investigate the role of initial water content (Shipitalo and Edwards, 1996), rainfall intensity (McIntosch et al., 1999), and soil water-repellence (van Dam et al. 1990; Dekker and Ritsema 1994) in triggering preferential flow or the effects of tillage and different crop rotations on the formation of macropores (Kamau et al. 1996; Turpin et al., 1998; Ogden et al., 1999; Iragavarapu et al. 1998). Usually, in such studies tracers are applied to the soil surface. At least to the author's knowledge, there are no studies in which the effects of preferential flow on the displacement of solutes located in the depth of a soil profile was studied experimentally.

2.6 References


Chapter 2


Chapter 2


Nitrogen Dynamics in Two Drained Fields with Humus-Rich Soils, a Case Study in the Furttal

Abstract

Drained humus rich soils are at the forefront of conflicts between intensive agricultural land use and protection of surface waters. Intensive crop production combined with high turnover of nutrients and short-circuiting of the seepage water to surface waters leads to a particular high risk of water pollution. Field N fluxes studied in the Furttal valley in Switzerland from 1995 through 1996 showed that mineralisation of organic soil N was a major source of nitrate in such soils. During the growing season 1996 about 150 and 300 kg N ha$^{-1}$ y$^{-1}$ were net mineralised in the main root horizon (0-40 cm depth) of two tile drained fields grown with different crops. Annual N exports via drain from these fields and additionally monitored drainage systems varied between 12 and 31 kg N ha$^{-1}$ y$^{-1}$ whereof a substantial portion (20-60%) was leached during the 6-month period from May through October. Since mineral N in these soils accumulated mainly in spring before plant uptake became effective, the risk of N leaching was very high at the beginning of the vegetation period. Thus, the problem of N leaching is not restricted to the non-growing season. The fact that only a small fraction of this pool was lost with the drainage water can be attributed mainly to the reduction of the pool by plant uptake during the growing season. After a 17-month monitoring period, total N losses via drain were about 5-7% of plant N uptake and 3-10% of net N mineralisation. Although N losses via drain were small in comparison to the rates of N turnover by soil microbial processes and plant uptake, they are not negligible from the point of view of water quality of the Furtbach. The discrepancy between the magnitude of these fluxes and turnover rates indicates that it will not be possible to control losses into the underground and drainage discharge by fine-tuning of agricultural management practices without

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reducing the intensity of land use.

Figure 3-1. View of the study site located at Otelfingen in the Furttal, Canton Zürich.
Nitrogen Dynamics in Two Drained Fields with Humus-Rich Soils

3.1 Introduction

In the past, large areas of wetland have been drained for agricultural use because their high organic matter and nutrient contents made them attractive for intensive crop production. The combination of intensive management, high turnover of nutrients and short-circuiting of the seepage water to surface waters in the same time produces a particular high risk of water pollution and eutrophication by this type of land use, especially by excessive leaching losses of nitrate.

It is generally assumed that nitrogen leaching during the growing season is negligible due to plant uptake of soil mineral N (Nmin) and high evapotranspiration rates leading to small soil mineral N pools and low net infiltration of precipitation water into soil (e.g. Kengni et al., 1994; Martin et al., 1994; Verhagen and Bouma, 1998; Kowalenko, 2000). Additionally, the main drainage period in many artificially drained systems is restricted to the non-growing season (Arlot, 1990) when microbial N turnover processes are reduced and nitrogen leaching depends largely on the previous accumulation of a mobile Nmin pool.

In recent years evidence increased that nutrients and agrochemicals were transported into subsoil and resource water also during the growing season. Such observations were mainly attributed to rapid transport of solutes through the root layer by preferential flow (e.g. Flury et al., 1995; Isensee and Sadeghi, 1995; Heatwole et al., 1997, Klocke et al., 1999; Shipitalo et al, 2000). Preferential flow phenomena have been observed not only in winter, when soil matrix was highly saturated with water, but also in dry summer periods, when rainfall intensities of summer storms exceeded the infiltration capacity of the bulk soil. This can be a problem of particular concern in fields with artificial drainage (Smettem et al., 1983; Richard and Steenhuis, 1988; Coles and Turdgill, 1985; Everts and Kanwar, 1990; Milburn et al., 1990; Magesan et al., 1995; Kumar et al., 1997). There, the drainpipes may act as artificial macropores connecting preferential pathways of the soil to surface water.

Whether preferential flow leads to preferential displacement of mineral N also depends on its accumulation and distribution within the soil profile. In drained wetlands the humus rich soil layers represent a particularly large pool of mobilisable nitrogen. Especially in summer, low groundwater table and high temperature promote soil aeration and decomposition of the “fossile” soil organic matter also in greater soil depths. Development of macro-porosity by formation of cracks and biopores, such as root and earthworm burrows, provide channels for preferential water flow and solute transport through the root zone. As a consequence, artificial drainage and intensive
Chapter 3

cultivation of these soils carries the heightened risk that large amounts of nutrients and agrochemicals are transferred from the fields to surface water bodies by-passing the filter and retention capacity of the soil matrix (e.g. Addiscott et al., 2000; Gentry et al., 2000; Kamra et al., 1999; Stamm et al., 1998).

These questions were taken up in a case study in the Furttal valley in Switzerland, where substantial nitrate losses via drainage systems were found not only during the non-growing season, but also during the growing season. In the basin of the Furttal valley north of Zürich about 250 ha are drained humic soils, which are under intensive, arable or vegetable production. The former wetland was reclaimed and brought under cultivation between 1920 and 1930. Today, the average organic matter content of the humus rich layers of these soils ranges between 10% and 17%. Monitoring the water quality of the creek Furtbach, the main drainage of the valley, showed that nitrate and ammonium concentrations regularly exceeded the Swiss quality standard, and about 45% of the annual N load had to be attributed to non-point-sources, such as the outflow from the field drains (Kupper, 1991). For certain drainage discharge events in July and August 1992, very high nitrate concentrations in the drain effluent were measured corresponding to N loads of 2.5-5 kg N per day. These measurements led to the hypothesis that mineralisation of organic matter may be major source of nitrate export during the cropping period, and that leaching of nitrate occurs mostly through preferential paths.

This paper presents the results of our field study in which we addressed the above questions by monitoring intensively soil nitrogen and water regime as well as drainage discharge over more than an year.
3.2 Method and Material

3.2.1 Study site

The basin of the Furttal valley north of Zürich is dominated by humic soils, which were reclaimed from former wetland soils by artificial drainage and taken under cultivation between 1920 and 1930. These soils are very fertile and suited for arable landuse (EJPD, 1975). Precipitation averages 1065 mm per year, mean air temperature is 8.5 °C, and the vegetation period lasts from 210 to 230 days.

In total, 42% (1’850 ha) of the area of the Furttal is under intensive agricultural and horticultural use including 500 ha of drained land. About half of the drained soils are high in humus content with an average organic matter content of the humus rich layers between 10% and 17%. Crops are mainly corn and maize (37%), non-grain crops, such as potatoes and sugar beet (28%) or grassland (30%) (BFS, 1995). For the nearby agglomeration of Zürich the Furttal represents an important source for supplying vegetable products. About 10% of the arable land are used for greenhouse and field grown vegetables (Figure 3-1). Average cattle density is low with 0.75 dairy cow equivalents per hectare.

The study area is located in Otelfingen near the creek Furtbach, which is the main drainage route of the valley. It belongs to a 57-hectare farm, which is cultivated according to the guidelines of integrated production (IP). The 11-year crop rotation includes mainly grain and fodder crops, intermittent by non-grain crops or field vegetables, such as sugar beet, potato, lettuce and preserved beans or peas.

The main soil types in the test area are classified as Humic Fluvisol and Mollic Gleysol (FAO, 1998). The texture of the subsoil varied strongly over short horizontal distance as well with depth. The thickness of the humus-rich topsoil ranged from 20-40 cm with sporadic lenses reaching to a depth of more than 100 cm. Table 3-1 shows some characteristics of two representative reference profiles recorded in the study area.
<table>
<thead>
<tr>
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<th>Silt [%]</th>
<th>Sand [%]</th>
<th>Bulk density [kg dm$^{-3}$]</th>
<th>Porosity [cm$^3$ cm$^{-3}$]</th>
<th>CaCO$_3$ [%]</th>
<th>C$_{org}$ [%]</th>
<th>C/N</th>
<th>Description</th>
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<td>67</td>
<td>9</td>
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</tr>
<tr>
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<td>21</td>
<td>62</td>
<td>17</td>
<td>1.236</td>
<td>0.537</td>
<td>44.8</td>
<td>0.9</td>
<td>n.d.</td>
<td>C(g)</td>
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Mollic Gleysol

<table>
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<tr>
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<th>Silt [%]</th>
<th>Sand [%]</th>
<th>Bulk density [kg dm$^{-3}$]</th>
<th>Porosity [cm$^3$ cm$^{-3}$]</th>
<th>CaCO$_3$ [%]</th>
<th>C$_{org}$ [%]</th>
<th>C/N</th>
<th>Description</th>
</tr>
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<td>39</td>
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<td>0.880</td>
<td>0.633</td>
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<td>37</td>
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<td>6.3</td>
<td>10</td>
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<td>7</td>
<td>18</td>
<td>75</td>
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<td>1.791</td>
<td>0.324</td>
<td>43.9</td>
<td>0.8</td>
<td>n.d.</td>
<td>C(g)</td>
</tr>
</tbody>
</table>

Humic Fluvisol

$C_{org}$ = organic carbon, C/N = ratio of organic carbon to organic nitrogen
† % dry matter of mineral soil, ‡ % dry matter of soil

3.2.2 Field monitoring

From May 1995 to December 1996 a campaign of field measurements was performed to monitor nutrient leaching from different drainage subsystems, soil mineral N and plant biomass pools as well as net N mineralisation in situ. Figure 3-2 gives a situation of the study area with the various points of observation and sampling. The drainage subcatchments FF I and FF II were dominated by a Mollic Gleysol, whereas the main soil type of the fields situated near the river Furthbach, i.e. FF III, FF IV (b and c), was a Humic Fluvisol.

Intensive monitoring studies were done on the drainage subcatchments FF II and FF IVa and IVb. In the study period, the fields underwent different management practices (see below). Soil mineral N (Nmin) pool was sampled along a diagonal transect (Figure 3-2, crosses), and N fluxes were determined by «sequential coring», as described below, combined with a split-plot design. This design consisted of two fields («plots» in the nomenclature of the split-plot design), i.e. FF II and FF IVa, and three replications («subplots») per field (Figure 3-2, dotted). During seven time periods N fluxes were studied simultaneously on each of the six subplots with the respective climate conditions as different «treatments». Five of the subplots were located nearby the water-regime monitoring blocks (Figure 3-2, rectangle) each provided with tensiometers,
TDR-probes and thermocouples. These blocks were aligned with respect to the main collectors II and IV, which led to different spacing, such as 29 m between the subplots on FF II, and 43 and 50 m between the subplots on FF IVa. Drainage outflow and water samples were taken in the manholes (Figure 3-2, closed circle) of the main collectors as well as in the pumping station connecting the drainage system to the creek (not shown in Figure 3-2).

Climatic conditions

Air temperature, humidity, radiation, wind speed and precipitation were recorded hourly at a nearby meteorological field station. The groundwater table was monitored continuously by a data logger connected to a piezometer.

Soil moisture and temperature regime

Each water regime monitoring block was provided with three replicates of tensiometer- and TDR-probes and one set of thermocouples at depths of 15, 30, 60, and 100 cm. In addition, tensiometers were installed below the soil surface at 5 cm depth. The respective pressure head, water content and soil temperature were recorded weekly.

Net nitrogen mineralisation in situ

Net mineralisation, leaching and plant uptake of soil nitrogen was measured using a modified version of the sequential in situ coring technique as described by Adams and Attiwil (1986) and Raison et al. (1987) at three replicate subplots on each of the two fields FF II and FF IVa. In this method, mineral N contents of soil cores subjected to different conditions over a chosen incubation period are compared to each other and to mineral N contents of samples taken at the beginning and the end of the observation period.
Figure 3-2. Scheme of the study site. Drainage subsystems FF II, IVa and IVb with the respective plots and transects for monitoring the water and nitrogen household (see legend, soil types: IU loamy silt, tU clay silt, IS loamy sand, sL sandy loam).
Nitrogen Dynamics in Two Drained Fields with Humus-Rich Soils

From July 1995 to November 1996 incubations were performed over seven periods of about six weeks length each. During the growing season 1996 the incubations followed each other without interruption, except if the respective field was about to be cultivated (Table 3-2).

Table 3-2. Time table of incubation periods and duration.

<table>
<thead>
<tr>
<th>Incubation</th>
<th>Subcatchment FF II</th>
<th>Subcatchment FF IVa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Begin [dd.mm.yy.]</td>
<td>End [dd.mm.yy.]</td>
</tr>
<tr>
<td>INC-1</td>
<td>05.07.95</td>
<td>03.08.95</td>
</tr>
<tr>
<td>INC-2</td>
<td>10.10.95</td>
<td>05.12.95</td>
</tr>
<tr>
<td>INC-3</td>
<td>27.03.96</td>
<td>07.05.96</td>
</tr>
<tr>
<td>INC-4</td>
<td>15.05.96</td>
<td>25.06.96</td>
</tr>
<tr>
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<td>08.08.96</td>
</tr>
<tr>
<td>INC-6</td>
<td>09.08.96</td>
<td>21.09.96</td>
</tr>
<tr>
<td>INC-7</td>
<td>28.09.96</td>
<td>09.11.96</td>
</tr>
</tbody>
</table>

At the start of each incubation period, samples were collected from bulk soil. At the same time, steel cylinders were driven into the soils at places of no plant cover, i.e. between plant rows, to exclude the intrusion of roots and N losses due to plant uptake. To minimise disturbance of soil structure and other artefacts due to the installation of the cylinders, we used tubes of a much larger size (25 cm in diameter, 40 cm in length) than in most previous studies. Half of the cylinders was covered by a roof in order to prevent nitrogen leaching by infiltrating water. At the end of each incubation period, soil samples were collected from the cylinders and from the unconfined and uncovered soil. Per replicate five soil cores (3 cm in diameter, 40 cm in length) were taken within a distance of 3-5 cm from the cylinders' outer boundary or a circle of about 20 cm in diameter, respectively.

In the laboratory the samples were cut into three slices corresponding to 0-5, 5-20 and 20-40 cm depth. The five samples per replicate were bulked per depth and sieved (8-10 mm). Chemical analyses of soil nitrate and ammonium were made in 0.01 M CaCl₂ extracts according to the Swiss Reference Methods (Eidgenössische Forschungsanstalten, 1995) using an autoanalyser (Alliance Instruments Nanterre, France). We determined nitrate by the hydrazine reduction method. The resulting azo dye was determined spectrophotometrically at 540 nm. Ammonium was determined using the modified Berthelot reaction and spectrophotometry at 660 nm.
Net mineralisation (NNM), net leaching (NNL) and plant uptake (PNU) of mineral nitrogen during the incubation period are then determined as the following differences:

\[
\text{NNM} = N_{\text{cov}} - N_{\text{init}} \quad \text{(Eq. 3-1)}
\]

\[
\text{NNL} = N_{\text{cov}} - N_{\text{open}} \quad \text{(Eq. 3-2)}
\]

\[
\text{PNU} = N_{\text{open}} - N_{\text{end}} \quad \text{(Eq. 3-3)}
\]

where \(N_{\text{init}}\) and \(N_{\text{end}}\) are the mineral N contents of the unconfined soil at the beginning and the end of the observation period, and \(N_{\text{cov}}\) and \(N_{\text{open}}\) are the mineral N contents of the cores taken from the covered and open cylinders at the end of the observation period, respectively. The calculation scheme is illustrated in Figure 3-3.

Figure 3-3. Calculation scheme of N turnover rates and N fluxes as the differences between initial mineral N concentration (\(N_{\text{init}}\)) and the final concentration (\(N_{\text{end}}\)) in the unconfined soil as well as in the open (\(N_{\text{open}}\)) and covered (\(N_{\text{cov}}\)) cylinders (see eqs. 3-1, 3-2, and 3-3).

It should be noted that NNM includes mineralisation, denitrification and immobilisation, and that NNL similarly represents the net effect of leaching minus inputs such as N deposition by rainfall. The method rests on the assumption that the confinement and coverage of the soil by the cylinders and their roofs does not affect the N turnover of the treated soil other than in the intended way.
Soil mineral N and plant N pools

From March through December 1996 the soil mineral N pool was estimated every two to three weeks in the subcatchments FF II, FF IVa, and FF IVb at 0-20, 20-40 and 40-70 cm depths (Table 3-3). These samples were collected systematically at twelve sampling points separated by neighbour distance of 15.7, 13.8, and 15.8 m along a diagonal transect. At each point, we took one soil sample per depth and bulked every four neighbouring samples of a given depth, so that we obtained a total of three composite samples per sampling time and depth. Chemical analyses of soil nitrate and ammonium were made as described above. Plant samples were collected from randomly selected plants at each soil sampling point. Like the soil samples, they were also pooled by three groups of every four neighbouring points each. After drying (at 60 °C) and grinding, subsamples of 1 to 2 mg were taken and analysed for total N by a CHNS-Analyser (CHNS-932, Leco Instrumente GmbH, Kirchheim, Germany).

Drainage water

Drainage water discharge was continuously recorded by water clocks installed in the access manholes of the main collectors. A detailed description of this and further installations monitoring the water regime of the different subcatchments is given by Schmied et al. (2000) and Kohler (in preparation). Weekly analysis of mineral nitrogen in the drainage water was done in the laboratory of the water protection authorities of the Canton Zürich\(^5\) by a Segmented Flow Analyser (SA 2000/4000, Skalar Analytik B.V., De Breda, NL). Phosphate concentrations were near detection limit and, thus, not considered further. Since nitrite concentrations were also very small and included in the nitrate measurements, they were not registered separately.

\(^5\) Amt für Abfall, Wasser, Energie und Luft (AWEL) des Kantons Zürich, Abteilung Gewässerschutz, Sektion Oberflächengewässer.
### Table 3-3. Time table of soil mineral N and plant biomass pools sampling, including crop and distance between neighboured sampling points.

<table>
<thead>
<tr>
<th>Subcatchment FF II</th>
<th>Date</th>
<th>Crop †</th>
<th>Subcatchment FF IVa</th>
<th>Date</th>
<th>Crop</th>
<th>Subcatchment FF IVb</th>
<th>Date</th>
<th>Crop †</th>
</tr>
</thead>
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<td></td>
<td>[dd.mm.yy.]</td>
<td>[-]</td>
<td></td>
<td>[dd.mm.yy.]</td>
<td>[-]</td>
<td></td>
</tr>
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<td>GLC</td>
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<td>GL</td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>01.11.95</td>
<td>GLC</td>
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<td>GL</td>
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<td></td>
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<tr>
<td></td>
<td></td>
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<td>GL</td>
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<td>GLC</td>
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<td>P/SM</td>
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<tr>
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<td>24.09.96</td>
<td>LET ‡</td>
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<td>GLC</td>
<td>18.12.96</td>
<td>-</td>
<td></td>
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<td></td>
</tr>
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</table>

15.7 m spacing †
13.8 m spacing
15.8 m spacing

† crop: SF sunflower, BS sugar beet, GLC grassland including clover, GL grassland, P potato, SM silo-maize

‡ LET: sampling occurred at harvest, i.e. June-9, June-17, September-17

†† Spacing: distance between neighboured sampling points along the transect
3.2.3 Land management

Detailed information on land management of the study area was obtained from the farmer's management control sheets. During the study period the crops on subcatchment FF II were grown according the rotation winter wheat, sunflower (catch crop), sugar beet and winter wheat. After harvesting the winter wheat and before sunflowers were sown on 10 August 1995 sewage sludge was applied (about 140 kg N ha\(^{-1}\)). The sunflowers were left until they were killed by frost in November. On December 14, the field was ploughed to a depth of about 20 cm to bury the frozen residues leading to a N input of 105 kg N ha\(^{-1}\). From 28 March 1996 sugar beet was grown and fertilised with a total of 107 kg mineral N per hectare over the growing season. Thereafter winter wheat was sown in November 1996.

At the beginning of the study, the field FF IVa was covered with one year old grassland, a mixture of ryegrass and clover. In April 1996 the field was ploughed to prepare the soil for lettuce, leading to an N input into soil of about 50 kg N ha\(^{-1}\). The field was divided into three lots on which lettuce was produced twice in the growing season. The planting data between the parcels differed 1 to 2 weeks. Thereafter, the same grass-clover mixture as grown before was sown on September 14. During the growing season 1996 about 260 kg N ha\(^{-1}\) was brought into the system by several fertiliser application.

On the field FF IVb grass was sown as a catch crop after the harvest of leguminous crops (preserved beans and peas) in August 1995. In the following spring the field was grazed by cattle, ploughed and manured partly with dung (about 100 kg N ha\(^{-1}\)) and partly with liquid manure (about 150 kg N ha\(^{-1}\)). Thereafter, the field was planted with potatoes, except for a small strip of maize. Two fertiliser applications in May and June 1996 led to a mineral N input of 129 kg N ha\(^{-1}\) in the potato and 84 kg N ha\(^{-1}\) in the maize crop.
Chapter 3

3.3 Results and Discussions

3.3.1 Climatic conditions

Selected climate data, i.e., daily and total precipitation, daily mean air temperature together with soil moisture and soil temperature measurements are shown in Figure 3-4. Precipitation was 913 mm during the study period from November 1995 to October 1996. This corresponds to only 86% of the average annual rainfall of 1065 mm.

3.3.2 Net nitrogen mineralisation in situ

The contribution of NNM to the pool of mineral soil N was substantial in both fields. During the growing season from May to October 1996 (220 days), net N mineralisation was about 300 kg N ha\(^{-1}\) in field FF II and 150 kg N ha\(^{-1}\) in field FF IV. The differences between the fields are probably a result of the management practice, i.e., the different inputs of organic material in the form of sewage sludge and plant residues.

Maximum NNM rates were found in spring and early summer when temperature was high and soil moisture was close to optimum conditions (Figure 3-5). Generally, highest rates occurred in the topsoil layer from 0-5 cm. On FF II, weekly NNM rates between 8 and 76 mg N per kg dry soil were measured in spring (incubations 3 and 4). After a nearly complete stop in summer, NNM gradually recovered in autumn. Variation of measured NNM rates are listed in Table 3-4.

Table 3-4. Statistics of weekly NNM rates per field and depth (N=21, i.e. 7 incubation periods x 3 replicates).

<table>
<thead>
<tr>
<th>Field</th>
<th>Depth [cm]</th>
<th>Mean [mg N kg(^{-1}) w(^{-1})]</th>
<th>Median</th>
<th>S.E.</th>
<th>Min.</th>
<th>Max.</th>
<th>CV [%]</th>
</tr>
</thead>
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<td>0-5</td>
<td>14.3</td>
<td>7.6</td>
<td>19.5</td>
<td>-15.0</td>
<td>75.6</td>
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</tr>
<tr>
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<td>5-20</td>
<td>2.3</td>
<td>2.1</td>
<td>2.2</td>
<td>-4.6</td>
<td>6.3</td>
<td>93.1</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>1.0</td>
<td>0.8</td>
<td>0.9</td>
<td>-0.2</td>
<td>3.5</td>
<td>87.5</td>
</tr>
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<td>FF IVa</td>
<td>0-5</td>
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<td>6.1</td>
<td>6.7</td>
<td>-13.7</td>
<td>15.3</td>
<td>147.6</td>
</tr>
<tr>
<td></td>
<td>5-20</td>
<td>1.0</td>
<td>1.0</td>
<td>4.1</td>
<td>-12.0</td>
<td>7.5</td>
<td>401.8</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>0.8</td>
<td>0.4</td>
<td>1.1</td>
<td>0.0</td>
<td>4.9</td>
<td>144.2</td>
</tr>
</tbody>
</table>

S.E. Standard Error, Min. Minimum, Max. Maximum, CV Coefficient of variation
Nitrogen Dynamics in Two Drained Fields with Humus-Rich Soils

Figure 3-4. Climate data from August 1995 through November 1996: Air and soil temperature, precipitation (PRE), potential evapotranspiration (ETP), soil pressure head ± standard deviation (HEAD), and ground water table (GWT). Data for soil temperature, pressure head and groundwater refer to the subcatchment FF II.
Figure 3-5. Variation of the mean NNM rates [mg N kg$^{-1}$ w$^{-1}$] ± one standard error between the seven incubation periods (Inc.) in the two fields FF II and FF IVa and the three sampling depths (0-5, 5-20, 20-40 cm). Crop: WW winter wheat, SF sunflower, SB sugar beet, GL grassland, LET lettuce. Note the different scaling of y-axes.
3.3.3 Nitrogen pools

In addition to the measurements on the subplots of the «sequential coring», which were located near the field-border, the Nmin pool down to 70 cm depth and the total nitrogen pool of the standing crop biomass were measured on the three study fields. With sugar beet (FF II) and potato (FF IVb) between 200 and 250 kg N ha\(^{-1}\) of mineral N accumulated in the soil compartment (0-70 cm depth) during spring before plant uptake became so effective that in autumn only less than 50 kg N ha\(^{-1}\) remained (Figure 3-6). Because of small uptake rates of the following winter wheat crop the Nmin pool of the soil gradually increased again after the harvest of the sugar beet and potatoes due to soil N mineralisation and decomposition of crop residues.

The data presented in Figure 3-6 show the delayed increase of soil mineral N due to plant residue mineralisation after the sunflowers on field FF II were ploughed under in winter 1995. However, the accumulation of mineral N in spring was not only due to mineralisation, but also to fertilisation. Repeated fertiliser applications to the lettuce culture, for instance, led to high mineral N contents in the topsoil of field IVa until late fall when the grass sown in September after the harvest of the vegetables started to grow.
Figure 3-6. Temporal dynamics of soil mineral N pool in 0-20, 20-40 and 40-70 cm depth and total N pool of the standing crops on the three study sites in [kg N ha^{-1}]. Arrows refer to fertiliser applications. SC soil cultivation, SF sunflowers, SB sugar beet, WW winter wheat, GL grassland, LET lettuce, P/SM potato incl. silo maize.
3.3.5 Quality of drainage water

The ammonium or nitrate concentrations in the weekly collected samples of drainage water regularly exceeded Swiss quality standards (GschV, 1999). The number of events exceeding these standards varied widely between the drainage subsystems (Figure 3-7).

About 15% of the samples collected from May 1995 to December 1997 in the subcatchment FF IVa and half of the samples taken in FF IVb exceeded the quality standard of 5.6 mg N l\(^{-1}\) for nitrate, while ammonium concentrations remained around detection limit. On the other hand, water samples from the pumping station and manhole II regularly exceeded also quality standards for ammonium, but rarely that for nitrate. In total, 49% of the samples of subcatchment FF II and 11% of total drainage system did not meet quality requirements of maximal 0.4 mg N l\(^{-1}\) (valid for water temperature smaller than 10 °C). On the three fields mineral N fertilisers were applied in the same form, i.e. ammonium-nitrate. We interpret the large amount of water samples with high ammonium concentrations in FF II to be due limited soil aeration of the Gleysol inhibiting nitrification, whereas ammonium oxidation was less restricted in the more sandy Fluvisol in FF IVa and FF IVb.

The constantly high nitrate concentration in collector IV can be attributed to the application of liquid manure in spring 1996 being quickly transported in the zone of fluctuating groundwater. Only a month later nitrate concentrations approximately doubled and then remained high with some fluctuations until the end of the observation period in December 1996. Peak values of about 20 mg N l\(^{-1}\) were reached in late autumn.

---

6 According to the Swiss “Gewässerschutzverordnung” (GschV, 1999) the quality standard for nitrate equals 5.6 mg N l\(^{-1}\). The standard for ammonium depends on the temperature of the water samples and equals 0.4 mg N l\(^{-1}\) at water temperature < 10 °C or 0.2 mg N l\(^{-1}\) at water temperature > 10 °C.
Figure 3-7. Weekly measurements of discharge and mineral N concentrations in the drainage water of the subsystems FF II, FF IVa, FF IVb and the drainage system as such. Quality standards (dashed lines) are 5.65 mg N l⁻¹ for nitrate and 0.4 mg N l⁻¹ for ammonium (water temperature <10 °C). Arrows refer to fertiliser applications.
3.3.6 N export via drainage

Figure 3-8 shows the cumulative water and mineral N fluxes of the total drainage system and three subcatchments from November 1995 to October 1996. The precipitation, which totalled 913 mm (Figure 3-8, top), led to a cumulative outflow Q of 230'564 m$^3$ at the pumping station, 5'882 m$^3$ at manhole II, 5'081 m$^3$ at manhole IVa, and 2'293 m$^3$ at IVb. To compare the area-averaged discharge in Figure 3-8 (centre) we divided cumulative outflow by catchment area. A 20 cm height difference between the neighbouring collectors III and IV at the respective manholes III and IVa and IVb (Figure 3-2) was found to explain a shift of the watershed between the two collectors from the theoretical position expected if they had been at the same altitude (Köhler, personal communication). The resulting deviation of the «effective» from the «theoretical» catchment area covered by the drains and collectors under the assumption of equal “ranges of influence” was substantial and made it necessary to adapt the subcatchment areas of IVa and IVb. Approximation of their size A was done as follows:

$$A = \frac{\text{measured outflow } Q}{\text{calculated net infiltration } I}$$

(Eq. 3-4)

where calculated net infiltration corresponds to the water balance shown in Table 3-5.

The estimated area of 1.41 ha (FF IVa) and 0.64 ha (FF IVb) represent the average «effective» subcatchment over the time period considered. Short-range fluctuations may occur especially during rainfall events with high precipitation intensities, when not only the collectors but also (part of) the field drains take effect. Such uncertainties must be included in the interpretation of events, such as the summer storm in July 1996. However, the «effective» and «theoretical» subcatchment areas for FF II are almost identical indicating the approximation applied to be valid.

Summing up the product of weekly measured drainage outflow and Nmin concentration, annual N exports with drainage discharge were calculated. Divided by the «effective» catchment areas, average fluxes of less than 20 kg N ha$^{-1}$ y$^{-1}$ were obtained for field FF II and FF IVa as well as for the drainage system as such, whereas average N loss for FF IVb was 28 kg N ha$^{-1}$ y$^{-1}$. Note that the latter value was strongly influenced by a single extreme event in July 1996.
Figure 3-8. Precipitation and curves of cumulative outflow and mineral N export for the drainage system (pumping station) and three different subcatchments. The arrow refers to a single rainfall event in July 1996.
Nitrogen Dynamics in Two Drained Fields with Humus-Rich Soils

Table 3-5. Annual water balance from November 1995 to October 1996 as well as «effective» and «theoretical» subcatchment areas.

<table>
<thead>
<tr>
<th></th>
<th>FF II</th>
<th>FF IVa</th>
<th>FF IVb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation P, in [m]</td>
<td>0.913</td>
<td>0.913</td>
<td>0.913</td>
</tr>
<tr>
<td>Actual evapotranspiration ETA, in [m]</td>
<td>0.558</td>
<td>0.553</td>
<td>0.553</td>
</tr>
<tr>
<td>Net infiltration (=P-ETA), in [m]</td>
<td>0.355</td>
<td>0.360</td>
<td>0.360</td>
</tr>
<tr>
<td>Cumulative discharge Q, in [m^3]</td>
<td>5882</td>
<td>5081</td>
<td>2293</td>
</tr>
<tr>
<td>«effective» subcatchment area [ha]</td>
<td>1.66</td>
<td>1.41</td>
<td>0.64</td>
</tr>
<tr>
<td>«theoretical» subcatchment area [ha]</td>
<td>1.59</td>
<td>3.32</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Given that precipitation during the study year was only 85% of the long-term average, but that plant growth and thus evapotranspiration were still not limited by soil water availability, the above figures of N export are in reasonable agreement with those given by Küpper (1991), who estimated that an area-average of 44 kg N ha^-1 y^-1 was exported from the agricultural section of the Furtbach catchment. Other values of N export via drains given in the literature range from 2-100 kg N ha^-1 y^-1 (Lammel, 1990; Wichtmann, 1994; de Vos et al., 2000; Zhao et al., 2000).

Such figures are subjected to uncertainties depending on sampling strategies. Our water meter, which was read weekly, captured cumulatively the entire amount of water leaving the system. But the nitrate and ammonium concentrations, which were measured in water samples taken every 5-10 days, do not represent the flux-weighted averages. Thus, large fluctuations of concentration could have led to significant bias in the estimates of N export. Since Kohler (in preparation) observed a positive correlation between the drainage discharge and nitrate concentration of the drainage water, N exports were likely to be underestimated in our study. Control measurements with high temporal resolution in collector II showed that N exports based on the weekly sampling interval were underestimated by 11% in the winter and by 14% in the summer half year. Independent of such bias, our results clearly confirmed our hypothesis that considerable export of nitrogen occurred during the growing season through the drainage system (Table 3-6) and that this export was mainly due to a few strong rainfall events. During the 6-month period from May through October 1996 about 20% of the total annual N export was transported via drainage into the Furtbach, while the respective loads of the subcatchments varied widely from 20-59%. Although many studies on N drainage have been published, we found only one comparing N losses of the growing and the non-growing season. However, similar to our findings Hayashi and Hatano (1999) found that about half of the annual N load exported from an onion field by subsurface drainage occurred during the vegetation period.
Table 3-6. Annual drainage outflow and Nmin export from November 1995 to October 1996 and half year periods. Values are corrected (+11% in the winter, and +14% in the summer period) for underestimation by weekly sampling interval, export.

<table>
<thead>
<tr>
<th>Flux - Site</th>
<th>Crops †</th>
<th>Area ‡</th>
<th>Annual Export</th>
<th>Winter Export</th>
<th>Summer Export</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[ha]</td>
<td>[mm] [%]</td>
<td>[mm] [ %]</td>
<td>[mm] [ %]</td>
</tr>
<tr>
<td>Drainage discharge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Pumping Station</td>
<td></td>
<td>57.50</td>
<td>401.0 [100]</td>
<td>278.8 [70]</td>
<td>122.2 [30]</td>
</tr>
<tr>
<td>- Manhole II</td>
<td>SF-SB-WW</td>
<td>1.59</td>
<td>369.9 [100]</td>
<td>261.0 [71]</td>
<td>108.9 [29]</td>
</tr>
<tr>
<td>- Manhole IVa</td>
<td>GL-LET-GL</td>
<td>1.41</td>
<td>360.1 [100]</td>
<td>227.2 [63]</td>
<td>132.9 [37]</td>
</tr>
<tr>
<td>- Manhole IVb</td>
<td>GL-P/SM-WW</td>
<td>0.64</td>
<td>360.1 [100]</td>
<td>225.6 [63]</td>
<td>134.5 [37]</td>
</tr>
<tr>
<td>Nmin-Export</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Pumping Station</td>
<td></td>
<td>57.50</td>
<td>18.4 [100]</td>
<td>14.0 [76]</td>
<td>4.4 [24]</td>
</tr>
<tr>
<td>- Manhole II</td>
<td>SF-SB-WW</td>
<td>1.59</td>
<td>13.7 [100]</td>
<td>10.8 [79]</td>
<td>2.8 [20]</td>
</tr>
<tr>
<td>- Manhole IVa</td>
<td>GL-LET-GL</td>
<td>1.41</td>
<td>11.9 [100]</td>
<td>6.6 [56]</td>
<td>5.3 [45]</td>
</tr>
<tr>
<td>- Manhole IVb</td>
<td>GL-P/SM-WW</td>
<td>0.64</td>
<td>31.3 [100]</td>
<td>13.0 [42]</td>
<td>18.3 [59]</td>
</tr>
</tbody>
</table>

† SF sunflowers, SB sugar beet, WW winter wheat, GL grassland, LET lettuce, P/SM potato/silo maize
‡ Reference Area, i.e. «effective» subcatchment area

3.3.7 Summary of results

Figure 3-9 summarises the results of N flux measurements in the main root zone of FF II and FF IVa and shows that most of the large amount of net mineralised N was taken up by plants, and only a minor fraction was lost by leaching. In quantifying N leaching by the sequential coring method it must be taken into account that this method only gives an assessment of net leaching (NNL), i.e. the difference between outputs and inputs with percolating solution. To obtain estimates of total leaching the values for NNL have to be increased at least by the amount of N input by deposition from the atmosphere. Assuming an annual deposition of 40 kg N ha⁻¹ y⁻¹, evenly distributed over the year, this makes a difference of +24 kg N ha⁻¹ for the study period (220 days), which is included in the leaching rates (Nexp) shown in Figure 3-9.

To account for incomplete ground cover of the root systems of the lettuce plants in tractor tracks, we assumed that plant N uptake (PNU) was limited to 80% of the area of FF IVa. With these assumptions the cumulative N balances displayed in Figure 3-9 were obtained from the sequential coring data. They show that during the growing season 1996 plant N uptake was about 2.6 (FF II) to 6.2 (FF IVa) times larger than losses by N leaching to deeper soil layers. Total N uptake by plants was even larger, as
N was taken up by roots also in the subsoil below 40 cm depth.

Notice, that during incubation the subplots were excluded from cultivation and fertilisation only occurred between some of the observation periods. This can be seen in Figure 3-9 by the step increase of the input curve between two measurements.

The balances of N fluxes on the scale of the subcatchment, summarised in Figure 3-10, include the subsoil compartment down to the collectors in 1.5 m depth on FF II and in 2 m depth on FF IVa. As in situ measurements of net mineralisation were available only for certain time periods, this term had to be estimated for the time between the incubation periods. Using the numerical model LEACHM (Hutson and Wagenet, 1991),

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Figure 3-9. N balance in the main root zone (0-40 cm) of the fields FF II and FF IVa for the growing season 1996. The balance is based on the N fluxes measured by the «sequential coring» method, corrected for N deposition and lower N uptake by the lettuce plants because of restricted root growth in the tractor tracks.
which is described in Chapter 4 of this thesis, the following values were calculated for NNMin the topsoil: 80 kg N ha\(^{-1}\) on FF II and 60 kg N ha\(^{-1}\) on FF IV for the first period from August to September 1995, and 40 kg N ha\(^{-1}\) on FF II and 15 kg N ha\(^{-1}\) on FF IV for the second period from December 1995 through March 1996. Likewise, NNMin rates were available only for the upper 40 cm of the soil and had to be estimated for the soil below this depth. Based on mineralisation studies (Chapter 5, this thesis) in undisturbed soil cores from one of the few humus rich subsoil lenses found in the fields under study, we estimated annual NNMin rates for the 40-70 cm soil layer of about 8 kg N ha\(^{-1}\) on FF II and 12 kg N ha\(^{-1}\) on FF IVa. Changes in the Nmin pool below 70, which had not been sampled, were not taken into account. The initial sizes of the mineral N pool was set equal to the measured Nmin content from 0-70 cm depth at the beginning of the accounting period.

![Graph showing N balance of the subcatchment](image)

Figure 3-10. N balance of the subcatchment, that is the soil compartment down to 1.5 m depth in FF II and 2.0 m depth in FF IVa for the study period.
Our results support the findings of other studies, which identified mineralisation of organic N in soil and in crop residues as a major source of nitrate (Powlson, 2000). In the 17-month monitoring period export of mineral N with the drainage water was the smallest term in the balance equation for both subcatchments, i.e. about 3% of net N mineralisation in FF II and 10% in FF IVa or 5% of plant N uptake in FF II and 7% in FF IVb. With respect to the general leakiness of nitrogen cycle (Davies, 2000) these results suggest an efficient use of nitrogen by the farmers cultivating the fields under study.

Figure 3-10 shows that from June 1996 on measured Nmin pool and N balance of FF II differed largely. Differences were about 200-300 kg N ha⁻¹. They may be attributed to sinks, such as a mineral N pool between the measurement depth in 70 cm and the collector II located in approx. 150 cm depth, to possible denitrification losses from this layer, and to immobilisation in plant root biomass not included by sampling strategies. Additionally, the NNM rates, which were measured on three subplots along the field border (Figure 3-2), may not hold for the entire field.

The likewise comparison in subcatchment FF IVa shows that substantial differences between measured Nmin pool and N balance occurred only in October 1996. Thereafter disagreement improved, while N uptake by the newly sown grassland and N export via drain increased. It is likely that the lacking nitrogen mass of about 110 kg N ha⁻¹ in October 1996 has been situated in the subsoil below 70 cm depth subjected to leaching via drain or to upwards transport in the root zone and subsequent plant uptake.

3.4 Conclusions

The results of the field studies did only partially agree with our expectations. Mineral N accumulated in spring before plant uptake became effective, and in autumn relatively small Nmin pools remained. Thus, as far as the availability of mobile N is concerned the risk of N leaching was very high at the beginning of the vegetation period. This mobile pool was primarily fed by fast decomposition of a large organic matter pool. The fact that only a very small fraction of this pool was lost with the drainage water can be attributed mainly to the reduction of the pool by plant uptake during the growing season.

With values ranging from 12-31 kg N ha⁻¹ y⁻¹ the N losses through the drainage systems were rather small also in comparison with values reported in the literature. Nonetheless, our results confirm the hypothesis that a substantial portion of the losses may occur
during the growing season and that the problem of N leaching is not restricted to the non-growing season. The observed drainage outflow and nutrient response curves also showed that high N loads are linked with only few strong rainfall events.

At the study site preferential flow played a major role. In a 2-year experiment Kohler (in preparation) monitored the fate of surface applied bromide on subcatchment FF II, and found that about 75% of the tracer lost with the drainage water was leached by preferential flow. Although not very effective in controlling the groundwater table, field drains made an important contribution to this export. Lying at 0.7-1.0 m depth and therefore nearer to the soil surface than the collectors, the field drains collected only 19% of the drainage outflow, whereas about half of the tracer lost through drainage were intercepted by them.

Although N losses via drain were not extensive and although they were almost negligible in comparison to the rates of N turnover by soil microbial processes and plant uptake, they are not negligible from the point of view of water quality and protection of the Furtbach. The discrepancy between the magnitude of these fluxes and turnover rates indicates that it will not be possible to control losses into the underground and drainage discharge by fine-tuning of agricultural management practices without reducing the intensity of land use.

3.5 References


Nitrogen Dynamics in Two Drained Fields with Humus-Rich Soils


Chapter 3


Inverse Estimation of Parameters in a Nitrogen Model Using Field Data

B. Schmied, K.C. Abbaspour, and R. Schulin


Abstract

An important step in numerical modeling is the determination of model parameters. Because of practical limitations, as well as time and financial constraints, inverse algorithms have in recent years presented an attractive alternative to direct methods of parameter estimation. In this study we linked the inverse algorithm of SUFI with the simulation program LEACHM to study nitrogen turnover of an agricultural field. Addressing the inherent modeling uncertainties, we introduce the concept of ‘conditioned parameter distributions’ as being a more appropriate alternative to ‘best-fit’ parameters. Conditioned parameter distributions are quantified within uncertainty domains, and the task of an inverse model then is to reduce or ‘condition’ this domain through minimization of an appropriate objective function. Propagating the uncertainty in the conditioned parameter distributions will result in simulations where most of the measurements are ‘respected’ or fall within the 95% confidence interval of the Bayesian distribution (95PCIBD). In this study we used measured pressure heads and NO₃ concentrations to estimate 12 hydraulic parameters and up to 14 nitrogen turnover related parameters. Most of the measurements in three soil layers fell within the 95PCIBD. Exceptions were some observed pressure heads corresponding to intense rainfall events and periods of soil freezing, as well as some high NO₃ concentrations in the subsoil between 40 and 70 cm depth. We attributed the discrepancies to processes that were not addressed by the simulation model such as freezing and short-circuiting due to macropore flow.
4.1. Introduction

Intensification of agriculture has led to an increased input of nitrogen (N) into agricultural soil-plant systems that greatly increased crop output, but also at the same time increased nitrogen losses to the environment. To balance the supply of nitrogen for optimal plant performance and minimal losses to the environment, various simulation models differing in representation of processes, numerical algorithms, complexity, and scale have been developed. Comparing earlier (Frissel and Van Veen, 1981) and more recent (Groot et al., 1991; Thomasson et al., 1991) approaches reveals that although numerical models in general have become more comprehensive, but still limitations exist as the result of inadequate description of simultaneous processes of N turnover (Hansen et al., 1995; Diekkrüger, 1995), and the incomplete definition and collection of model input parameters (De Willingen, 1991).

Serious problems in modeling N transfer through soil-crop systems are currently posed by the lack of understanding of soil biological processes (Otter-Nacke and Kuhlmann, 1991; De Willigen, 1991), the influence of physical soil factors (Van Veen and Kuikman, 1990; Verberne et al., 1990; Ladd et al., 1993), and the nature of decomposing substrates (Amato and Ladd, 1992; Jensen, 1994; Motavalli et al., 1995). The more exactly a model tries to describe the processes involved, the more complex it gets and, hence, the more difficult it becomes to use. Greater model complexity also means introduction of more parameters. Model parameters are generally unknown and difficult to measure, especially for field problems.

To estimate model parameters of a field study, inverse modeling offers sometimes the only viable choice because of time, expenses, practical limitations and inadequacy of laboratory methods. Since N turnover is strongly affected by micro-environmental conditions, additional difficulties arise from the heterogeneity of soil properties, even on very small geographical scales (Becket and Webster, 1971). Neglecting spatial variability can lead to unsatisfactory and often erroneous prediction results (Addiscott et al., 1991; Finke, 1993; Huwe and Totsche, 1995; Abbaspour et al., 1998).

We found relatively few publications that described inverse estimation of hydraulic and transport properties using data from field experiments (Feddes et al., 1993; Romano, 1993; Zijlstra and Dane, 1996; Lehmann and Ackerer, 1997, Simunek et al., 1998). Abbaspour et al. (1999) estimated hydraulic, transport and plant parameters from a lysimeter experiment. To our knowledge only one study was performed to estimate N-turnover rates from a soil column leaching experiment by inverse modeling (Yamaguchi et al., 1992).
The objectives of this paper were to investigate the applicability of inverse estimation of parameters to a complex soil-plant system in the field, and to obtain model parameters which would describe our field observations of pressure head and nitrate concentration. To estimate the unknown parameters we linked the nitrogen turnover model LEACHM (Hutson and Wagenet, 1992) with the sequential uncertainty fitting algorithm SUFI proposed by Abbaspour et al. (1997).

4.2. Material and methods

The database used in this paper is from a field experiment in which we studied nitrogen fluxes (net mineralization, drainage losses, plant uptake) and pools (ammonia and nitrate) in a formerly wetland area in the Canton Zurich, Switzerland. Schmied (2001) gives a detailed description of the project’s context and results including sampling strategies and chemical analysis of the different nitrogen species. Here, we will give only a brief overview of the experiment.

The following data were collected from March through December 1996 on a 1.6-ha field planted with sugarbeet. The soil mineral N pool was sampled every two to three weeks at 0-20 cm, 20-40 cm, and 40-70 cm depths. These samples were taken systematically in a distance of 15.7 m on twelve sampling points along a diagonal transect. At each point, we took one soil sample per depth and bulked every four neighboring samples for a total of three composite samples per sampling time. Chemical analyses of soil nitrate and ammonium were made in 0.01 M CaCl₂ extracts according to the Swiss Reference Methods (Eidgenössische Forschungsanstalten, 1996) using an Autoanalyser (Alliance Instruments Nanterre, France). We determined nitrate by the hydrazine reduction method resulting in a colored azo dye that was measured spectrophotometrically at 540 nm. Ammonia was determined using the modified Berthelot reaction and spectrophotometry at 660 nm. To estimate plant N uptake, plant samples were collected from randomly selected plants at each soil sampling point. As for the soil samples, the plant samples were also pooled for every four neighboring samples. After drying (at 60 °C) and grinding, total N content of sub-samples of 1 to 2 mg plant materials were determined by a CHNS-Analyser (CHNS-932, Leco Instrumente GmbH, Kirchheim, Germany). An overview of the sampling schedule along with the measured soil nitrate and plant nitrogen contents is given in Table 4-1.

Relevant soil properties are presented in Table 4-2. Air temperature, humidity, radiation, wind speed and precipitation were recorded hourly at a nearby meteorological station. The groundwater table was monitored continuously by a data logger connected to a piezometer. Pressure heads at 5, 15, 30, and 60 cm depths were recorded on a weekly
basis with tensiometers installed on three different plots with three replications per plot.

Table 4-1. Sampling schedule along with soil nitrate N and plant total N pools

<table>
<thead>
<tr>
<th>Date</th>
<th>Soil nitrate N</th>
<th>Plant N</th>
</tr>
</thead>
<tbody>
<tr>
<td>[mm/dd/yy]</td>
<td>0 - 20 cm</td>
<td>20 - 40 cm</td>
</tr>
<tr>
<td>03/26/96</td>
<td>15.2 ±4.3</td>
<td>15.4 ±4.8</td>
</tr>
<tr>
<td>04/09/96</td>
<td>39.7 ±13.1</td>
<td>21.6 ±5.4</td>
</tr>
<tr>
<td>04/23/96</td>
<td>51.4 ±22.3</td>
<td>28.1 ±12.5</td>
</tr>
<tr>
<td>05/07/96</td>
<td>42.0 ±11.4</td>
<td>27.4 ±7.0</td>
</tr>
<tr>
<td>05/28/96</td>
<td>49.1 ±4.1</td>
<td>35.9 ±7.2</td>
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<tr>
<td>06/12/96</td>
<td>39.5 ±23.5</td>
<td>24.0 ±14.5</td>
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<td>07/03/96</td>
<td>5.2 ±2.7</td>
<td>9.1 ±3.2</td>
</tr>
<tr>
<td>07/17/96</td>
<td>4.1 ±0.9</td>
<td>5.8 ±2.4</td>
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<td>6.3 ±4.5</td>
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<tr>
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<td>7.3 ±5.1</td>
<td>6.4 ±3.4</td>
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<tr>
<td>11/09/96</td>
<td>8.7 ±5.4</td>
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</tr>
<tr>
<td>12/18/96</td>
<td>7.4 ±2.4</td>
<td>9.2 ±3.6</td>
</tr>
</tbody>
</table>

† Values are means of three bulked samples ± one standard deviation.

Table 4-2. Soil profile description. †

<table>
<thead>
<tr>
<th>Depth</th>
<th>( \rho_b ) g cm(^{-3} )</th>
<th>E</th>
<th>CaCO(_3 )</th>
<th>pH</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
<th>Org. C</th>
<th>C/N</th>
</tr>
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<tbody>
<tr>
<td>cm</td>
<td>g cm(^{-3} )</td>
<td>g g(^{-1} )</td>
<td>%</td>
<td>%</td>
<td>g 100g(^{-1} )</td>
<td>15</td>
<td>0.70</td>
<td>0.71</td>
<td>0.23</td>
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<td>30</td>
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</tr>
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<td>0.55</td>
<td>7.0</td>
<td>22</td>
<td>67</td>
<td>9</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>1.23</td>
<td>0.54</td>
<td>0.45</td>
<td>-</td>
<td>21</td>
<td>62</td>
<td>17</td>
<td>0.9</td>
<td>-</td>
</tr>
</tbody>
</table>

† \( \rho_b \) bulk density; E porosity; Org. C organic carbon; C/N ratio of organic carbon to organic nitrogen; texture classes according to USDA classification.

Management data were obtained from the farmer's management control sheets. Crops were rotated as: winter wheat - sunflower (catch crop) - sugarbeet - winter wheat. After harvesting the winter wheat sunflower was sown in August 1995 as a catch crop. After the first frost was over, the soil was plowed in mid December 1995, burying the plant residues in the top 20 cm of soil. The field was left fallow until 28 March 1996, when the sugarbeet was sown. The sugarbeet harvest lasted about 6 weeks, from mid September to the end of October 1996, followed by the seeding of winter wheat in November.
4.3. Simulation techniques

4.3.1 Model description

The program LEACTM (Hutson and Wagenet, 1992) consists of several sub-models. In the present study we used the sub-models LEACHW and LEACHN. LEACHW simulates soil water regime on the basis of a numerical solution of the Richards equation:

\[
\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[ K(\theta) \frac{\partial H}{\partial z} \right] - U(z, t) \tag{Eq. 4-1}
\]

where \( \theta \) is volumetric water content \((L^3 m^{-3})\), \( H \) is total hydraulic head \((L)\), \( K \) is hydraulic conductivity \((L m^{-1})\), \( t \) is time \((T)\), \( z \) is depth \((m)\), positive downwards, and \( U \) is a sink term representing water lost by transpiration \((T^{-1})\).

Soil water retention functions are parameterized according to the model of Hutson and Cass (1987), and the hydraulic conductivity function is given by Campbell (1974). See Appendix 1 for details of the equations.

The upper boundary condition was assigned as atmospheric with rainfall and evapotranspiration, and for the lower boundary condition the hydraulic head was prescribed according to the measured moving water table.

Potential evapotranspiration was calculated from the recorded climate data according to the model of Allen et al. (1994). A crop cover fraction was used to partition potential evapotranspiration into potential evaporation and transpiration. It was assumed that evapotranspiration started at 0.3 day and ended at 0.8 day, and that during this period potential evapotranspiration flux density varied sinusoidally. A factor representing the ratio of maximum actual to potential transpiration \( (R_\ell) \) allowed an increased transpiration to compensate for reduced surface evaporation under dry conditions (Hutson and Wagenet, 1992).

Solute transport is simulated by a numerical solution to the following form of the convection-dispersion equation:

\[
\frac{\partial (\theta + \rho K_d + \varepsilon K'_h) c}{\partial t} = \frac{\partial}{\partial z} \left[ D(\theta, q) \frac{\partial c}{\partial z} - q c \right] \pm \phi \tag{Eq. 4-2}
\]

where \( c \) is solute concentration in the solution \((M m^{-3})\), \( \rho \) is soil bulk density \((M m^{-3})\), \( K_d \) is the solute partition coefficient between the liquid and solid phases \((m^{-1})\), \( \varepsilon \) is the gas-filled soil porosity, \( K'_h \) is a modified Henry’s law constant, \( q \) is the Darcian flux \((m s^{-1})\), \( D(\theta, q) \) is the dispersion coefficient \((m^2 s^{-1})\), \( z \) is the soil depth \((m)\), and \( \phi \) indicates the source/sink term \((M m^{-3} s^{-1})\).
Figure 4-1. Carbon and nitrogen flowchart of LEACHN.
Nitrogen transformation in LEACHN follows the concept of Johnsson et al. (1987). The different organic and mineral N pools and the fluxes between the pools are illustrated in Figure 4-1. In general, organic matter turnover processes are described by first-order kinetics of the following form:

\[ \frac{dC_i}{dt} = k_i e_0 e_T C_i \]  

(Eq. 4-3)

where \( k_i (T^{-1}) \) is the constant basic reaction rate for the organic carbon pool \( C_i (M) \), \( e_0 \) and \( e_T \) are two correction functions accounting for the influence of water content and temperature, respectively. The latter dependence is considered as a \( Q_{10} \) type function.

N mineralization is assumed to follow the rate of organic matter decomposition and the C/N ratios of three different pools described as litter, easily degradable manure, and relatively stables humus according to the equations given in Appendix 1. An overview of the main input data required by LEACHM is also given in Appendix 2.

4.3.2 Inverse Parameter Estimation by SUFI

The simulation model described above contains a number of unknown parameters which were estimated by the inverse program SUFI (Abbaspour et al., 1997). An important feature of the SUFI program is that it is forward and repeatedly invokes the simulation program. Also, SUFI provides opportunities which prevent falling into local minima (Abbaspour et al., 1997; 2000).

The essential steps carried out by SUFI for parameter identification can be shortly described as follows. First, each parameter \( p_i \) \((i = 1, ..., n) \) is depicted as an uncertain variable defined within a domain of uncertainty based on prior information. Then an objective function, quantifying the deviation of simulated from observed values, is minimized. The following steps are carried out repeatedly:

1. For every single parameter \( p_i \), the uncertainty domain is divided into a number \( m_{pi} \) of user-specified strata of equal width. Parameter values are defined by the first moment of each stratum.
2. For every possible combination of parameter values, \( M = m_{p1} m_{p2} \cdots m_{pn} \), the simulation model is run, and the value of the objective function is calculated for each run. Using the \( M \) simulations, the 95% confidence interval of the Bayesian distribution (Benjamin and Cornell, 1970) of the objective function as well as any desired model variable such as water content or pressure head are calculated.
3. The user identifies a critical value of the objective function, and all the parameter combinations producing values of the objective function below the critical value...
are recorded as successful. Parameter strata not meeting the critical condition are eliminated resulting in updated, narrower uncertainty domains for each parameter.

4. The above steps are repeated again with the updated parameter domains of step 3 until no further improvements to the objective function are achieved.

The number of iterations depends on the stratification strategy, which is problem-dependent. The larger the number of strata the faster the convergence, however, at the price of a higher computational cost. Estimated parameter domains are independent of the stratification strategy. For inverse analysis, SUFI can be combined with different simulation programs. In the present study we linked SUFI with LEACHW and LEACHN to estimate the unknown hydraulic, chemical and biological parameters.

4.3.3 Conditioned parameter distribution versus fitted parameters

The first iteration of SUFI is based on a prior estimate of the uncertainty domain of the model parameters and therefore, because of the often large initial uncertainties, the 95\% confidence interval of the Bayesian distribution (95PCIBD) of any model variable is large. This is shown by the space within the example curves ‘a’ in Figure 4-2 that is used to demonstrate this concept.

Figure 4-2. Simulations based on the ‘conditioned parameter distribution’ concept versus the ‘best-fit parameters’. Best-fit parameters produce simulations, which usually miss most of the measurements, that is curve ‘d’. Whereas conditioned parameter distributions produce simulations, which respect most of the measurements, that is curves ‘c’.
As iterations proceed, the uncertainty domain of the parameters become smaller as they are more and more conditioned on the measurements of the variable(s) used in the objective function. Thus, ‘conditioned parameter distributions’ in the context of this study refer to parameter distributions such that, when propagated stochastically through a simulation program, the 95PCIIBD of the simulated variable would contain all, or most of the measured points (i.e., curves ‘c’ in Figure 4-2). In SUFI, the iterations can be continued until the upper and the lower limits of the 95PCIIBD coincide to a single curve. This curve is produced by a set of single-valued parameters generally referred to as ‘best-fit parameters’ (curve ‘d’ in Figure 4-2).

However, as illustrated by curve ‘d’ in Figure 4-2, fitted parameters produce simulations that often miss most of the measured points. In our opinion, fitted parameters are inadequate for analysis of environmental problems if used without the uncertainty associated with them. In least square optimization programs, the covariance of the parameter matrix and hence the 95% confidence interval associated with each parameter are based on linear regression analysis. The problem, therefore, with the calculated parameter uncertainties are that they hold only approximately for the non-linear analysis (Kool and Parker, 1988). Instead, we suggest obtaining conditioned parameter distributions, where most of the data points are respected within the 95PCIIBD.

4.4. Results and Discussions

The data on climate variables and management practices used as input in the simulations with LEACHW and LEACHF, are shown in Figure 4-3. It can be seen that the groundwater table responded quickly to precipitation events. Measured soil nitrate and plant N contents are listed in Table 4-1.

4.4.1 Estimation of parameters related to the water regime

In LEACHW, parameters describing the hydraulic properties of a soil are given by $a$, $b$ and $K_s$ in Eqs. (A 4-1.1) to (A 4-1.5). These parameters were treated as unknown random variables. To take into account plant water uptake we had three more unknown parameters, i.e. the crop cover at maturity (CC), the relative root depth (RD), and the ratio of maximum actual to potential transpiration ($R_T$). Other crop parameters were estimated from literature data (see Appendix 2). Since the simulated profile was divided into three different layers, there were twelve unknown parameters to estimate. The objective function $g(h)$ for LEACHW was expressed as:

$$g(h) = \frac{1}{n} \sqrt{\sum_{i=1}^{n} \sum_{j=1}^{n} (h_{ij}^m - h_{ij})^2}$$  \hspace{1cm} (Eq. 4-4)
where \( h^n \) is the measured pressure head, \( h^p \) is the simulated pressure head, \( \tau \) is the number of measurements over time, \( s \) is the number of measurements over space, and \( n \) is the total number of measurements (\( \tau \) times \( s \)).

Figure 4-3. Measured data from August 1995 to December 1996. (a) Field management data. (b) Mean daily temperature. (c) Water fluxes: daily precipitation, cumulative precipitation, and evapotranspiration. (d) Ground water table measured as distance below surface.
Parameter estimation was performed using the pressure head data measured for the period of March to December 1996. The initial uncertainty domains for the unknown parameters, the final uncertainty domains (conditioned parameter distributions), and the estimated best-fits are given in Table 4-3. For lack of information, the initial distribution of each parameter was assumed to be uniform within its uncertainty domain. Figure 4-4 shows the simulation results for three depths along with the measured data. The 95PCIBD for the pressure head contains most but not all of the measured data points. Some of the fast system responses, especially after intensive rainfall events, could not be captured regardless of how much the uncertainties of the parameters were increased.

Table 4-3. LEACHW input parameters estimated by inverse analysis: initial uncertainty domains, final uncertainty domains (conditioned parameters), best-fit parameter values.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Code</th>
<th>Unit</th>
<th>initial UD † (conditioned parameters)</th>
<th>final UD † (conditioned parameters)</th>
<th>best-fit (fitted parameters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Campbell’s constant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- layer 0-20 cm</td>
<td>a_1</td>
<td>kPa</td>
<td>[-0.20, -0.01]</td>
<td>[-0.224, -0.075]</td>
<td>-0.149</td>
</tr>
<tr>
<td>- layer 20-40 cm</td>
<td>a_2</td>
<td>kPa</td>
<td>[-0.40, -0.10]</td>
<td>[-0.278, -0.093]</td>
<td>-0.185</td>
</tr>
<tr>
<td>- layer 40-70 cm</td>
<td>a_3</td>
<td>kPa</td>
<td>[-0.50, -0.10]</td>
<td>[-0.513, -0.003]</td>
<td>-0.258</td>
</tr>
<tr>
<td>Campbell’s exponent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- layer 0-20 cm</td>
<td>b_1</td>
<td>[-]</td>
<td>[18.0, 20.0]</td>
<td>[19.57, 23.93]</td>
<td>21.75</td>
</tr>
<tr>
<td>- layer 20-40 cm</td>
<td>b_2</td>
<td>[-]</td>
<td>[15.0, 17.0]</td>
<td>[28.35, 34.65]</td>
<td>31.50</td>
</tr>
<tr>
<td>- layer 40-70 cm</td>
<td>b_3</td>
<td>[-]</td>
<td>[8.0, 10.0]</td>
<td>[18.0, 22.0]</td>
<td>20.00</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- layer 0-20 cm</td>
<td>Ks_1</td>
<td>[mm d⁻¹]</td>
<td>[8500, 18500]</td>
<td>[12060, 14740]</td>
<td>13400</td>
</tr>
<tr>
<td>- layer 20-40 cm</td>
<td>Ks_2</td>
<td>[mm d⁻¹]</td>
<td>[6000, 10000]</td>
<td>[2656, 3135]</td>
<td>2850</td>
</tr>
<tr>
<td>- layer 40-70 cm</td>
<td>Ks_3</td>
<td>[mm d⁻¹]</td>
<td>[2000, 6000]</td>
<td>[2025, 2475]</td>
<td>2250</td>
</tr>
<tr>
<td>Crop cover</td>
<td>CC</td>
<td>[-]</td>
<td>[1.20, 1.80]</td>
<td>[1.260, 1.540]</td>
<td>1.40</td>
</tr>
<tr>
<td>Relative root depth</td>
<td>RD</td>
<td>[-]</td>
<td>[0.10, 0.30]</td>
<td>[0.171, 0.209]</td>
<td>0.19</td>
</tr>
<tr>
<td>Max. ratio actual to potential transpiration</td>
<td>Rᵦ</td>
<td>[-]</td>
<td>[1.1, 1.3]</td>
<td>[1.395, 1.705]</td>
<td>1.55</td>
</tr>
<tr>
<td>Value of the objective function</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.54</td>
</tr>
</tbody>
</table>

† UD = uncertainty domains

The parameter distributions conditioned on the measured data from March to December 1996 were then validated by simulating pressure heads for the period of August 1995 to March 1996. This means that the conditional parameters (Table 4-3) were propagated by a Monte Carlo procedure using the August 1995 to March 1996 climate, ground-
Chapter 4

water, and agricultural data. The validation results for the three depths are shown in Figure 4-5. In the context of the conditioned parameter distributions, a validation is considered successful if all of the measured data points would fall within the 95PCIBD. In Figure 4-5, the validation result shows that most of the measurements fell within the 95PCIBD, with the exception of a freezing period in January 1996 and after an intensive rainfall event in August 1995. The discrepancies between the measured and the simulated pressure heads in this case may at least have two causes, inadequate inversely estimated parameters and inadequate characterization of hydraulic processes in the simulation model.

For the case of the inversely estimated parameters, the program SUFI, being a forward model, is always stable. However, given the large number of parameters in this study there is a good chance that the parameters at the absolute minimum of the objective function were not obtained, albeit by employing procedures such as tunneling (see Abbaspour et al., 1999b). To check if the discrepancies, observed in both the calibration and the validation data sets, were caused by inadequate parameters we increased the uncertainty of all parameters by a large interval and propagating the uncertainties through the LEACHW model. The 95PCIBD still could not account for some observations in the June, July, and August of 1996 (Figure 4-4) in the calibration data set and January of 1996 and August of 1995 (Figure 4-5) in the validation data set. Since LEACHW assumes water flow to take place in a homogenous single-region porous medium, we decided that the discrepancies were caused by the inadequate accounting of the hydraulic processes such as preferential flow and freezing, the latter occurring in January of 1996. Preferential flow may have been triggered by intensive rainfall events which occurred during 1995 and 1996.
Inverse Estimation of Parameters in a Nitrogen Model Using Field Data

Figure 4-4. LEACHW calibration (March 1996 - December 1996). Simulation of pressure head with conditional hydraulic and plant parameters showing the 95% confidence interval of the Bayesian distribution for the pressure head (curves). Symbols represent the measured data ± one standard deviation.
Figure 4-5. LEACHW validation (August 1995 - March 1996). Simulation of pressure head with conditional hydraulic and plant parameters determined based on observations of March 1996 - December 1996 time period. Curves are the 95% confidence interval of the Bayesian distribution of the simulated pressure heads. Symbols represent the measurements ± one standard deviation.
In inverse modeling, it is important to realize that we are only adjusting the unknown parameters to obtain a good fit, where as often certain hydraulic or chemical processes can only account for some observations. In field situations especially, non-uniform hydraulic and chemical processes may influence much of the observations, and it would be futile to try to account for them by adjusting parameters of a model that applies to homogenous and uniform conditions. For this reason care should be taken in identifying the existing hydraulic and chemical processes at work and using appropriate models. Hydraulic processes (see Kätterer, 2001) and the soil profile system (see Abbaspour et al., 2000) can also be treated as unknown random variables by invoking different models which handle different processes. We are planning further modeling work with the program MACRO-N (Larsson, 1999) which accounts for macropore flow and soil freezing. An interesting experience of the authors with inverse modeling of field problems is that so far it was not possible to obtain good fits by the force of parameter fitting alone if important hydraulic, chemical, or system dependent processes were neglected (Abbaspour et al., 1999, 2000). We consider this to be an important and positive aspect of inverse modeling, one that could make inverse modeling a tool for the analyses of the system and the processes as well as a parameter estimation routine.

4.4.2 Estimation of parameters related to nitrogen turnover

After conditioning the hydraulic parameters for LEACHW, we used SUFI to estimate the parameters of the nitrogen sub-model LEACFN. To assess the importance of different processes in soil N dynamics several scenarios of different complexity were considered. Scenario S1 represents the simplest scenario involving only one organic matter pool (i.e., measured soil organic C and N were considered to belong to the humus pool) and ignoring any water and temperature dependence of the reaction rates ($e_0$ and $e_T$ in Eq. 4-3). In the other scenarios, adding a fast decomposing litter pool (scenario S2), plus adjusting the reaction rates for water and temperature effects (scenario S3) included further processes. The objective function used in these scenarios was expressed as:

$$g(NO_j) = \frac{1}{n} \sqrt{\sum_{i=1}^{s} \sum_{j=1}^{k} \left( NO_j^m - NO_j^p \right)^2}$$

(Eq. 4-5)

where superscripts $m$ and $p$ stand for measured and simulated variables, $\tau$ is the number of measurements over time, $s$ is the number of measurements over space, and $n$ is the total number of measurements ($\tau$ times $s$).

Finally, in scenario S4 we investigated the effect of including plant N uptake as a
second variable in the objective function on parameter estimates, using the following objective function:

\[ g(NO_3, NUP) = \frac{1}{n} \left( \sum_{i=1}^{s} \sum_{j=1}^{s'} \left( NO_3^m_{ij} - NO_3^p_{ij} \right)^2 \right) \cdot \frac{1}{k} \left( \sum_{i=1}^{s} \sum_{j=1}^{s'} \left( NUP^m_{ij} - NUP^p_{ij} \right)^2 \right) \] (Eq. 4-6)

where \( NUP \) is the plant N uptake, \( t \) and \( s \) are the number of measured NO\(_3\) over time and space, respectively, \( t' \) and \( s' \) are the number of measured NUP over time and space, respectively, \( n = t s \), and \( k = t's' \). The above multiplicative form of the objective function was first tested by Abbaspour et al. (1999) and found to produce reasonable results without the need for calculating any weights for different variables.

The final results of parameter estimation are given in Table 4-4. Simulated and measured NO\(_3\) data are compared in Figures 4-6 and 4-7. Note that the measured data are averages of 3 data points per depth. In general, simulations with best-fit parameters (Figure 4-6) were almost always within the range of measurements ± one standard deviation in the first and second layers. All scenarios underestimated the nitrate concentration in the subsoil indicating that, as discussed before, either the model assumptions were inadequate, or given the large number of parameters to estimate we did not achieve the global minimum of the objective functions.

Scenario S1 (without litter pool) resulted in a final parameter combination with unreasonably high values for the nitrification rate constant \( K_{nit} \) and the soil solution distribution coefficient \( K_{d(NO_3)} \). The value of the objective function for scenario S1 was 0.92 (kg N ha\(^{-1}\)). A major improvement was achieved in scenario S2 with the addition of a fast decomposing litter pool. In this scenario, the value of the objective function decreased to 0.80 (kg N ha\(^{-1}\)) and simulated NO\(_3\) values were closer to the measured averages. Since in scenario S3 the various N turnover rate coefficients were made dependent on temperature and soil water content, the simulation results were expected to be further improved. The new value of the objective function was 0.67 (kg N ha\(^{-1}\)) due to a higher nitrification rate indicating better estimates of the measured points in the period of litter mineralization. However, estimates of the other parameters in S2 and S3 were fairly close to each other.

The 95PCIBD for scenarios S1 and S2 are shown in Figure 4-7. Propagating the final uncertainty domains in the parameters related to litter mineralization to the simulation outputs resulted in a 95PCIBD which respected most of the measurements in the period when the litter pool was relevant (spring/early summer). But regardless of any increases in the uncertainty domains of N turnover and the hydraulic parameters, the observed high NO\(_3\) averages in the 40 to 70 cm-depth could not be matched. This emphasizes the
point we made earlier with respect to hydraulic parameters, meaning that the discrepancies are probably process rather than parameter dependent.

Table 4-4. LEACHN input parameters estimated by inverse analysis for different scenarios.

<table>
<thead>
<tr>
<th>Specification#</th>
<th>Code</th>
<th>Unit</th>
<th>Scenario</th>
<th>Literature values$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>S1</td>
<td>S2</td>
</tr>
<tr>
<td>Distr. coeff. soil /sol. NH4</td>
<td>$K_{diss}$</td>
<td>dm$^3$ kg$^{-1}$</td>
<td>27.0$^f$</td>
<td>3.3</td>
</tr>
<tr>
<td>Nitrification rate</td>
<td>$k_{nit}$</td>
<td>d$^3$</td>
<td>&gt;200</td>
<td>0.174</td>
</tr>
<tr>
<td>Denitrification rate</td>
<td>$k_{den}$</td>
<td>d$^3$</td>
<td>0.00973</td>
<td>0.0756</td>
</tr>
<tr>
<td>Mineralization rate humus</td>
<td>$k_{hum}$</td>
<td>d$^3$</td>
<td>5.31E-5</td>
<td>5.94E-5</td>
</tr>
<tr>
<td>Mineralization rate litter</td>
<td>$k_{litter}$</td>
<td>d$^3$</td>
<td>-</td>
<td>0.0607</td>
</tr>
<tr>
<td>Initial ratio N$\text{in}$ / N$\text{org}$</td>
<td>$N_{pool}$</td>
<td>%</td>
<td>-</td>
<td>2.38</td>
</tr>
<tr>
<td>Initial ratio C$\text{in}$ / C$\text{org}$</td>
<td>$C_{pool}$</td>
<td>%</td>
<td>-</td>
<td>3.75</td>
</tr>
<tr>
<td>Synthesis efficiency</td>
<td>$f_s$</td>
<td>-</td>
<td>-</td>
<td>0.683</td>
</tr>
<tr>
<td>Humification factor</td>
<td>$f_h$</td>
<td>-</td>
<td>-</td>
<td>0.210</td>
</tr>
<tr>
<td>Q10-factor</td>
<td>$Q_{10}$</td>
<td>-</td>
<td>-</td>
<td>1.50</td>
</tr>
<tr>
<td>High end of opt. We range</td>
<td>$HE_{opt}$</td>
<td>%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Low end of opt. We range</td>
<td>$LE_{opt}$</td>
<td>kPa</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Min. matric potential</td>
<td>$LE_{min}$</td>
<td>kPa</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rel. transf. rate saturation</td>
<td>$tr_{SAT}$</td>
<td>-</td>
<td>-</td>
<td>&gt;1.0$^f$</td>
</tr>
<tr>
<td>No. of estimated parameters</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Variables in objective fn.</td>
<td>-</td>
<td>-</td>
<td>NO$_3$</td>
<td>NO$_2$</td>
</tr>
<tr>
<td>Value of objective fn.</td>
<td>0.92</td>
<td>0.80</td>
<td>0.67</td>
<td>0.76*46.6</td>
</tr>
</tbody>
</table>

# For abbreviations see Appendix 2.

§ Single parameter values or parameter ranges (lowest; highest) according to Johnsson et al. (1987), Borg et al. (1990), Hutson and Wagenet (1992), Lotse et al (1992), Bradbury et al. (1993), Wu et al. (1998).

† Fixed to 3.0.

‡ Fixed to 1.0.
Figure 4-6. LEACHN calibration (March 1996 - December 1996). Simulations of NO$_3$ concentrations are based on the fitted parameters for Scenarios S1, S2 and S3. Symbols represent the measurements ± one standard deviation.
Figure 4-7. Simulations of NO$_3$ using the conditional parameters in Table 4-4 for scenarios S1 and S2. Symbols represent the measurements ± one standard deviation.
We used the parameter set obtained in S3 (litter pool plus environmental adjustments) to simulate the total plant N uptake (Figure 4-8). Simulation results underestimated total plant N content by about 100 kg N ha\(^{-1}\). Since plant uptake is a major sink for mineral N, it was expected that scenario S4, which included \(NUP\) in the objective function, would perform better than S3 in predicting total plant N uptake. For scenario S4, the root mean square error between the measured and simulated NO\(_3\) increased from 0.67 (in scenario S3) to 0.76 (Table 4-4). As expected, the estimate of the total plant N content showed a significant improvement, and the difference between simulated and measured total NUP decreased from 100 (in scenario S3) to 10 kg N ha\(^{-1}\) (Figure 4-8). Although during the vegetation period, the observed dynamics of NUP was still not very well described.

A comparison of the parameter estimates obtained in S4 with those of S3 (Table 4-4) shows that incorporation of NUP into the objective function forced a better match of plant N uptake by approximately doubling the nitrification rate, while at the same time the soil solution distribution coefficient reduced by more than half. Otherwise, the parameter estimates of S3 and S4 obtained by means of the SUFI algorithm are fairly similar to each other and also in close agreement with values reported in the literature (Table 4-4). The results above illustrate the conditionality of the estimated parameters on the formulation of the objective function and, thus, the importance of choosing it carefully (see also Abbaspour et al., 1999).

4.4.3 Sensitivity Analysis

We performed a sensitivity analysis by varying the parameters one by one from their optimal values by ± 50%. Figure 4-9 shows the results of this analysis for the six most sensitive parameters in scenario S4. It can be seen that the parameters related to the litter pool and its mineralization (i.e., \(N_{pool}\), \(C_{pool}\), \(f_e\), \(f_h\), and \(k_{hn}\)) and the denitrification rate \((k_{den})\) are the most sensitive. Also, but not shown in Figure 4-9, very sensitive parameters were found to be the humus mineralization rate and the \(Q_N\) factor which accounts for the temperature dependence of the rate coefficients. The hydraulic and crop parameters estimated in LEACHW were not sensitive relative to soil NO\(_3\) and plant N uptake with the exception of the Campbell's exponent in the uppermost layer \(b_1\) and the relative root depth factor \(RD\).
Inverse Estimation of Parameters in a Nitrogen Model Using Field Data

Figure 4-8. Simulation of plant N uptake using parameters in scenarios S3 and S4. Measurements of the plant total N pool are mean values ± one standard deviation. Simulation results are represented as the 95% confidential interval of the Bayesian distribution for plant uptake.

Figure 4-9. Sensitivity analysis for scenario S4 showing the 5 most sensitive parameters. For abbreviations see Appendix 2.
4.5 Conclusions

The inverse parameter estimation algorithm of SUFI was linked with LEACHW and LEACHN to estimate, respectively, hydraulic and nitrogen turnover parameters of an agricultural field. The conditioned parameter distributions led to good descriptions for both the observed pressure heads and the NO\textsubscript{3} concentrations in the soil solution at different layers in the top 70-cm of the field soil under study. The exceptions, however, were some pressure heads corresponding to intense rainfall events and periods of soil freezing, and some high NO\textsubscript{3} concentrations at 40 to 70 cm-depth. These deviations, we concluded, were process rather than parameter dependent. Future studies are being designed with a nitrogen model that takes preferential flow and soil freezing into account.

In this paper we introduced the concept of ‘conditioned parameter distributions’ versus ‘best-fit’ parameters. We maintain that conditioned parameter distributions are more appropriate than best-fit parameters for describing environmental processes, because of the inherent uncertainty associated with the quantification of the parameters and because parameter distributions expressed in conditioned form allow for probabilistic interpretation as demanded in the framework of risk analyses.

4.6 References


Inverse Estimation of Parameters in a Nitrogen Model Using Field Data


Inverse Estimation of Parameters in a Nitrogen Model Using Field Data


Appendix 1: Equations

Soil water retention functions according to the model of Hutson and Cass (1987):

\[
h = \frac{a(1 - \theta / \theta_s)^{1/2}(\theta_e / \theta_s)^{-h}}{(1 - \theta_e / \theta_s)^{1/2}} \quad \text{hc} < h \leq 0 \\
h = a(\theta / \theta_s)^{-b} \quad h \leq \text{hc}
\]

(A 4-1.1)  
(A 4-1.2)

where \(a\) and \(b\) are constants, \(h\) is the pressure head (L), \(\theta_s\) is the saturated water content (L^3 L^-1), and \((h_c, \theta_c)\) is the intersection point calculated according to:

\[
h_c = a\left[2b / (1 + 2b)\right]^{-b} \quad (A 4-1.3)
\]

\[
\theta_c = 2b \theta_s / (1 + 2b) \quad (A 4-1.4)
\]

Soil hydraulic conductivity function according to Campbell (1974),

\[
K(\theta) = K_s (\theta / \theta_s)^{(2b+3)} 
\]

(A 4-1.5)

where \(K_s\) is the saturated hydraulic conductivity (L T^-1).

Equations describing N mineralization are expressed as:

\[
\frac{dN_{l_l}}{dt} = \left[\frac{N_{l_l}}{C_{l_l}} + \frac{f_c}{r_o} (1 - f_h)\right] k_{l_l} e_\theta e_\tau C_{l_l} 
\]

(A 4-1.6)

\[
\frac{dN_{man}}{dt} = \left[\frac{N_{man}}{C_{man}} + \frac{f_c}{r_o} (1 - f_h)\right] k_{man} e_\theta e_\tau C_{man} 
\]

(A 4-1.7)

\[
\frac{dN_{hum}}{dt} = \frac{f_c f_h}{r_o} \left[k_{l_l} C_{l_l} + k_{man} C_{man} - k_{hum} N_{hum}\right] e_\theta e_\tau 
\]

(A 4-1.8)

where \(N\) and \(C\) are the concentration of nitrogen and carbon, respectively, \(k\) is the reaction rate for C mineralization for the three different organic matter pools assigned by the subscripts \(l_l\) (litter), \(man\) (manure), and \(hum\) (humus), \(f_c\) is the fraction of organic carbon that is converted to humus and biomass, \(f_h\) is the humification factor, and \(r_o\) is the C/N ratio of humus and microbial biomass.
Appendix 2: Input parameters LEACHM (to be continued).

<table>
<thead>
<tr>
<th>MODEL - Compartment</th>
<th>Properties</th>
<th>Specification</th>
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<th>Unit</th>
<th>Source</th>
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## Appendix 2 (continued)

### MODEL - Compartment

#### - Properties

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#### LEACHN - SOIL

- Transport parameters
- Chemical properties

#### LEACHN - CROP

- plant N uptake
- Potential N uptake

#### LEACHN - NITROGEN TRANSFORMATIONS

- Reaction rates
- Constants
- Correction functions

### Source:
- calc (calculated), mfs (management fact sheet), meas (measured), lit (literature), est (parameter estimation by inverse analysis).
- drivar (driving variables for LEACHM program), Tab. 3 and Tab. 4 see respective Tables.
- Texture classes according to USDA classification.

---

<table>
<thead>
<tr>
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Net Nitrogen Mineralisation in Undisturbed Soil Cores, Monoliths and in the Field as Affected by Soil Moisture

B. Schmied, T. Kätterer and R. Schulin

Submitted to Nutrient Cycling in Agroecosystems

Abstract

The contribution of “old” and “new” organic matter to nitrogen export from former wetland soils was estimated in situ in a drained Mollic Gleysol and ex situ using undisturbed soil cores and monoliths. Net nitrogen mineralisation (NNM) and its moisture dependence were determined in the soil cores, taken in the organic-rich layer at 45-55 cm depth. The resulting response function was used to estimate NNM in two undisturbed soil monoliths excavated at 28-80 cm depth and kept under different moisture regimes. To stay abreast of changes in soil temperature a quadratic temperature response function was assumed a priori.

The NNM rate constants, estimated in each monolith for four depths assuming first-order kinetics, did not significantly differ from those obtained for the soil cores. In combination with the above response functions simulation of NNM under the conditions of the in situ experiment with a one-pool model gave good agreement with field incubation results obtained for the depth 20-40 cm indicating the predominance of “old” organic matter. For the topsoil (0-20 cm) it was necessary to account separately for “new” material by assuming a second pool of organic matter with a higher turnover rate. The calibrated two-pool model estimated that about 340 kg N ha⁻¹ were mineralised during the experimental year in the upper 40 cm of the soil, of which about 48% derived from the fast decomposing material. The results suggest that the overall N mineralisation in the field can be well estimated by numerical modelling using lab-determined rate coefficients and response functions. This was also true for the mostly undisturbed soil layer below the plough layer, whereas the agreement with the short-range dynamics in the topsoil was weak.
5.1 Introduction

Large areas of wetland have been drained for agricultural use because high organic matter and nutrient contents made them very suitable for intensive production. The same factors, however, also often result in particular high risk for the quality of surface and ground water resources due to excessive organic matter mineralisation and subsequent leaching of surplus mineralised N. During the growing season (micro)environmental conditions (such as higher soil temperature, root activity and sufficient oxygen supply because of soil drying), increase microbiological activity and thus N turnover processes also in greater soil depths. Accumulation of mineral N occurs depending on the interaction of the nitrogen turnover processes subsumed as net N mineralisation (NNM) that is mineralisation (ammonification and subsequent nitrification), immobilisation and denitrification. In the absence of plant uptake this mineral N pool is exposed to leaching below the root zone.

In general, N leaching in moderate climate conditions is considered to occur mainly during the non-growing season when precipitation largely exceeds evapotranspiration. This notion is supported by many studies monitoring N leaching to ground- and surface water (e.g. Verhagen and Bouma, 1998; Martin et al., 1994; Kengni et al. 1994). Nowadays, it is well documented that displacement of solutes may occur through preferential flow paths in a wide range soil types under various climatic conditions (e.g. Beven and Germann, 1982; Van Genuchten et al., 1990; Flury et al., 1994; Stamm et al., 1998, Ritsema, 1999). Thus, N losses during the growing season may be more important than previously believed because of preferential transport of mineral N originating from mineralisation of soil organic matter. Although many reports on N drainage have been published, there are few on annual N export and even less dealing with N losses during the vegetation period.

The present study was in particular motivated by findings from monitoring the outflow of various drainage compartments in the Furttal north of Zürich. In the basin of the Furttal valley about 250 ha are drained humic soils, which are under intensive, arable or vegetable production. The former wetland was reclaimed and brought under cultivation between 1920 and 1930. Today, the average organic matter content of the humus rich layer of these soils ranges between 10% and 17%. Measurements showed that 20 to 58% of the annual N losses via drainage was exported from May through October 1996 (Schmied et al., 1999). These findings led to the hypothesis that mineralisation of organic matter, especially the "old" material originating from the former wetland soil, may be the major source of observed nitrate export during the vegetation period.

In this paper, we present the results of three mineralisation studies in situ in the main
root horizon (0-40 cm) of an arable field and *ex situ* with undisturbed soil cores and monoliths originating from the subsoil of a 100-cm organic-rich layer. To interpret the field incubation tests a simple model approach was chosen, while model parameterisation was based on the laboratory experiments. The aim of this study was to determine to what extent "old" stabilised (soil-incorporated) and "new" labile (plant-residual, sewage sludge) soil organic matter contributes to net N mineralisation in the growing season. Additionally, we wanted to test the hypothesis that N mineralisation rates and their dependence on soil moisture as estimated in small undisturbed soil cores in the laboratory also apply to undisturbed monoliths as well as in the field below the plough layer where cultivation and climate effects are small. For the results of related transport studies performed simultaneously we refer to Kätterer et al. (2001) and Schmied (2001, cf. this thesis chapter 6).

5.2 Material and methods

5.2.1 Study site

The 1.6 ha study site was located in the basin of the Furttal valley. The main soil type was classified as Mollic Gleysol. Below the humic plough layer only little remains of the former peat soil. In general, the mineral soil begins between 30 to 40 cm depth already, only locally the organic soil still reaches about 100 cm depth (Table 5-1). Groundwater levels usually vary between 1.5 m (i.e. from the depth of the drain collectors) to 0.5 m below surface. The pH is buffered by carbonate in the entire profile.

The area is intensively used for agriculture and horticulture. At the beginning of the field study winter wheat was harvested in July 1995 and the straw was removed. The amount of harvest residues, stubble and below-ground stem bases, were not quantified but assumed to correspond to 1500 kg C and 15 kg N ha\(^{-1}\), respectively (Table 5-2). Root biomass was assumed to contribute with 600 kg C and 15 kg N. On 10 August 1995, sewage sludge was applied (28 m\(^3\) ha\(^{-1}\)). We assumed that the sludge contained 10% organic C and 0.5% organic N. After tillage, sunflowers were sown as a catch crop and ploughed under after the first frost at 14 December 1995. Sunflower residues were incorporated into the upper 20 cm of the soil. According to the analysis of 12 randomly selected sunflowers including coarse roots this corresponded to 1840 C and 105 kg N ha\(^{-1}\). Fine roots not recovered by sampling were assumed to have added another 200 kg C and 10 kg N ha\(^{-1}\). On 28 March 1996 sugarbeets were sown.
Table 5-1. Mean values of soil properties.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth [cm]</th>
<th>( \rho_b ) [kg dm(^{-3})]</th>
<th>( \theta_s ) [-]</th>
<th>pH</th>
<th>Clay [%]</th>
<th>Silt [%]</th>
<th>Sand [%]</th>
<th>CaCO(_3) [g g(^{-1})]</th>
<th>C(_{\text{tot}}) [g 100g(^{-1})]</th>
<th>C(_{\text{org}}) [g 100g(^{-1})]</th>
<th>N(_{\text{tot}}) [-]</th>
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<tr>
<td>Ap</td>
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<td>7.2</td>
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Abbreviations: \( \rho_b \) = bulk density; \( \theta_s \) = porosity; C\(_{\text{org}}\) = organic carbon; N\(_{\text{tot}}\) = total soil N; C/N = C/N ratio of organic matter; n.d. = no data.

Table 5-2. Measured and assumed C and N pools.

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<thead>
<tr>
<th>Soil C and N pool respectively input</th>
<th>Organic C [kg C ha(^{-1})]</th>
<th>Nitrogen [kg N ha(^{-1})]</th>
<th>C/N [-]</th>
<th>Incorporation depth [cm]</th>
<th>date [mmm-yy]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil organic carbon and nitrogen †</td>
<td>29638</td>
<td>2964</td>
<td>10</td>
<td>0-10</td>
<td>Jul-95</td>
</tr>
<tr>
<td>0-5 cm depth</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-20 cm depth</td>
<td>98800</td>
<td>9880</td>
<td>10</td>
<td>0-10</td>
<td>Jul-95</td>
</tr>
<tr>
<td>20-40 cm depth</td>
<td>88210</td>
<td>7351</td>
<td>12</td>
<td>0-10</td>
<td>Jul-95</td>
</tr>
<tr>
<td>C and N input</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Harvest residues, stubble and below-</td>
<td>4000</td>
<td>40</td>
<td>100</td>
<td>0-10</td>
<td>Jul-95</td>
</tr>
<tr>
<td>ground stem bases (winter wheat) ‡</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Root residues (winter wheat) ‡</td>
<td>600</td>
<td>15</td>
<td>40</td>
<td>0-10</td>
<td>Jul-95</td>
</tr>
<tr>
<td>Sewage sludge (28 m(^3) ha(^{-1})¶</td>
<td>840</td>
<td>84</td>
<td>10</td>
<td>0-10</td>
<td>Aug-95</td>
</tr>
<tr>
<td>Plant residues (sunflowers) #</td>
<td>1840</td>
<td>105</td>
<td>18</td>
<td>0-20</td>
<td>Dec-95</td>
</tr>
<tr>
<td>Root residues (sunflowers) ‡</td>
<td>200</td>
<td>10</td>
<td>20</td>
<td>0-20</td>
<td>Dec-95</td>
</tr>
</tbody>
</table>

† calculated from bulk density and averaged C and N content per layer measured at the beginning of each incubation periods.
‡ assumed according to literature (FAL, 1987; Walther et al., 1994)
¶ calculated from sewage sludge application and assumed C and N content (see text)
# measured (see text)
Air temperature, humidity, radiation, wind speed and precipitation were recorded hourly in a nearby meteorological field station. Groundwater levels were recorded continuously through a piezometer coupled to a data logger. Thermocouples, TDR-probes and tensiometers were installed on two plots with three replications per plot at 15, 30, and 60 cm depth, the latter additionally at 5 cm depth. Readings were taken weekly.

5.2.2 Methods

Ex situ mineralisation in undisturbed soil cores

On 21 October 1997, 55 undisturbed soil cores (basal area 22.3 cm², length 10 cm) were taken at 45 to 55 cm soil depth from a profile in which the humus rich horizon reached to 0.9 m depth. Samples were carried to the laboratory in colding boxes at about 5°C. Fifty cores were cut into halves of equal length which were fitted tightly into plastic tubes of about 100 ml volume. The remaining five samples were cut into quarters and fitted into steel tubes of 2.4 cm length and 55 ml volume. Porous plastic gauze fastened by rubber bands was used to hold the soil within the tubes. The soil cores were put into distilled water to saturate from below for two days. Then they were drained on a porous plate with the low end of the sample cores at 1 cm above water level. After weighing the 100-ml cores were randomly assigned to five groups with ten pairs each. These groups were each equilibrated at one of the following water potentials applied by hanging water columns to the lower end of the samples, i.e. -20, -80, -160, -345 or -690 hPa. The 55-ml cores were adjusted to equilibrate with -1000 hPa. After equilibration, one randomly selected sample per pair of the 100-ml cores and two per quartet of the 55-ml cores were analysed for ammonium and nitrate using an Autoanalyser (Alliance Instruments Nanterre, France).

The remaining samples were incubated in gas-tight glass vessels at a constant temperature of 15°C. After three and six weeks five samples per moisture level were extracted with 0.01 M CaCl₂ and the extracts were analysed for ammonium and nitrate. During incubation, CO₂ evolution was measured daily in each vessel using wave length modulation (MicroSensonic, Dietikon, Switzerland). To prevent anaerobic conditions, all samples were aerated as soon as CO₂ concentrations in the headspace exceeded 2000 ppm.

At the end of the experiment, samples were dried at 105 °C for 24 hours, weighed and analysed for total C and N using a CHNS-Analyser (CHNS-932, Leco Instrumente GmbH, Kirchheim, Germany). The same samples were used to calculate dry bulk density and saturated water content (weight difference between the saturated and dried samples by their volume).
Net N mineralisation rates, $k_h$ [d$^{-1}$], were calculated by pairs for each incubation period ($\Delta t$=three and six weeks, respectively) by

$$k_h = \left[ \frac{\Delta N_{\text{min}}}{(N_{\text{org}} + \Delta N_{\text{min}}) \Delta t} \right]_h$$

(Eq. 5-1)

where $\Delta N_{\text{min}}$ is the change in mineral N of the samples during the incubation, $N_{\text{org}}$ is the total organic N pool in the soil measured at the end of the experiment, and the subscript $h$ refers to the water potential of the samples. Then the average rate constants for each moisture level ($k_h$) was calculated. The ratios ($r_h$) between $k_h$ and the mean maximum rate constant ($k$) were calculated.

$$r_h = \frac{k_h'}{k}$$

(Eq. 5-2)

A response function was fitted to the $r_h$-values by a non-linear regression model (NLIN, SAS, 1982):

$$r(h) = \begin{cases} 1 + a(h - h_{\text{max}}) & : h < h_{\text{max}} \\ 1 + b(\log_{10}(h) - \log_{10}(h_{\text{max}})) & : h \geq h_{\text{max}} \end{cases}$$

(Eq. 5-3)

where $h$ is the soil water tension in hPa, $h_{\text{max}}$ is the tension at which $k$ was highest and $a$ and $b$ are fitting parameters.

**Ex situ mineralisation in subsoil monoliths**

Two undisturbed soil monoliths of 25 l volume (height 52 cm; basal area 487 cm$^2$) were excavated at 28 to 80 cm depth at a distance of about 2 m from where the small soil cores were taken showing similar soil properties (Table 5-3). Two TDR probes, thermocouples and tensiometers were installed horizontally at 6, 21, 36 and 46 cm below the soil surface in each monolith, connected to a data logger (Schmied, 2001; cf. this thesis chapter 6). After conditioning with several pore volumes of a 0.005 g l$^{-1}$ CaCO$_3$ solution the columns were incubated at room temperature (15-23°C). One column (WET) was covered with a disc during the incubation to prevent water loss from the surface, whereas the other column (DRY) was not protected against surface evaporation. The water potential applied by hanging water columns at the lower boundaries were different, i.e. -10 hPa for the WET and -70 hPa for the DRY. This treatment led to water potentials at 6 cm depth of maximal -66 hPa in WET and -368 hPa in DRY. Although the cover on the ‘wet’ column was not completely gas-tight it was removed every two to three days for about one hour to improve gas exchange. After
44 days of incubation, breakthrough and elution curves of mineralised nitrate and sulfate, and differently applied bromide, chloride and deuterium tracers were recorded as described elsewhere (Kätterer et al., 2001; Schmied, 2001) before the monoliths were used for further incubation tests.

Table 5-3. Bulk density and total C and N pools in the soil samples used for the in situ («sequential coring») and ex situ («undisturbed soil cores» and «soil monoliths») experiments. Mean values, coefficients of variation (CV, %), C/N-ratios and numbers of replicates (No.) at different in situ depths in the profile.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth [cm]</th>
<th>Bulk density mean [g cm⁻³]</th>
<th>Total Carbon mean [g N 100g⁻¹]</th>
<th>Total Nitrogen mean [g N 100g⁻¹]</th>
<th>C/N No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequential coring</td>
<td>0-5</td>
<td>0.72 3</td>
<td>15.6</td>
<td>0.89</td>
<td>12 17 9</td>
</tr>
<tr>
<td></td>
<td>5-20</td>
<td>0.70 2</td>
<td>15.7</td>
<td>0.90</td>
<td>14 17 9</td>
</tr>
<tr>
<td></td>
<td>20-40</td>
<td>0.80 19</td>
<td>12.9</td>
<td>0.46</td>
<td>64 28 9</td>
</tr>
<tr>
<td>Undisturbed cores</td>
<td>45-55</td>
<td>0.55 29</td>
<td>15.9</td>
<td>0.89</td>
<td>32 18 50</td>
</tr>
<tr>
<td>Dry monolith</td>
<td>28-41</td>
<td>0.62 8</td>
<td>17.8</td>
<td>1.19</td>
<td>31 15 2</td>
</tr>
<tr>
<td></td>
<td>41-54</td>
<td>0.58 6</td>
<td>14.7</td>
<td>0.97</td>
<td>2 15 2</td>
</tr>
<tr>
<td></td>
<td>54-67</td>
<td>0.57 9</td>
<td>13.6</td>
<td>0.79</td>
<td>9 17 2</td>
</tr>
<tr>
<td></td>
<td>67-80</td>
<td>0.39 2</td>
<td>18.1</td>
<td>1.05</td>
<td>6 17 2</td>
</tr>
<tr>
<td>Wet monolith</td>
<td>28-41</td>
<td>0.53 2</td>
<td>14.6</td>
<td>0.95</td>
<td>4 15 2</td>
</tr>
<tr>
<td></td>
<td>41-54</td>
<td>0.66 10</td>
<td>13.9</td>
<td>0.82</td>
<td>1 17 2</td>
</tr>
<tr>
<td></td>
<td>54-67</td>
<td>0.50 8</td>
<td>15.0</td>
<td>112</td>
<td>0.83 10 18 2</td>
</tr>
<tr>
<td></td>
<td>67-80</td>
<td>0.39 9</td>
<td>22.0</td>
<td>1.32</td>
<td>11 17 2</td>
</tr>
</tbody>
</table>

During the incubations, soil solution samples were extracted through tensiometer cups and analysed for nitrate by ion chromatography (DX-100, Dionex Switzerland, Olten, Switzerland).

At the end of the experiments, samples were taken from the two monoliths by vertical coring the entire profile. In the two vertical sections where the TDR-probes had been installed, four soil cores were taken about 2 cm from the columns’ outer boundary progressively in depth with an auger (5 cm in diameter), cut into 1-4 cm-thick slices and dried at 105 °C. The dried soil samples were analysed for total C and N. In addition, 100-ml soil cores were collected with steel cylinders taken from the two sections where the tensiometers had been installed for the determination of dry bulk density.

Room and soil temperatures varied between 15 and 23 °C during the incubations. To describe the temperature dependence of mineralisation the relative reaction rate \( r(T) \)
was assumed \textit{a priori} to follow the function proposed by Ratkowsky et al. (1982), i.e.

\[
  r_T = \frac{(T - T_{\text{min}})^2}{(T_{\text{ref}} - T_{\text{min}})^2}, \quad T > T_{\text{min}}
\]  

(Eq. 5-4)

where \( T \) is the soil temperature, \( T_{\text{min}} \) is the minimum temperature below which microbial activity is assumed to be zero, and \( T_{\text{ref}} \) is the temperature to which all measurements are referred to. Here, the reference temperature was set to 15 °C as in the incubations of the soil cores. The value for \( T_{\text{min}} \) was chosen to be -5 °C, according to data given by Díaz-Raviña et al. (1994), Lomander et al. (1998), Persson (1999), and Seyferth and Persson (1999).

Daily values for \( r(T) \) and for the function \( r(h) \) parameterised for the soil cores (Eq. 5-3) were calculated

\[
r(h, T) = r(h) r(T)
\]  

(Eq. 5-5)

and used as modifiers of the mineralisation rate constants \( (k) \). In contrast to the soil cores, the \( r \)-values in the monoliths varied with time. Thus, we had to integrate \( r(h, T) \) over time before calculating the evolution of mineral N in the monoliths. Since analysis of selected soil solution samples showed that ammonium concentrations were always below detection limit, a possible contribution of ammonium was neglected in the following calculations. That is, we assumed the amount of adsorbed ammonium remaining constant and mineralised ammonium being nitrified. Further, the nitrate concentrations measured at 6, 21, 36 and 46 cm depth were considered to represent a layer of 12, 20, 8 and 12 cm.

The following equation was fitted to the resident amount of \( \text{NO}_3^- \) measured during the two incubation periods at four depths in both monoliths by optimising \( k \) for each depth, treatment and period:

\[
  N_{\text{min}} = N_{\text{min,init}} + N_{\text{org}} \left(1 - e^{-k \int r(h) \, dt} \right)
\]  

(Eq. 5-6)

The resulting \( k \)-values were subjected to analysis of variance.

\textbf{In situ mineralisation}

Net N mineralisation was measured \textit{in situ} on three plots using the «sequential coring» method proposed by Raison et al. (1987). The experimental layout was designed as a split-plot with six treatments (time periods) and three plots (replicates per field). To
prevent N uptake by plants as well as water infiltration and leaching, steel cylinders (diameter 25 cm, length 40 cm) were pushed down into the soil and covered with plastic roofs.

Mineral N was determined in five soil samples per plot (0-40 cm depth) taken in the bulk soil at the beginning and inside the cylinders at the end of the 6-week incubation period. This procedure was repeated six times from October 1995 through October 1996.

Directly after sampling, the soil samples were put into cold boxes and brought into the laboratory where they were cut into three horizontal sections, that is 0-5 cm, 5-20 and 20-40 cm depth. From each plot the five samples per depth were bulked, sieved (5-10 mm) and extracted immediately with 0.01 M CaCl₂. Nitrate and ammonium concentrations in the extracts were analysed spectrophotometrically using an Autoanalyser (Alliance Instruments Nanterre, France).

NNM was calculated as the difference between mineral N measured in the unconfined soil at the beginning of each incubation period and that in the covered cylinders at the end of each incubation period.

The contribution of stabilised soil organic matter originating mainly from the former wetland soil (further referred to as humus) to total N mineralisation was estimated from Eq. 5-7 assuming that the same rate constant, $k$, and response functions, $r(h,T)$, were valid in the field as in the soil monoliths and taking measurements of soil water tension and temperature at 5, 15 and 30 cm depth as input values for the three depth layers 0-5, 5-20 and 20-40 cm, respectively. Total organic N storage in the three layers was calculated from measured bulk density and total N concentrations shown in Table 5-3.

To calculate the contribution of soil labile organic matter from litter to total N mineralisation, we assumed that decomposition followed first order kinetics with respect to C concentration:

$$\frac{dC}{dt} = k_r r(h,T)C(f_r - 1)$$  \hspace{1cm} (Eq. 5-7)

where $f_r$ refers to the efficiency of microbial biomass synthesis being recycled within the litter C pool,

$$f_r = (1 - f_h) f_c$$  \hspace{1cm} (Eq. 5-8)

with $f_c$ referring to the efficiency of microbial synthesis and $f_h$ representing the carbon humification fraction.
N fluxes were driven by C fluxes according to the C/N ratios of decomposing litter, \((C/N)_i\), and of the recycled C, \(q\).

\[
\frac{dN}{dt} = k_i r(h,T)C_i \left[ \frac{f_c}{\frac{N}{C}} \right] \quad \text{(Eq. 5-9)}
\]

In our calculation we used the same temperature and moisture response function \(r(h,T)\) for N mineralisation of litter as for the organic matter in the subsoil monoliths.

Daily values of net mineralised litter N were calculated between 10 August 1995 and 9 November 1996. Initial values for C and N were estimated as shown in Table 5-2. The inputs from previous crop residues and sewage sludge application were distributed between the three layers according to a root distribution linearly decreasing with depth and shallow soil cultivation (about 10 cm depth) prior to sowing of sunflowers. On 14 December 1995, the field was ploughed and the respective C and N input from sunflower residues, which have been grown as a catch crop after the winter wheat, were incorporated into the upper 20 cm of the soil.

The two parameters \(f_c\) (0.68) and \(f_h\) (0.21) were set according to previous simulation studies (Schmied et al., 2000). The unknown reaction rate constant, \(k_i\) and parameter \(q\) were estimated by minimising the sum of squared differences between measured and simulated net N mineralisation of the six incubation periods.

### 5.3 Results and discussion

#### 5.3.1 Carbon and net nitrogen mineralisation in undisturbed soil cores

Experimental net N mineralisation rates in the soil cores were on average maximal with \(k = 4.3 \times 10^{-5} \text{ d}^{-1}\) at 80 hPa water tension (Figure 5-1a) and a variance of 5.0 \times 10^{-5}. The overall average of the soil cores was 3.0 \times 10^{-5} \text{ d}^{-1} and its variance 8.4 \times 10^{-6}. Rates tended to be higher during the first three-week period, but this difference was not significant due to the relatively large variance of the measurements. By the same reasons also the differences between water tensions were significantly only between –80 and –690 hPa. The normalised response of net N mineralisation rates to soil water tension was described according to Eq. 5-3 and fitted parameter values of \(a\) (0.0058) and \(b\) (-0.48) (Figure 5-1b).

CO₂-evolution rates did not tend to change during a given experiment (Figure 5-1c). They were highest at the highest moisture, –20 hPa, and tended to show a second maximum at tensions of –690 hPa. The fact that less N was net mineralised per unit C at –20 hPa than at –80 hPa water tension can be explained by a higher rate of denitrifica-
tation due to low oxygen availability. The same argument applies to the tendency for decreased NNM rates with longer incubation time. Additionally, a (minor) part of the measured CO₂-evolution may be attributed to the disintegration of carbonate caused by the protons formed during decomposition and nitrification.

![Bar chart showing Net N mineralisation](image)

![Graph showing Soil water response](image)

![Graph showing CO₂ evolution](image)

Figure 5-1. Mineralisation in undisturbed soil cores incubated at different soil water tensions. Values are given as mean and standard error. (a) Net N mineralisation NNM. (b) Measured and modelled (Eq. 5-3) response of NNM to soil water tension. Parameters values for the fitted equation were a=0.0058; b= -0.48. (c) CO₂ evolution.
5.3.2 Net N mineralisation in the monoliths

Recording of soil water tensions was limited by the measurement range of the tensiometers especially at 6 cm depth in DRY. Therefore, we used the relationship between soil water contents and soil water tensions to estimate the values needed for the moisture response (Eq. 5-3) of N mineralisation in the monoliths. The respective water characteristics parameters and corresponding water retention curves were adapted from Schmied (2001, cf. this thesis chapter 6) and are shown in Figure 5-2 and Table 5-4.

![Graph showing soil water retention characteristics](image-url)

Figure 5-2. Measured (symbols) and estimated (lines) soil water retention characteristics functions at four depths in the Dry (———) and Wet (-------) columns: 6 cm (square); 21 cm (circle); 36 cm (star); 46 cm (dot). Parameter values for the functions are presented in Table 5-4.
Net Nitrogen Mineralisation in Undisturbed Soil Cores, Monoliths and in the Field

The experimental net N mineralisation rate constants of the two monoliths were very similar to those estimated for the soil cores. The average value of $k$ for both monoliths, incubation periods and all depths was $4.2 \times 10^{-5}$ d$^{-1}$ and its variance $1.4 \times 10^{-10}$, neglecting the value for 46 cm in the wet column as an outlier (Table 5-5).

Table 5-4. Water retention parameters for the ‘dry’ and ‘wet’ monoliths at four depth. Values were adapted from Schmied (2001, cf. this thesis chapter 6).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol Units</th>
<th>Dry</th>
<th>Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6 cm</td>
<td>21 cm</td>
</tr>
<tr>
<td>Saturated water content</td>
<td>$\theta_s$</td>
<td>m$^3$ m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Boundary water content</td>
<td>$\theta_b$</td>
<td>m$^3$ m$^{-3}$</td>
<td>0.711</td>
</tr>
<tr>
<td>Boundary pressure head</td>
<td>$\psi_b$</td>
<td>cm</td>
<td>43.6</td>
</tr>
<tr>
<td>Pore size distribution index</td>
<td>$\alpha$</td>
<td></td>
<td>0.102</td>
</tr>
</tbody>
</table>

Table 5-5. Estimated net N mineralisation constants ($k$) in the ‘dry’ and ‘wet’ monolith during two incubation periods. Saturation is the mean water filled pore space in the soil and Temperature is the mean of all records during the corresponding incubation period.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Period</th>
<th>Duration (d$^{-1}$)</th>
<th>Depth (cm)</th>
<th>Saturation (%)</th>
<th>Temperature ($^\circ$C)</th>
<th>$k$ (10$^{-5}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>1</td>
<td>62</td>
<td>6</td>
<td>66</td>
<td>16.3</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>62</td>
<td>21</td>
<td>88</td>
<td>16.8</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>62</td>
<td>36</td>
<td>91</td>
<td>16.9</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>62</td>
<td>46</td>
<td>92</td>
<td>16.9</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16</td>
<td>6</td>
<td>74</td>
<td>19.1</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16</td>
<td>21</td>
<td>87</td>
<td>19.4</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16</td>
<td>36</td>
<td>89</td>
<td>19.5</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16</td>
<td>46</td>
<td>90</td>
<td>19.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Wet</td>
<td>1</td>
<td>46</td>
<td>6</td>
<td>83</td>
<td>16.3</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>46</td>
<td>21</td>
<td>89</td>
<td>16.8</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>46</td>
<td>36</td>
<td>96</td>
<td>16.9</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>46</td>
<td>46</td>
<td>97</td>
<td>16.9</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>32</td>
<td>6</td>
<td>88</td>
<td>19.1</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>32</td>
<td>21</td>
<td>92</td>
<td>19.4</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>32</td>
<td>36</td>
<td>98</td>
<td>19.5</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>32</td>
<td>46</td>
<td>99</td>
<td>19.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Analysis of variance did not reveal any significant differences between monoliths, incubation periods and depths with respect to \( k \). Insofar, at least, the response functions successfully accounted for the variations in soil moisture and temperature. Also the dynamics of net N mineralisation was reasonably well described by the model (Figure 5-3). The low value of \( k \) at depth 46 cm in WET during the second incubation (Table 5-5) was probably due to increased denitrification, since more than 99% of the pore volume at this depth was water saturated. Estimation of our moisture response function for such conditions, which were outside the calibration range, therefore should be considered as unsafe.

Figure 5-3. Measured (Meas) and simulated (Sim) net N mineralisation in the ‘dry’ and ‘wet’ monolith at four depths during two incubation periods.
In combination with the above moisture and temperature response functions we calculated annual net N mineralisation in the humus rich subsoil, that is 40-70 cm depth, under the *in situ* conditions from November 1995 through October 1996. Calculations were based on field measurements of water potential and soil temperature at 60 cm depth as well as average values for organic N content and bulk density (cf. Table 5-3) and gave an annual NNM rate of 40 kg N per hectare and decimetre soil. Since the humus rich layer of the field under study reached in about 15% of the sampling points to 50 cm and in about 2% of the sampling to 70 cm depth, we assumed an annual N release from the 40-70 cm layer of about 8 kg N ha\(^{-1}\) y\(^{-1}\) only.

### 5.3.3 In situ net N mineralisation

For the humus decomposition the reaction rate \(k\) (4.2 \(\times 10^{-5}\) d\(^{-1}\)) as calibrated in the monoliths was used. The unknown rate constant for litter decomposition \(k_l\) (0.07 d\(^{-1}\)) and the parameter \(q\) (8) were estimated by minimising the sum of squared differences between measured and simulated NNM of the six incubation periods. According to the simulations 345.7 kg N ha\(^{-1}\) were mineralised during the study period, whereof 52% derived from humus. Simulations closely matched the total amounts of N mineralised in the upper 40 cm of the profile measured (346.1 kg N ha\(^{-1}\)). While this was also true for the six incubation periods, measurements and simulations per 0-5, 5-20 and 20-40 cm depth differed considerably during partial periods (Figure 5-4).

For the incubation periods in spring and early summer the fitted model underestimated net N mineralisation at 0-5 cm depth and overestimated it at 5-20 cm depth. At 5-20 cm depth humus mineralisation alone almost corresponded to measured NNM and litter mineralisation seemed to be the reason for overestimation. Preferential allocation of the litter input to the upper 5 cm would result in a much better fit between simulations and measurements, but we could not find a rationale for this.

Since the labile organic material is highly dynamic in the field due to litter input from growing and senescent plants and manure, differences between the simulated and measured field NNM curves may have been due to soil litter dynamics not accounted by the model. In addition, short-time wetting-drying processes eventually leading to N flushes especially in the uppermost soil layer (Mary & Recous, 1994) were not included in the model.
Figure 5-4. Net N mineralisation measured *in situ* (mean ± standard error) and simulated from humus and litter during six periods between 9 October 1995 and 8 November 1996.
A third source of error may lie in the sequential in situ coring method itself. Considering that estimates of net N mineralisation are based on measurements of soil mineral N, the NNM rates in the surface layer may be masked by nitrate import due to upward movement of capillary water. Especially during the growing season the evaporating water at the soil surface may have led to nitrate accumulation, while the droughty soils may have inhibited redistribution by diffusion. However, the inadequate modelling of N dynamics in the topsoil would probably improve if upward nitrate transport and more differentiation of fast decomposing organic matter pools and factors affecting decomposition rates in the surface layer was included in the model.

At 20-40 cm depth the one-pool model, that is humus decomposition, explained the amount and temporal patterns of in situ NNM reasonably well. Thus, decay of litter affected total NNM rates only marginally, whereas net N mineralisation in the upper two layers was almost entirely governed by this process. Overestimation of NNM, especially during period 4, may have been due to N immobilisation driven by carbon-rich root turnover and exudation from the sugarbeet roots, a process that was not considered properly by the overall NNM-rate used here.

5.4 Conclusions

The net N mineralisation rates estimated from ex situ incubations of undisturbed subsoil cores or monoliths were, after correction for moisture and temperature, able to describe NNM measured below the plough layer in situ. This result suggests, that N turnover in 20-40 cm depth was dominated by humus decomposition. Partitioning the organic matter conceptionally into two separate pools, that is a fast decomposing “litter” and a slowly decomposing “humus” pool, fitted the overall NNM (0-40 cm depth, six incubation periods) also fairly well. But simulations did not honour the dynamics of litter turnover in the topsoil. This may be due to an experimental artefact of the sequential in situ coring technique: Upward moving capillary water may evaporate at the soil surface leading to nitrate accumulation in the uppermost soil layer and, thus, an augmentation of the mineral N pool originating from local mineralisation. Therefore, the inadequate modelling of N turnover processes in the topsoil may be improved by the inclusion of upward N transport. In addition, more differentiation of fast decomposing organic matter pools and factors affecting decomposition rates in the surface layer may be needed.

Net N mineralisation in the field was higher than that usually reported for mineral soils under similar climatic conditions (e.g. Hoffmann et al., 1996) but lower than reported for drained and intensively used wetlands (Okruzko, 1989; Wild & Pfadenhauer, 1997).
This seems to be reasonable since the soil investigated here is in transition, from a wetland to a mineral soil. Correspondingly, contribution of the "fossile" organic matter in the subsoil to the mobile N pool was of minor importance because there were only few places where the organic soil still reaches about 100 cm depth.

We conclude, that overall net N mineralisation of soil organic matter in the main root layer \textit{in situ} and its dependence on soil moisture can be estimated from undisturbed soil cores incubated \textit{ex situ}. The simple one-pool (humus) model approach could describe temporal NNM dynamics reasonably well in layers where the N turnover processes are not predominated by litter decomposition.

5.5 Acknowledgements

Many thanks to the involved co-workers of the Swiss Federal Institute of Technology in Zürich, especially to Martin Keller (equipment), Anna Grünwald (analysis) and Emir Sokolovic (assistance) of Institute of Terrestrial Ecology and Elisabeth Mayer (analysis) of the Institute of Plant Science.

5.6 References


Multiple Tracer Transport through Undisturbed Soil Columns under Different Initial Moisture Conditions and Application Modes

B. T. Schmied, K.C. Abbaspour, T. Kätterer and R. Schulin
Prepared for publication in Journal of Contaminant Hydrology

Abstract

Leaching of nitrate and other soluble chemicals from agricultural soils is an important water protection problem. In this study we tested the hypothesis that the leaching characteristics may strongly depend on the way solutes are applied to the soil, in particular in dry soils. Two leaching experiments were conducted with one monolith being initially wet, the other dry, when infiltration started and three mobile tracers being applied, each in a different way, that is by the infiltrating water (deuterium, D), placed on the soil surface (bromide, Br), and injected in the soil matrix at 5 cm depth (chloride, Cl).

The water content in the ‘WET’ column rapidly equilibrated to stable values, reflecting steady-state conditions. In the ‘DRY’ column moisture distribution was still far from equilibrium conditions long after the infiltration front had reached the bottom of the column.

The elution curves of the tracers were also influenced by initial moisture status, in particular for Cl. Apparently, a large fraction of the tracer had been bypassed in the initial phase of infiltration in ‘DRY’, indicating a higher degree of flow through preferential paths. The early breakthrough of D and Br combined with a tailing at later stages is typical of transport with incomplete mixing or local non-equilibrium between pore domains of different mobility.

Elution curves for the ‘WET’ column were well described by the convection-dispersion equation (CDE) although flow conditions were transient at the beginning. For the ‘DRY’ column, however, neither the CDE, nor the two-region model, which both assume steady-state flow, adequately described the experimentally observed leaching characteristics of chloride.
6.1 Introduction

Drained humic soils are at the forefront of conflicts between intensive agricultural land use and protection of water resources. Increasing the rates of water removal and decreasing the level of water tables, drainage systems promote soil aeration and development of macro-porosity by formation of cracks and biopores, such as root and earthworm channels. While these processes are desirable from the viewpoint of agriculture, as they improve growth conditions for crops, they also intensify mineralisation of organic matter previously accumulated under anaerobic conditions of water-logging and provide channels for preferential water flow and solute transport through the root zone. Consequently, artificial drainage and intensive cultivation of these soils carries the heightened risk that large amounts of agrochemicals are transferred from the fields to surface water bodies by-passing the filter and retention capacity of the soil matrix (e.g. Addiscott et al., 2000; Gentry et al., 2000; Kamra et al., 1999; Stamm et al., 1998). In this context, nitrate is a water pollutant of particular concern due to its high mobility, large turnover rates and intensive use as fertiliser. The study presented here was motivated by recent observations in the Furttal valley in Switzerland where substantial nitrate losses via drainage systems were found not only during the non-growing season, but contrary to the widely accepted opinion also during the growing season.

The basin of the Furttal valley north of Zürich is dominated by drained humic gley soils, which are under intensive, arable or vegetable production. The former wetland was reclaimed and brought under cultivation between 1920 and 1930. Nitrate concentrations in the valley's creek, which is the main drainage route of the valley, regularly exceeds the Swiss quality standard of 5.65 mg NO$_3$-N l$^{-1}$ (Kupper, 1991). Estimations showed that about 45% of the nitrogen load in the creek originates from the non-point sources, such as the outflow from the field drains. For certain drainage discharge events in July and August 1992, very high nitrate concentrations in the drain effluent were measured. These measurements led to the hypothesis that mineralisation of organic matter may be the major source of nitrate export during the cropping period, and that leaching of nitrate occurs mostly through preferential paths.

In recent years several tracer experiments were designed to study the movement of water through preferential paths. Many of these studies investigated the role of natural soil structure in general (e.g. Chen et al., 1999; Gupta et al., 1999; Wojick et al., 1998), or specific structural features such as clay pans (Wilkinson and Blevins, 1999) and macropores (Ghodrati et al., 1999; Iqbal, 1999) for triggering and occurrence of preferential flow. Some authors also looked into effects of agricultural practices on the formation of macropores conducting preferential flow, for instance, tillage (Ogden et
Multiple Tracer Transport through Undisturbed Soil Columns

al., 1999; Turpin et al., 1998; Kamau et al., 1996) and crop rotation (Iragavarapu et al., 1998; Kamau et al., 1996). Others focused on the role of variables, such as initial water content and rainfall intensity (e.g. McIntosch et al., 1999; Shipitalo and Edwards, 1996; Flury et al., 1994, Edwards et al., 1993), and water-repellency of the soil material (van Dam et al. 1990, Dekker and Ritsema, 1994). The above works were mostly based on the surface-applied tracers, and only few studies investigated the influence of the method of tracer application on the transport processes. For instance, Kamau et al. (1996) studied the effect of ponding versus spraying on the solute transport. Recently, Waddell et al. (2000) compared different irrigation-fertilisation methods in-situ by varying the kind of N fertilisers, which were applied differently (spread on the surface, incorporated into the plough layer, dripped into the root zone), and irrigation treatments (sprinkling, drip placement at the surface and in 25 cm depth). Unfortunately, the varying amount of infiltrated water between the irrigation treatments masks the effects of application method. To our knowledge no investigations were done to study temporal patterns of solute throughput in the outflow of surface-applied materials and chemicals initially present within the soil profile, that is soil-born solutes such as mineralised nitrate or heavy metals resulting from weathering.

Using a multiple tracer experiment under controlled laboratory conditions, our objective was in particular to study the influence of solute exposure to infiltrating water, that is tracer application mode, and initial soil moisture on the travel time distribution of the solutes. Two leaching experiments were conducted in undisturbed soil monoliths from the Furttal Valley with three mobile tracers and initially wet and dry moisture conditions. Elution curves were recorded simultaneously for deuterium (D), bromide (Br) and chloride (Cl), which were applied in different ways, that is dissolved in the sprinkling solution (D), spread over the soil surface (Br) or injected below the surface (Cl). In this paper we present the experimental results and show that the elution curves of all three tracers are well described by the classical convection-dispersion equation (CDE) under the initially wet conditions, in agreement with Wieringa (1977), whereas simple steady-flow models failed to account for under the initially dry conditions. In another paper (Kätterer et al., 2001) we analyse these curves in terms of more complex transport models accounting for transient conditions also studied the solute elution curves using two different simulation models where transient conditions as well as macropore flow.
6.2 Materials and Methods

6.2.1 Experimental set-up

Two undisturbed soil monoliths were excavated from a depth of 28 to 80 cm in an artificially drained, arable field in the Furttal valley. The samples were encased in steel cylinders (height 52 cm, basal area 487 cm²) and transported to the laboratory. The experimental site was drained and reclaimed in the 1920s, since when the thickness of the hums-rich topsoil has decreased to about 40 cm in average, though in some places there is still a 100-cm organic-rich layer. The soil columns were taken in one of these lenses to study mineralisation of the soil organic matter, initially assuming a relatively homogeneous soil profile for this depth. Data on soil properties of the field and the two monoliths are given in Table 6-1 and 6-2.

Table 6-1. Characteristic soil properties measured in the field in August 1997 at 28-80 cm depth, that is the depth where the soil monoliths were taken from.

<table>
<thead>
<tr>
<th>Depth [cm]</th>
<th>pH</th>
<th>Clay [%]</th>
<th>Silt [%]</th>
<th>Sand [%]</th>
<th>Class</th>
<th>Bulk density [g cm⁻³]</th>
<th>Porosity [%]</th>
<th>Organic C [g 100g⁻¹ dry soil]</th>
<th>Total N [g 100g⁻¹ dry soil]</th>
<th>C/N #</th>
</tr>
</thead>
<tbody>
<tr>
<td>28-38</td>
<td>7.0</td>
<td>30</td>
<td>46</td>
<td>24</td>
<td>c. loam</td>
<td>0.69</td>
<td>0.69</td>
<td>16.1</td>
<td>1.1</td>
<td>15</td>
</tr>
<tr>
<td>38-48</td>
<td>7.3</td>
<td>12</td>
<td>53</td>
<td>34</td>
<td>s. loam</td>
<td>0.78</td>
<td>0.69</td>
<td>6.8</td>
<td>0.9</td>
<td>8</td>
</tr>
<tr>
<td>48-58</td>
<td>7.3</td>
<td>12</td>
<td>54</td>
<td>34</td>
<td>s. loam</td>
<td>0.72</td>
<td>0.71</td>
<td>6.7</td>
<td>0.8</td>
<td>8</td>
</tr>
<tr>
<td>58-68</td>
<td>7.1</td>
<td>12</td>
<td>49</td>
<td>39</td>
<td>loam</td>
<td>0.47</td>
<td>0.81</td>
<td>6.6</td>
<td>1.2</td>
<td>6</td>
</tr>
<tr>
<td>68-78</td>
<td>6.9</td>
<td>24</td>
<td>54</td>
<td>22</td>
<td>s. loam</td>
<td>0.40</td>
<td>0.80</td>
<td>20.8</td>
<td>1.0</td>
<td>21</td>
</tr>
</tbody>
</table>

† Texture class according to SSSA (1998) with c. = clay, s. = silt
‡ Porosity = 1–ρs/ρb, where ρs is bulk density and ρb is solid density (=2.4 g cm⁻³);
# C/N = C/N ratio of organic matter.

Table 6-2. Bulk density and total C and N pools in the soil monoliths measured at the end of the experiment in April 1999. Mean values, coefficients of variation (CV, %), C/N-ratios are based on two to four replicates per depth.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth [cm]</th>
<th>Bulk density [g cm⁻³]</th>
<th>Porosity [cm³ cm⁻³]</th>
<th>Total C [g 100g⁻¹ dry soil]</th>
<th>Total N [g 100g⁻¹ dry soil]</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry monolith</td>
<td>0-13</td>
<td>0.62 ± 8</td>
<td>0.74 ± 3</td>
<td>17.8 ± 36</td>
<td>1.19 ± 31</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>13-26</td>
<td>0.58 ± 6</td>
<td>0.77 ± 2</td>
<td>14.7 ± 5</td>
<td>0.97 ± 2</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>26-39</td>
<td>0.57 ± 9</td>
<td>0.78 ± 2</td>
<td>13.6 ± 7</td>
<td>0.79 ± 9</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>39-52</td>
<td>0.39 ± 2</td>
<td>0.82 ± 0</td>
<td>18.1 ± 7</td>
<td>1.05 ± 6</td>
<td>17</td>
</tr>
<tr>
<td>Wet monolith</td>
<td>0-13</td>
<td>0.53 ± 2</td>
<td>0.77 ± 1</td>
<td>14.6 ± 4</td>
<td>0.95 ± 4</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>13-26</td>
<td>0.66 ± 10</td>
<td>0.74 ± 4</td>
<td>13.9 ± 5</td>
<td>0.82 ± 1</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>26-39</td>
<td>0.50 ± 8</td>
<td>0.80 ± 2</td>
<td>15.0 ± 112</td>
<td>0.83 ± 10</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>39-52</td>
<td>0.39 ± 2</td>
<td>0.82 ± 2</td>
<td>22.0 ± 7</td>
<td>1.32 ± 11</td>
<td>17</td>
</tr>
</tbody>
</table>
To measure soil water content, water tension and temperature two TDR probes, two tensiometers, and one thermocouple were installed horizontally in the columns at depths of 6, 21, 36 and 46 cm and connected to a data logger as illustrated in Figure 6-1. Irrigation occurred through a rotating sprinkler head installed above the top of each column. At the bottom, the columns were held by a tension plate, which was connected to a hanging water column. Electrical conductivity of the discharge was monitored online by an electrode installed in the outflow section and connected to a data logger.

Figure 6-1. Experimental set-up of the soil columns and instrumentation per measurement level. Size dimensions are in mm.

6.2.2 Soil water regime

After instrumentation, the water table was raised slowly from below to saturate the soil columns over a three-day period using de-ionised water containing 0.005 g l⁻¹ CaCO₃. The TDR and tensiometer measurements were simultaneously collected during this wetting and the later drying period (that is incubation, see below) in 10-30 minutes.
Chapter 6

intervals. The respective water retention curves for the two soil columns were determined by curve fitting using the Brooks and Corey (1964) formulation as modified for low tensions by Jarvis (1994):

\[
\psi(e) = \begin{cases} 
\psi_b \left( \frac{\theta_s - \theta}{\theta_s - \theta_h} \right)^{1/\lambda} & \psi_h < \psi \leq \psi_s \\
\psi_b \left( \frac{\theta - \theta_r}{\theta_h - \theta_r} \right)^{1/\lambda} & \psi_r < \psi \leq \psi_h 
\end{cases}
\]  
(Eq. 6-1)

where \( \theta \) is the water content (cm\(^3\) cm\(^{-3}\)), \( \psi \) is the water tension (cm), \( \lambda \) is the pore size distribution index, \( \theta_r \) is the residual water content (cm\(^3\) cm\(^{-3}\)), \( \theta_s \) is the saturated water content (cm\(^3\) cm\(^{-3}\)), \( \psi_b \) is the water tension at the boundary between the soil matrix and macropores, and \( \psi_h \) is the water content (cm\(^3\) cm\(^{-3}\)) corresponding to \( \psi_h \).

The effective saturated hydraulic conductivity, \( K_s \), was estimated by measuring discharge under constant head conditions at the soil surface (2-cm ponding water).

After obtaining the water retention curves, several pore volumes of water were percolated through each soil column until the salt concentration in the soil solution was negligible. Prior to the tracer experiments the columns were incubated for 4-8 weeks at room temperature to start off two treatments, that is, to establish different initial soil moisture conditions. One column (further referred to as WET) was covered with a disc during incubation to prevent evaporative water losses from the surface, whereas the other column (DRY) was left uncovered. A constant suction was applied by means of a hanging water column during incubation at the bottom of the WET (10 hPa) and the DRY (70 hPa) column. Although the cover on WEI was not gas-tight, it was removed every two to three days for about one hour to allow gas exchange to take place with the room atmosphere. During incubation, nitrogen mineralisation was monitored by taking samples of soil solution from the tensiometer ports and analysing them for nitrate as described elsewhere (Schmied et al., 2001; cf. Chapter 5 of this thesis).

6.2.3 Tracer elution curves

One hour before starting the irrigation, we injected a total of 10 ml of highly concentrated CaCl\(_2\) solution (16.3 g Cl m\(^{-2}\)) through 84 evenly distributed syringes at a depth of 5 cm into the soil. Then thirty minutes before irrigation started, bromide was evenly spread over the soil surface as solid CaBr\(_2\) (6.3 g Br m\(^{-2}\)). The third tracer, deuterium water, was continuously applied at a concentration of about 0.04% with the irrigation water.
Irrigation was maintained with constant pumping rates for 54 hours at intensities of about 17 mm h\(^{-1}\) (WET) and 19 mm h\(^{-1}\) (DRY). During this time water content, water tension, and discharge conductivity were measured every ten minutes, and soil solution was sampled from the tensiometers (two replicates at four depths) at 2, 9, 18, 36 and 54 hours after the start of the irrigation. Then infiltration was stopped after changes in the electrical conductivity of the discharge were approximately zero. To account for the varying infiltration rates \(q_{in}\) and the transient conditions, results were plotted against dimensionless time \(T (T = vt/L)\) representing pore volumes (PV), where \(L\) is the length of the monolith, \(t\) is time and pore-water velocity \(v\) was defined as the ratio of infiltration to water content in the soil column measured during the leaching experiment, that is \(v = q_{in}/\theta\).

The concentrations of chloride, bromide, nitrate and sulfate in the discharge water and in the extracts from the tensiometers were determined by ion chromatography (DX-100, Dionex, Olten, Switzerland). For deuterium analysis 0.5 µl of sample solution were injected into a chromium reactor at 850 °C yielding hydrogen gas (H/Device, Finnigan, Bremen, Germany). The D/H isotope ratio of the sample \(R_{sa}\) was determined with an isotope-ratio mass-spectrometer (delta S, Finnigan, Bremen, Germany) and reported in a \(\delta_{sa}\) notation, that is the per mille deviations of the sample from a standard (V-SMOW) with an isotope ratio \(R^1\) of 1.557x10\(^{-4}\)

\[
R_{sa} = R^1 \left( \frac{\delta_{sa}}{1000} + 1 \right) \quad \text{(Eq. 6-2)}
\]

D concentration is reported as mass density

\[
c_D = R_D \left( \frac{R_{sa}}{R_{soil} + 1} \right) \quad \text{(Eq. 6-3)}
\]

where \(R_D\) is the mass density of D in pure deuterium water (0.22 g cm\(^{-3}\)). To account for the deuterium and chloride in the background water the concentration \(c\) was evaluated as

\[
c = c_{dis} - \frac{q_{soil}}{q_{dis}} c_0 \quad \text{(Eq. 6-4)}
\]

where \(c_{dis}\) is the measured concentration in the discharge \(q_{dis}\), and \(c_0\) is the average residual concentration measured at 6, 21, 36, and 46 cm depth before irrigation started. The ratio \(q_{soil}/q_{dis}\) is the proportion of original soil water in the discharge calculated as
\[ \frac{q_{\text{soil}}}{q_{\text{dis}}} = 1 - \frac{R_{\text{dis}} - R_{\text{soil}}}{R_{\text{pr}} - R_{\text{soil}}} \]  
(Eq. 6-5)

with \( R \) representing the isotopic ratio in the discharge \( (R_{\text{dis}}) \), the original soil water \( (R_{\text{soil}}) \) and the irrigation water \( (R_{\text{pr}} = 3.850 \times 10^{-4}) \).

### 6.2.4 Physical and chemical analysis

After the breakthrough experiment, both columns were sampled destructively by coring the entire profile to obtain total C, N and S, residual chloride and bromide, and dry bulk density. Samples for chemical analysis were taken from the two vertical sections with previous TDR installations about 2 cm from the columns' outer boundary. After drying at 105 °C for 24 hours total C, N and S were determined in ground subsamples using a CHNS-Analyser (CHNS-932, Leco Instrument GmbH, Kirchheim, Germany). Residual Cl and Br were analysed in water extracts using ion chromatography (DX-100, Dionex, Olten, Switzerland). Dry bulk density was determined from 100-ml soil cores collected with steel cylinders from the two sections where the tensiometers had been installed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Wetting conditions</th>
<th>Drying conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>21</td>
</tr>
<tr>
<td>Saturated water content</td>
<td>( \theta_s )</td>
<td>m³ m⁻³</td>
<td>0.634</td>
<td>0.702</td>
</tr>
<tr>
<td>Boundary water content</td>
<td>( \theta_b )</td>
<td>m³ m⁻³</td>
<td>0.541</td>
<td>0.636</td>
</tr>
<tr>
<td>Boundary pressure head</td>
<td>( \psi_b )</td>
<td>hPa</td>
<td>9.62</td>
<td>19.9</td>
</tr>
<tr>
<td>Pore size distribution index</td>
<td>( \lambda )</td>
<td>-</td>
<td>0.024</td>
<td>0.014</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Wetting conditions</th>
<th>Drying conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>21</td>
</tr>
<tr>
<td>Saturated water content</td>
<td>( \theta_s )</td>
<td>m³ m⁻³</td>
<td>0.711</td>
<td>0.700</td>
</tr>
<tr>
<td>Boundary water content</td>
<td>( \theta_b )</td>
<td>m³ m⁻³</td>
<td>0.616</td>
<td>0.647</td>
</tr>
<tr>
<td>Boundary pressure head</td>
<td>( \psi_b )</td>
<td>hPa</td>
<td>4.57</td>
<td>15.2</td>
</tr>
<tr>
<td>Pore size distribution index</td>
<td>( \lambda )</td>
<td>-</td>
<td>0.042</td>
<td>0.015</td>
</tr>
</tbody>
</table>

\( \dagger \) Boundary water content was fitted during wetting and assumed to be constant during drying conditions.
6.3 Results and discussion

6.3.1 Soil water regime

The water retention curves were determined from the simultaneous measurements of pressure head and water content recorded during initial wetting and drying cycles prior to the transport experiments. Saturated water content \( \theta_s \), boundary water content \( \theta_b \) and boundary pressure head \( \psi_b \) all tended to increase slightly with depth (Figure 6-2 and Table 6-3), as bulk density \( p_b \) tended to decrease (Table 6-2). Only small differences were, however, found between the two columns. Average porosity was 0.78 for the WET and 0.77 for the DRY column, and the effective saturated hydraulic conductivity \( K_s \) was 810 cm d\(^{-1}\) for the WET and 800 cm d\(^{-1}\) for the DRY soil monolith.

Figure 6-3 shows that the water content in the initially wet column rapidly attained steady-state equilibrium, that is, after only 7% of a pore volume (0.07PV) after infiltration started. Almost no change was observed at the lowest monitoring depth in response to the infiltration, while water contents at 6, 21 and 36 cm depths increased by 0.083, 0.045 and 0.038 (cm\(^3\) cm\(^{-3}\)), respectively. Outflow started to increase after infiltration of 0.065PV, at the same time when the water content at 36 cm depth indicated steady-state. During the experiment, total water content increased by 6.9% of the initial soil water content.

The initially dry column showed similar, but as expected larger changes in water content, which also required more time. Total changes of the water content in the uppermost monitoring depth were about 73% of the initial soil water, whereas the deeper soil layers increased by 14-16%. In contrast to the initially wet column, the water contents in the upper two monitoring depths reacted faster, but with steadily decreasing rate. The latter may be due water repellence of the dry soil surface, which was deduced from the formation of droplets observed at the beginning of the infiltration, limiting infiltration in the upper soil layer. While at 36 and 46 cm depth steady-state equilibrium was reached after 0.10PV and 0.13PV, the water content of the uppermost layer continued to increase very slowly until the end of the experiment. Outflow started to increase at 0.10PV, that is at the same time as the water content at 36 cm depth reached a steady-state condition, but clearly before the bottom layer was saturated. These data show that the infiltrating solution was rapidly transferred deep into the DRY column and that moisture distribution was still far from equilibrium conditions long after the infiltration front had reached the bottom of the column. These are clear signs of preferential flow.
Figure 6-2. Measured (symbols) and estimated (lines) soil water retention characteristics functions at four depths in the initially WET and DRY column. Black symbols and solid lines refer to wetting conditions, open symbols and dotted lines to drying conditions. The curves were determined from pressure head and water content data using the modified Brooks and Corey (1964) function. The respective parameters for each monolith and depth are presented in Table 6-3.
Multiple Tracer Transport through Undisturbed Soil Columns

Figure 6-3. Measured water content per depth versus dimensionless time in the initially WET and DRY column. The graphs at the bottom represent blow-ups of water content curves during the first 0.15PV.
6.3.2 Tracer elution curves

Figure 6-4 compares the normalised tracer concentrations in the discharge for the two columns. The normalised values of D breakthrough curves refer to the input concentration of D in the irrigation water \(c/c_0\); Br and Cl elution curves were normalised by scaling the area below the curve to a value of 1. Graphs show that the initial wetness influenced the concentration response curves of the solutes, in particular for chloride, which had been injected below the surface. Elution of Cl from the initially dry column was slower and more spread over time than from the initially wet column. Obviously a much larger fraction of the tracer had been bypassed in the initial phase of infiltration in the DRY column, indicating a higher degree of flow through preferential pathways. The elution of the other two tracers, which were applied with the infiltrating water or directly spread onto the soil surface, was more rapid at the beginning, but slower at the end. The early breakthrough combined with a tailing at later stages is typical for transport with incomplete mixing or local non-equilibrium between pore domains of different mobility.

Non-equilibrium transport in the DRY column was also indicated by the relative position of the inflection-points of the tracer elution curves. The inflection-point of the D breakthrough curve occurred clearly earlier in the DRY (0.632PV) than in the WET column (0.991PV). Despite their very different application modes the concentration response curves of Cl and Br from the initially wet column yielded almost identical shapes of the travel time curves and were also similar to bromide breakthrough in DRY. But the maximum concentrations in WET were observed at 0.721PV for Cl and 0.775PV for Br, that is later than the peak of Br curve in DRY which occurred at 0.607PV.

The normalised elution curves of chloride and bromide may be interpreted as the travel time distribution for an initial unit mass pulse applied at the surface for Br and at 5 cm depth below the column surface for Cl, whereas the normalised deuterium curves correspond to cumulative distributions. The mean travel time of surface applied tracers Br and D was smaller in DRY than in WET reflecting faster transport, whereas the large mean travel time of chloride in DRY was due to its location within zones which were by-passed by water flow, at least in the beginning of water infiltration (in Figure 6-4 given in brackets).
Figure 6-4. Solute concentration response for deuterium (D), bromide (Br) and chloride (Cl) in the WET and DRY soil column normalised as relative concentration C/C₀ (unit input concentration C₀) for D and scaled area below the curve to a value of 1 (unit area) for Cl and Br. The mean travel time of the solutes are given in brackets.
6.3.3 Direct comparison of travel time distributions

In contrast to bromide and chloride, deuterium was applied continuously and not as a point input. To compare Br and Cl with D elution curves, therefore, we integrated the curves. For comparison of the resulting cumulative travel time distributions we used Q-Q-plots, in which each point represents a certain quantile of eluted solute relative to the total amount of solute applied. Its co-ordinates are the times (that is pore volumes) at which this quantile has been eluted for the two solutes compared. A straight line means that the time required to elute same quantiles of solute mass were proportional. For conservative tracers with linear sorption, the slope of the Q-Q-plot then would represent the ratio between their retardation factors.

An almost perfectly straight line resulted from the comparison of bromide and chloride elution from the initially wet column, except for the last part of the curve which represents the quantiles close to complete elution (Figure 6-5, left). Due to the long tailing of the elution curves the Q-Q-plots become very sensitive to uncertainties in the mass balance (Table 6-4) in this last part. Thus, deviations from linearity of the last few points of the Q-Q-plots should not be overinterpreted. Considering this, all three solutes display more or less similar shapes of their cumulative travel time distribution in the initially wet column, despite of the different application modes.

Table 6-4. Mass balances for water and solutes.

<table>
<thead>
<tr>
<th></th>
<th>Water [mm]</th>
<th>Deuterium [g D m⁻²]</th>
<th>Bromide [g Br m⁻²]</th>
<th>Chloride [g Cl m⁻²]</th>
<th>Nitrate [g N m⁻²]</th>
<th>Sulfate [g S m⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>COLUMN</td>
<td>WET  DRY</td>
<td>WET  DRY</td>
<td>WET  DRY</td>
<td>WET  DRY</td>
<td>WET  DRY</td>
<td>WET  DRY</td>
</tr>
<tr>
<td>Input</td>
<td>917 1063</td>
<td>76.82 90.05</td>
<td>6.32 4.93</td>
<td>16.28 16.28</td>
<td>0.00 0.00</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>Output</td>
<td>876 995</td>
<td>54.53 64.19</td>
<td>5.62 4.97</td>
<td>16.85 17.82</td>
<td>15.71 31.73</td>
<td>5.58 10.72</td>
</tr>
<tr>
<td>Initial</td>
<td>336 291</td>
<td>10.55 9.23</td>
<td>0.00 0.00</td>
<td>0.24 0.29</td>
<td>16.98 26.59</td>
<td>5.36 9.78</td>
</tr>
<tr>
<td>End</td>
<td>359 362</td>
<td>30.02 30.63</td>
<td>0.13 0.20</td>
<td>0.70 0.87</td>
<td>0.18 0.39</td>
<td>0.23 0.60</td>
</tr>
<tr>
<td>Balance</td>
<td>18 -3</td>
<td>2.82 4.46</td>
<td>0.57 -0.24</td>
<td>-1.03 -2.12</td>
<td>1.09 -5.53</td>
<td>-0.45 -1.54</td>
</tr>
<tr>
<td>(in %)†</td>
<td>(2%) (0%)</td>
<td>(4%) (5%)</td>
<td>(9%) (-5%)</td>
<td>(-6%) (-13%)</td>
<td>(6%) (-21%)</td>
<td>(-8%) (-16%)</td>
</tr>
</tbody>
</table>

† Balance = Input + Initial pool – Output – End pool; in brackets given in % of input respectively initial pool.
Multiple Tracer Transport through Undisturbed Soil Columns

Initially WET column

Initially DRY column

Bromide - Chloride

Relative time Br [-]

Relative time Cl [-]

y = 0.938x

Bromide - Deuterium

Relative time Br [-]

Relative time D [-]

y = 0.841x

Chloride - Deuterium

Relative time Cl [-]

Relative time D [-]

y = 0.824x

y = 1.198x

Figure 6-5. Q-Q-plots. Pair wise comparison of tracer distribution in the WET and DRY monolith.
In the initially dry column bromide showed a rather different behaviour compared to chloride (Figure 6-5, right). Interestingly, chloride and deuterium gave an almost perfectly linear Q-Q-plot for the initially dry column. However, chloride was retarded by a factor of about 1.2 in this column, whereas it was eluted much faster than deuterium under initially wet conditions. On the other hand, retardation of deuterium relative to bromide as well as the shapes of their Q-Q-relationships were almost the same under both conditions.

These results indicate that transport conditions changed drastically in the early stage of the elution experiment when the wetting front moved down through the DRY column. Whereas the elution curve of deuterium that was applied continuously represents an average over all phases of the experiment, all of the bromide was exposed to the initial conditions at the soil surface and, thus, subjected to at least some degree of water-repellence according to our visual inspection. The retardation of chloride elution indicates that infiltration was initially channelled along few preferential pathways, bypassing most of the chloride residing in the soil matrix below the surface. This behaviour fits well to the two-phase wetting kinetics observed with the TDR probes (cf. Figure 6-3).

While we cannot rule out that the transient conditions at the beginning of the infiltration in the WET column may have caused some effects on transport similar as in the initially dry column, such effects did not show up in the resulting elution curves and would, thus, have been negligible. Faster elution of bromide and chloride in comparison to deuterium was to be expected due to effects of anion exclusion and slight sorption of deuterium as well as initial location of the tracer.

### 6.3.4 Parameterization by a steady-flow transport model

Following Wieringa (1977) we tried to describe, parametrize and compare the observed elution curves in terms of steady-flow transport models for the sake of parsimony, starting with the classical convection-dispersion equation (CDE). The CDE for a linearly sorbing tracer in equilibrium in normalised form is given as

\[
R \frac{\partial C}{\partial T} = \frac{1}{P} \frac{\partial^3 C}{\partial Z^3} - \frac{\partial C}{\partial Z} \quad \text{(Eq. 6-6)}
\]

where \( C \) is the relative concentration \((c/c_0)\), \( c \) is the actual concentration, \( c_0 \) is the concentration in the tracer pulse or step, \( Z \) represents the dimensionless spatial co-ordinate \((z/L)\), \( L \) is the length of the column, and \( T \) refers to the dimensionless time \((vt/L)\). This model is based on the assumption of complete local mixing/equilibrium leading to a Fickian type of dispersion \( D \) which is accounted for by the dimensionless Peclet number.
$P (vL/D)$. The constant retardation factor $R$ is the only other parameter. It accounts for linear adsorption, including "negative adsorption" due to, for instance, the repulsion of anions from negatively charged soil sites (anion exclusion) or hydrophobia.

Estimation of transport parameters was achieved by using the inverse modelling option of the CXTFIT equilibrium code (Tonde et al., 1995). The initial concentrations of the solutes within the profile were calculated by assuming the tracer masses being dissolved in the original soil water at 0-0.1 cm depth (Br) and 4.75-5.25 cm depth (Cl). Similarly, initial values for nitrate and sulfate concentrations (see below) were distributed stepwise according to measurements at 6, 21, 36, and 46 cm depth. The inlet condition for D was given as step input. The only parameter accounting for boundary conditions was pore velocity $v$, which was set to 2.613 mm h$^{-1}$ (WET) and 3.037 mm h$^{-1}$ (DRY) according to the average ratio of infiltration to water content in the soil monolith.

We proceeded by first fitting the deuterium breakthrough curve, that is, the Peclet number $P$ and retardation coefficient $R$ for both columns. Then, the bromide and chloride elution curves were simulated, fixing $P$ to the values found for deuterium and fitting $R$ separately for bromide and chloride. In a second modelling effort we estimated both the Peclet number and the retardation factor simultaneously to test if including a second parameter would improve the results for Br and Cl.

Simulated breakthrough curves of D agreed very well ($r^2=0.998$) with the measurements for both columns (Figure 6-6). Similar $R$ values were obtained, whereas the dispersion coefficients ($=vL/P$) represented by $P$ in Table 6-5 differed significantly. The smaller Peclet number in the DRY soil column agrees with the findings of Maciejewsky (1993) and Fesch et al. (1998) insofar, that hydrodynamic dispersion increases with decreasing water content.

For the WET column the fits of Br and Cl elution curves improved, when both $P$ and $R$ were fitted. The $P$-values obtained were smaller than that for D which can be attributed to some initial dispersal of the two anions in the soil. In the DRY column fitting of both transport parameters slightly improved the mass balance, while the correlation between simulated and measured values thereby decreased.
Figure 6-6. Measured (symbols) and calculated (lines) tracer elution curves in the initially WET and DRY soil monoliths based on CXTFIT-estimated transport parameters with the equilibrium (1-region) and the non-equilibrium (2-region) CDE model. Dotted lines refer to the 1-region model; solid lines to the 2-region model (Toride et al., 1995). The fitted model parameters were listed in brackets.
For bromide we obtained similar $R$-values for the WET and the DRY column being smaller than 1 due to anion exclusion (Table 6-5). For chloride $R$ in the WET column was comparable to the bromide retardation coefficients. To describe the long tailing of the chloride elution curve in the DRY column the model required almost twice as large $R$-values than for the initially wet column. This reflects that the chloride was at least initially by-passed by the infiltrating water. Apart from this, however, all the fitted retardation coefficients were in the range of respective values reported in the literature (e.g. Schulin et al., 1987).

Table 6-5. CXTFIT: Initial and fitted parameters for equilibrium and non-equilibrium CDE models. †

<table>
<thead>
<tr>
<th>Model</th>
<th>Symbol</th>
<th>WET</th>
<th>DRY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Initial concentration (mg cm⁻³)</td>
<td>$C$</td>
<td>0.0</td>
<td>11.7</td>
</tr>
<tr>
<td>- Initial tracer location</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of Br and Cl (cm)</td>
<td>$v$</td>
<td>2.61</td>
<td>2.61</td>
</tr>
<tr>
<td>Mean pore velocity (cm h⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Retardation coefficient (-)</td>
<td>$R$</td>
<td>1.057</td>
<td>0.838</td>
</tr>
<tr>
<td>=&gt; Regression coefficient $r^2$</td>
<td></td>
<td>0.998</td>
<td>0.899</td>
</tr>
<tr>
<td>Non-equilibrium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Retardation coefficient (-)</td>
<td>$R$</td>
<td>1.197</td>
<td>0.787</td>
</tr>
<tr>
<td>- Partitioning coefficient (-)</td>
<td>$\beta$</td>
<td>0.997</td>
<td>0.182</td>
</tr>
<tr>
<td>- Mass transfer coefficient (-)</td>
<td>$\omega$</td>
<td>0.000</td>
<td>6.148</td>
</tr>
<tr>
<td>=&gt; Regression coefficient $r^2$</td>
<td></td>
<td>0.997</td>
<td>0.993</td>
</tr>
</tbody>
</table>

† fixed according to values fitted for D respectively Br.

Goodness of fit was sensitive to the input values of initial tracer pools and $r^2$ improved when the initial concentration values for Br and Cl were assuming the initial soil water content being larger than measured (results not shown). In the case of bromide this may have a physical meaning, inasmuch as part of the surface applied CaBr₂ salt probably dissolves only in the first infiltration water.

Additionally the hypothesis was tested that a two-region model was needed to improve the description of the elution curves by using the following physical non-equilibrium model proposed by van Genuchten and Wieringa (1976):
Therefore, we proceeded in the same way as described above including two more variables to fit, namely the relative fraction of mobile water $\beta$ and the dimensionless mass transfer coefficient $\omega$ defining the solute transfer velocity between the two regions. $C$, $T$, $Z$ and $R=R_m=R_{im}$ are defined as above, and the subscripts $m$ and $im$ refer to the mobile and immobile water phase. Note that $P$ is the Peclet number for the mobile phase.

We obtained almost perfect fits of elution curves for the DRY column (Figure 6-6 right, dotted line). Only Cl tailing was clearly overestimated. But the unreasonable high value for fitted chloride retardation (Table 6-5) showed that partitioning the pore space into mobile and immobile domains alone was not sufficient to account for the underlying physics of the transport processes. Due to correlation between some parameters non-uniqueness and numerical instability was observed when three or four transport parameters of the deuterium BTC in WET were fitted. Depending on the starting values given for the fitting parameters the relative fraction of mobile water $\beta$ approximated either one or zero, while the mass transfer coefficient complementarily tended towards zero or large values. Additionally, a large degree of uncertainty was associated with the fitted values. Thus, in Table 6-5 only one parameter combination out of several solutions for deuterium is shown. To keep as much consistency and plausibility as possible, we used the bromide elution curve to determine values for $P$, $\omega$ and $\beta$, which were then taken as fixed values in fitting the elution curve of CI (Figure 6-6 left, dotted line).

While fitting allowed to reproduce the shapes of the various elution curves reasonably well with a consistent set of values for $P$, $\omega$ and $\beta$, it required implausible values for $R$. For chloride it was clearly above and for bromide below the range of physically meaningful values. In the case of chloride, this may be at least partially due to the fact that CXTF automatically assumes that initially present solutes are in local equilibrium between mobile and immobile regions at the beginning of elution. This assumption may be appropriate for steady-state flow conditions, but would probably not have been adequate for the transient situation at the beginning of infiltration in the initially dry column, where the major portion of the chloride should have been expected to reside in the effectively immobile water of the matrix, by-passed by the chloride-free solution infiltrating through previously void flow channels between those regions. As the
assumption of initial equilibrium distribution of the injected chloride would have overestimated the physical mobility of this solute increasing the retardation factor $R$ would be an attempt of the fitting routine to compensate for this.

In the case of bromide, the low $R$-value can be interpreted as a compensation of the model to account for the initially much more pronounced preferential leaching than during later stages of the infiltration. As the other parameters were the same for all solutes, and thus, represent some sort of average conditions over the elution experiment, only the retardation factor was available to account for differences between solutes.

Finally we used the resulting parameter set in Table 6-5 to simulate the respective nitrate ($\text{NO}_3$) and sulfate ($\text{SO}_4$) curves in Figure 6-7. Simulations agreed well with measurements. Since initial $\text{NO}_3$ and $\text{SO}_4$ pools were distributed within the entire column length, the elution curves were affected only marginally by the transient conditions in the uppermost layer of the DRY column. Experimental artefacts may have contributed to discrepancy between fitted and measured concentration values at the beginning of elution, such as entrapped air in the outlet tubes caused by the application of a hydraulic pressure head at the lower boundary of -70 hPa in DRY. Additionally, initial nitrate and sulfate distribution were subjected to large spatial heterogeneity and, thus, quite uncertain. In the DRY column 21% of the initial nitrate and 16% of the initial sulfate were not recovered at the end according to the mass balances for water and solutes in Table 6-4.

The modelling results show that under the conditions of the initial wet column the steady-flow form of the CDF provided a consistent description of the normalised elution curves of the various solutes investigated. Deviations from this model due to the initial increase in water content were negligible if they occurred. This was quite different under the much more transient conditions of the initially dry column. In this case, no consistent descriptions was achieved with neither of the two models used. To some degree, this was probably due to the above discussed fact that CXTFIT automatically assumes equilibrium between mobile and immobile regions as conditions for solutes initially present in the columns. It could have been more appropriate to assume that the major portion was located in the immobile region because the “mobile region” was actually only created with the start of the infiltration and by definition of the mobile-immobile concept should not have mixed well with the resident water in the column.
Figure 6-7. Measured (symbols) and calculated (lines) nitrate and sulfate concentration curves in the initially WET and DRY soil monoliths based on the fitted transport parameters in Table 6-5 for the dual-porosity model.

However, further analysis with the MACRO model, which allows for transient and macropore flow and, thus, also for more flexibility with respect to the initial distribution of resident solutes, showed that this did not suffice for a complete solution to the problem (Kätterer et al, 2001). With MACRO, it was possible to give a physically plausible and consistent description of all elution curves except for the leaching of bromide through the initially dry column. The parameter set which simultaneously fitted the other curves failed to account for the early arrival of the bromide. Obviously, even MACRO was not able to fully cope with the change of transport conditions in the DRY column, i.e. that an obviously very pronounced condition of by-pass flow at the beginning of the infiltration gradually extenuated as infiltration continued. The main cause for this change, which was already inferred from the comparison of the Q-Q-plots
above, is most likely the increase in wettability of initially water-repellent matrix surfaces in the DRY column during the experiment.

6.4 Conclusions

Initial dryness of the soil clearly affected the transport and elution behaviour of the solutes depending on the mode of application. The early breakthrough of the surface applied tracers in the DRY column combined with a tailing at later stages is typical for transport with incomplete mixing, that is local non-equilibrium between pore domains of different mobility. The fact that in the same time the chemically similar chloride, which had been injected just beneath the soil surface, was strongly retarded gives strong evidence that indeed by-pass flow in particular during the first stages of infiltration was the main process responsible for the differences in tracer translocation. In the WET column the surface-applied Br was transported similar to the Cl indicating that steady-state conditions at the location of tracer placement did hardly affect the transport mechanisms.

The phenomenon in the initially dry column may be interpreted as some irrigation water moved faster, bypassing the soil matrix through preferential flow paths due to physical heterogeneity. Strong flow channelling in the DRY column can be attributed to macropores arising from shrinking and water-repellency at surface exposed to dry air. Water repellency must be considered as major factor inhibiting infiltration of water into the matrix of desiccated organic or humus-rich soils (Dekker et al. 1999, Dekker and Ritsema 1996, van Dam et al. 1990).

Since solute response curves represent the net effect of the transport processes, they do not allow resolution of individual mechanisms contributing to the overall behaviour. In the DRY column, chemical or physical heterogeneity seems to play an important role for chloride placed at the 5 cm depth. Whereas in the WET column, the near saturated flow conditions imparted a degree of homogeneity. Thus, the similarity between the Br response in DRY and the Br and Cl response in WET may be caused by the net effect of different processes. In DRY, fast solute transport may be caused by bromide being carried in the water flowing through preferential paths, whereas the transport in the WET column was probably governed by the convective-dispersive mechanism and fast transport was due to the large hydraulic conductivity of the soil matrix and partially also to the anion exclusion effect.

Application of the steady-state transport models using the CXTFIT code led to reasonable descriptions of the observed elution curves under initially moist conditions, which were not far from steady-state equilibrium of the infiltration. For the initial dry soil,
Chapter 6

neither the equilibrium nor the non-equilibrium model could adequately describe the experimentally observed leaching characteristics of chloride. To some degree, this was probably due to the inadequate description of the initial distribution of resident solutes, since the simulation codes used in automatically assume equilibrium between mobile and immobile regions as conditions for solutes initially present in the columns. Even a model allowing for transient and macropore flow and, thus, also for more flexibility with respect to the initial conditions, was not able to fully cope with the change of transport conditions in the initially dry column at the beginning of the infiltration (Kätterer et al., 2001).

Irrespective of the likely mechanisms involved our results also have important practical relevance with respect to the field application of fertilisers. They show that if such amendments are applied on the surface of desiccated soils then there is a high risk that a heavy rainfall occurring shortly afterwards may leach them into the subsoil, by-passing the filter and absorption capacity of the root zone. This risk is much lesser if these substances have been already worked into the soil as often done with fertilisers applied with sowing. Top dressings in humus-rich soils during dry periods in summer should be avoided at all. This assumptions hold also for mineral N released from decomposed plant residues which have not been incorporated into the soil. However, if biological activities such as nitrification are concentrated along preferential flow paths, as suggested by findings of Hagedorn (1999) and Bundt (2000), also N mineralised within the soil may be subject to a high risk of leaching by preferential flow.

6.5 Acknowledgements

Financial support was received from Kanton Zürich and from ETH Zürich. We thank Rolf Siegwolf and Matthias Saurer of the Paul Scherrer Institute (PSI) in Villigen, Switzerland, for their help in kindly measuring deuterium.

6.6 References


Multiple Tracer Transport through Undisturbed Soil Columns


Single- and Dual-Porosity Modelling of Multiple Tracer transport through Soil columns: Effects of Initial Moisture and Mode of Application

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Published in European Journal of Soil Science (2001) 52: 25-36

Abstract

We investigated the effect of initial moisture contents and mode of application on the displacement of multiple conservative tracers through undisturbed columns of a Mollic Gleysol. Bromide was applied at the soil surface and chloride was injected at 5 cm depth. The columns were irrigated with deuterium-enriched water. A dual-porosity model and two single-porosity models were calibrated separately to Br\textsuperscript{-} and Cl\textsuperscript{-} elution curves in the two columns.

Elution curves were almost identical for Br\textsuperscript{-} and Cl\textsuperscript{-} under initially wet conditions, whereas the displacement of Br\textsuperscript{-} was faster than that of Cl\textsuperscript{-} in the initially dry column, indicating rapid transport with preferential flow. Only the dual-porosity model described the long-tailing breakthrough of Cl\textsuperscript{-} in the initially dry column adequately. The parameter values giving acceptable fits for ‘Br dry’ were not compatible with the description of the three other elution curves, which could be adequately modelled with a single set of parameter values.

The estimated set of common parameters was validated by comparing with the elution curves of deuterium water, nitrate and sulphate, as well as with resident tracer concentrations at four depths. The results showed that solutes can be displaced much faster when applied at the surface of initially dry soil than when applied to wet soil or when resident in the soil matrix. The simulation results suggest that solute transport under initially dry conditions was governed by preferential flow of infiltration water through macropores by-passing the matrix due to shrinkage cracks and water repellence of matrix surfaces.
Chapter 7

7.1 Introduction

Evidence is accumulating that solutes move faster than predicted by approaches based on area-averaged water potentials (e.g. Beven & Germann, 1982; van Genuchten et al., 1990; Jury & Flühler, 1992). Nutrients and pesticides into water can be displaced through preferential flow paths in soils varying widely in texture and structure under various climatic conditions (Ritsema, 1999), especially in artificially drained fields (Smettem et al., 1983; Richard & Steenhuis, 1988; Milburn et al., 1990; Coles & Trudgill, 1985; Kumar et al., 1997, Magesan et al., 1995; Everts & Kanwar, 1990). Many factors, such as soil surface properties and water content, rain intensities, the time interval between rain events, the distribution of solutes within the profile may trigger preferential flow (Magesan et al., 1995; Bouma, 1990; Coles & Trudgill, 1985; Bronswijk et al., 1995).

We have investigated two of these factors in a laboratory experiment using undisturbed soil columns from a drained wetland, where preferential flow results from water repellence and shrinkage upon drying. We studied the occurrence of preferential flow in this soil during infiltration under dry and moist initial conditions and its role in the displacement of solutes applied at the soil surface or resident within its matrix. The main objective was to test under which of these conditions (surface and sub-surface application of tracers; initially dry and wet soil) one-domain models cannot describe solute transport, and, thus, preferential flow paths must be considered when describing vertical solute transport.

7.2 Soil properties, experimental set-up and measurements

The soil used for this study is a Mollic Gleysol from an arable field in the Furttal, near Zürich. It was drained and reclaimed for cultivation in the 1920s, since when the thickness of the humus-rich horizon has decreased to about 40 cm on average, though in some places there is still a 100-cm organic-rich layer. Two undisturbed columns of soil were taken at one of these places from 28-80 cm depth. They were encased in steel cylinders (diameter 24.9 cm; height 52 cm) and installed in the laboratory. The average carbon content in the columns was about 11% and dry bulk density decreased with depth from about 0.7 to 0.4 g cm$^{-3}$. 

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A brief description of the experimental set-up is given below. Two TDR (time domain reflectometry) probes, two thermocouples and two tensiometers were installed horizontally at each of the four depths, 6, 21, 36 and 46 cm below the soil surface in each cylinder and connected to a data logger. The columns were saturated from below by stepwise raising of the water table over 3 days. The water retention characteristic curves were obtained from TDR and tensiometer measurements during this period. The saturated hydraulic conductivity, $K_s$, was estimated for each column under constant head conditions at the soil surface (ponded under 2 cm water).

One column was covered with a steel lid to prevent water loss from the surface, whereas the other column was left open for evaporation. Both columns were kept at room temperature (15-23°C) for about 3 months.

A bromide pulse was applied as solid CaBr$_2$ at the soil surface (5.17 and 5.75 g Br$^-$ m$^{-2}$ in the initially dry and wet column, respectively) and a chloride pulse (18.34 and 17.31 g Cl$^-$ m$^{-2}$ in the initially dry and wet column, respectively) was injected through 84 evenly distributed syringe injections of highly concentrated (20%) CaCl$_2$ solution into a depth of 5 cm. About 1 hour after applying the solutes, the columns were irrigated with deuterium-labelled water (see below). Irrigation rates were about 20 mm per hour, corresponding to about 6% of $K_s$. 

7.3 Simulation models

We used two one-dimensional flow and transport models to interpret and analyse the experimental results: HYDRUS (Vogel et al., 1996) and in MACRO (Jarvis, 1994), which differ (as applied here) with respect to the uniformity of the flow domain. HYDRUS assumes only a single flow domain described by the Richards equation. MACRO is based on the concept of two different domains: a micropore or matrix domain in which flow is governed by the Richards equation as in HYDRUS and a macropore domain which drains the excess of water upon saturation of the matrix by gravity flow.

In both models, Richards’ equation is solved numerically for one-dimensional water flow:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left( K \left( \frac{\partial \psi}{\partial z} - 1 \right) \right) + S \quad ,
$$

(Eq. 7-1)

where \( \theta \) is the volumetric water content, \( K \) is the hydraulic conductivity, \( \psi \) is the hydraulic pressure head, \( S \) is a term and \( z \) is depth (positive downwards). MACRO uses Richards’ equation only to describe water fluxes in micropores. For the macropore region, a simplified approach is used, with fluxes predicted by assuming no changes in \( \psi \) with depth, \( \partial \psi / \partial z = 0 \), i.e. a unit pressure head, laminar flow under gravity.

In MACRO, \( S \) includes water exchange (\( S_w \)) between micro- and macropores. The flux from macro- to micropores is given by

$$S_w = \left( \frac{3 D_w}{d^2} \gamma_m \right) (\theta_b - \theta_{mi}) \quad ,
$$

(Eq. 7-2)

where \( d \) is the effective ‘diffusion path length’, \( \theta_b \) and \( \theta_{mi} \) are the saturated and actual water content in micropores, respectively, \( D_w \) is effective water diffusivity, and \( \gamma_m \) is a scaling factor introduced to match the approximate and exact solutions to the diffusion problem and set to an average value of 0.8 within the program (see Jarvis, 1994, for details). Water flow in the opposite direction, i.e. from micro- into macropores, is simply the water content exceeding \( \theta_b \), i.e. \( \psi - \theta_b \), that is immediately routed into the macropores. Dispersion in the macropores is neglected in the model since solute transport is assumed to be dominated by convection.

In HYDRUS, soil water retention, \( \theta(\psi) \), is described by the model of van Genuchten (1980), given by
Single- and Dual-Porosity Modelling of Multiple Tracer Transport

\[ \theta(\psi) = \theta_s + \frac{\theta_s - \theta_r}{\left(1 + |\alpha\psi|^{\lambda}\right)^{\lambda-1}} \quad ; \quad \psi > 0 \]  

(Eq. 7-3)

\[ \theta(\psi) = \theta_r \quad ; \quad \psi \leq 0 \]

which is combined with the model of Mualem (1976) to yield the hydraulic conductivity function:

\[ K(\psi) = K_s S_c^n \left[ 1 - \left(1 - \frac{1}{S_c^{\lambda}}\right)^{\frac{\lambda-1}{\lambda}} \right] \]

(Eq. 7-4)

where \( \theta_s \) and \( \theta_r \) are the saturated and residual water content, respectively, \( K_s \) is the saturated hydraulic conductivity, \( \alpha \) is the inverse of the air-entry value, \( \lambda \) is a pore size distribution index, \( n \) is an empirical curve shape parameter (expressing pore connectivity) and \( S_c \) is the effective water content, \( S_c = (\theta - \theta_r)/(\theta_b - \theta_r) \).

In MACRO, different functions are used for the micro- and macropore regions. The water retention characteristics for the micropores, \( \psi_{mi}(\theta) \), are given by the Brooks & Corey (1964) function:

\[ \psi_{mi}(\theta) = \psi_b S_{mi}^{\frac{\lambda-1}{\lambda}} \quad ; \quad \theta_r \leq \theta \leq \theta_b \]  

(Eq. 7-5)

where

\[ S_{mi} = \frac{\theta - \theta_r}{\theta_b - \theta_r} \quad ; \quad \theta_r \leq \theta \leq \theta_b \]  

(Eq. 7-6)

As in HYDRUS, the hydraulic conductivity function, \( K_{mi} \), is derived from the retention curve by way of the Mualem (1976) model, yielding

\[ K_{mi} = K_b S_{mi}^{-a+2+\frac{1}{\lambda}} \]

(Eq. 7-7)

where \( K_b \) is the hydraulic conductivity of the saturated matrix.

Since macropore domain flow is driven by gravity and occurs only under matrix-saturated conditions, no retention curve is required. Thus, the hydraulic conductivity of the macropores, \( K_{ma} \), is given by a simple power law expression of the degree of saturation in the macropores (\( S_{ma} \)):

\[ K_{ma} = (K_s - K_b) S_{ma}^{\alpha} \quad ; \quad \theta_b < \theta \leq \theta_s \]  

(Eq. 7-8)
where
\[ S_{ma} = \frac{\theta_{ma}}{\theta_s - \theta_b} \]  
(Eq. 7-9)

and \( n^* \) is an empirical parameter describing the connectivity between the pores.

The critical boundary hydraulic head at which micropores begin to drain \( (\psi_b) \) corresponds to the air-entry value, i.e. \( 1/\alpha \) in Equation 7-3.

Solute transport in HYDRUS is fully described by the standard convection–dispersion equation for non-sorbing tracers:
\[ \frac{\partial \theta c}{\partial t} = \frac{\partial}{\partial z} \left( D \theta \frac{\partial c}{\partial z} - q c \right) \pm U \]  
(Eq. 7-10)

where \( c \) is the solute concentration in the liquid phase, \( q \) is the Darcian water flow rate, \( U \) is a sink term (set to zero in the HYDRUS application), and \( D \) is the dispersion coefficient given by
\[ D = \epsilon \frac{q}{\theta} + D_0 \tau \]  
(Eq. 7-11)

where \( \epsilon \) is the dispersivity, \( D_0 \) is the ionic diffusion coefficient in free water and the tortuosity factor \( (\tau = \theta^{7/3}/\theta_s^2) \) is calculated following Millington & Quirk (1961).

In MACRO solutes in micropores are transported according to Equation 7-10, whereas dispersion is not considered in the macropore flow domain. The source or sink term \( (U) \) in Equation 7-10 accounts for mass transfer between the flow domains and represents diffusion and mass flow by
\[ U = \left( \frac{3}{d^2} \frac{D_s \theta_{ma}}{\theta_s} \right) (c_{ma} - c_m') + S_w c' \]  
(Eq. 7-12)

where the prime notation indicates either solute concentration in macro- or micropores depending on the direction of water flow \( S_w \), and \( D_e \) is an effective diffusion coefficient determined by
\[ D_e = D_0 \tau S_{ma} \]  
(Eq. 7-13)

In MACRO, infiltration into micropores at the upper boundary is limited by \( K_b \). The portion of rain or irrigation exceeding \( K_b \) is directed into macropores. We calculated the solute concentration of the water infiltrating into macropores \( (c_{ma}') \) assuming complete mixing of the infiltrating water with water stored in the ‘mixing depth’, \( z_d \), i.e. a shallow layer at the soil surface:
where $Q_d$ is the amount of solute stored in the ‘mixing depth’, $R$ is the amount of rain or irrigation reaching the surface within time interval $\Delta t$, $c_r$ is the concentration in the rain or irrigation water and $\theta_l$ is the water content in the layer $z_l$. The amount of solute added to or removed from the micropores in the top layer within time interval $\Delta t$ is then calculated as the difference:

$$Q_{mi(t)} = R c_r - I_{ma} c_{ma}^*$$  \hspace{1cm} (Eq. 7-15)

where $I_{ma}$ is the infiltration in macropores.
Chapter 7

7.4 Model parameterization

7.4.1 Boundary conditions and initial values

Water flux at the upper boundary was set equal to the irrigation rate. A constant head of -70 hPa was set at the lower boundary of the initially dry column and one of -10 hPa at the lower boundary of the initially wet column.

In simulations with HYDRUS, the soil profiles were represented by 52 elements of equal length. To reduce computation time for the complex MACRO model, discretization was limited to ten layers with increasing thickness from top to bottom.

We set initial water contents from measured values, assuming that measurements at 6, 21, 36 and 46 cm depth represented the depth layers 0-12, 12-32, 32-40, 40-52 cm, respectively, except for the 0-12 cm layer of the initially dry column. Here, the initial water content was assumed to increase with depth with a gradient of 0.01 cm\(^{-1}\), matching the measured value at 6 cm.

The amounts of bromide and chloride applied were given as initial conditions in the layers 0-1 and 5-7 cm, respectively, assuming uniform distribution within these layers. At all other depths the initial concentration of these two tracers was set to zero.

The initial amounts of nitrate and sulphate calculated from concentration measurements and water content at the four depths differed by up to 20% from the eluted amounts. We scaled the initial amounts at each depth with the same factor to correspond to the measured amount eluted.

7.4.2 Hydraulic properties estimated from measurements

The saturated hydraulic conductivity (\(K_s = 33.6 \text{ cm h}^{-1}\)) averaged over the column length under ponding water differed by less than 5% between the two columns and was set equal for all depths in both columns.

The hydraulic parameters of the retention curves (\(\theta_e, \theta_h, \psi_b\) and \(\lambda\)) were estimated from TDR and tensiometer measurements at four depths during imbibition (Table 7-1) and the residual water content (\(\theta_r\)) was set to zero. The water content \(\theta_s\) was set according to that observed at zero tension, and \(\lambda, \theta_h\) and \(\psi_b\) were estimated by curve-fitting using non-linear regression analysis. In both columns, the steepness of the retention curve \(\psi(\theta)\) increased with depth. For example, at 50 hPa pressure head, about 17% of the water stored at saturation was released at 6 cm depth according to the retention curves. The corresponding water release was about 9% at 21 cm, 5% at 36 cm, and 3% at 46 cm. Thus, the large pore fraction decreased with depth.
7.4.3 Identification of unknown parameters

The values of the unknown water and solute transport parameters were estimated by inverse modelling using the Sequential Uncertainty domain parameter FItting program SUFI of Abbaspour et al. (1997). Each unknown parameter was assumed to be uniformly distributed within an initially defined uncertainty range. The upper and lower bounds of the uncertainty range were chosen on the basis of our experience. To reduce the number of unknown parameters, we aggregated the depth layers within the models into one (i.e. parameter values were the same for all depths) or two (i.e. one value for the upper layer and one for the lower part of the columns).

The HYDRUS and MACRO models were run with an exhaustive sampling scheme (Abbaspour et al., 1997), and for each run a goal function, \( g \), was calculated as

\[
  g = \sum_{i=1}^{h} \left[ e_i^m - s_i^p \right],
\]

(Eq. 7-16)

where \( h \) denotes the number of measurements for each elution curve and \( s_i \) are the measured (superscript \( m \)) and predicted (superscript \( p \)) fluxes or concentrations. We assumed that a solution was reached when the reduction in the values of \( g \) for successive iterations was less than 5%.
Table 7-1. Values of hydraulic parameters for the initially dry and wet columns used in the permeo simulations according to data derived during a period of wetting the columns from below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Initially dry column</th>
<th>Initially wet column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated water content</td>
<td></td>
<td>0.005</td>
<td>0.000</td>
</tr>
<tr>
<td>Boundary water content</td>
<td></td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity</td>
<td>K_s</td>
<td>0.014</td>
<td>0.014</td>
</tr>
<tr>
<td>Poresizedistribution index</td>
<td>X</td>
<td>0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>Boundary pressure head</td>
<td>y</td>
<td>0.71</td>
<td>0.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>0.0-12</th>
<th>12-24</th>
<th>24-40</th>
<th>40-52</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.29</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>3.36</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>4.25</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>6.91</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>7.29</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
</tbody>
</table>
7.4.4 Modelling strategy

The basic concept was to calibrate the simulation models based on the elution curves of Br\(^-\) and Cl\(^-\) for both columns separately (Figure 7-1). The validity of the calibrated models was then tested by comparing simulations with measurements of resident tracer concentrations at the four depths 6, 21, 36 and 46 cm and, furthermore, by comparison of simulations with measured breakthrough of deuterium (applied with the irrigation water) as well as elution curves of nitrate and sulphate which were present in the soil columns at the beginning of irrigation.

Figure 7-1. Flow chart for the model applications. Deuterium = D.
7.5 Model calibration

The normalised accumulated elution curves for \( \text{Br}^- \) and \( \text{Cl}^- \) in initially wet column (Wet) were almost identical (Figure 7-2). About 50% of these ions had been leached after about 15 hours. After 30 hours, about 95% of \( \text{Br}^- \) and \( \text{Cl}^- \) had been leached. However, in the initially dry column (Dry), the elution curves of the two tracers differed considerably. The shape of the \( \text{Br}^- \) elution curve in Dry was similar to that in Wet, but \( \text{Br}^- \) was transported faster in Dry than in Wet (Figure 7-2). Chloride, on the other hand, was eluted more slowly in Dry than in Wet. The elution curve of \( \text{Cl}^- \) in Dry showed a long tail indicating that the chloride injected at 5 cm was largely by-passed by the infiltration (Feyen et al., 1998). This by-pass infiltration resulted in a preferential displacement of bromide, that had been applied at the surface.

The concentration elution curves of both tracers in Wet and that of \( \text{Br}^- \) in Dry were adequately reproduced by HYDRUS, but this model failed to describe the elution of \( \text{Cl}^- \) in Dry (Figure 7-3). Running MACRO in single-domain mode gave similar results (Figure 7-3). Differences in the best-fit simulations between the two one-domain models were due to differences in calibration. For example, only two water retention curves were used for the whole column length in HYDRUS, whereas four curves were used in MACRO. The water retention functions also differed between the two models, and the parameter values were considered as unknowns in the former and set \( \textit{a priori} \) in the latter model. Also, the saturated hydraulic conductivity was fitted to the elution curves in HYDRUS, and it was set according to measurements in the MACRO application. Thus, there appeared to be other processes involved than those implemented in the one-domain models, at least for \( \text{Cl}^- \) in Dry since the simulation resulted in a poor fit to the measurements despite the differences in the models and their calibration procedures.

All further analyses were done with MACRO in the two-domain mode. The inverse procedure was used to estimate the values of nine unknown parameters simultaneously, but separately for the \( \text{Br}^- \) and \( \text{Cl}^- \) elution curves in the initially dry and wet column, respectively (Table 7-2). This resulted in an almost perfect agreement between simulated and measured elution curves when using wide bounds of the parameter strata (not shown). Thus, MACRO accounted for the processes necessary to explain the behaviour of the solute breakthrough curves, even that of \( \text{Cl}^- \) in Dry.
Figure 7-2. Normalized accumulated experimental elution curves for Br⁻ and Cl⁻ in the initially dry and wet columns.

Figure 7-3. Experimental elution curves for Br⁻ and Cl⁻ in the initially dry soil column and simulation results using HYDRUS and MACRO run in one pore domain. Optimised parameter values for Br⁻ using HYDRUS were: \( \alpha = 0.0255 \); \( \alpha = 0.0450 \); \( \lambda_1 = 1.32 \); \( \lambda_2 = 1.25 \); \( K_{s1} = 65 \text{ cm/h} \); \( K_{s2} = 58 \text{ cm/h} \) and dispersivity = 1.65 cm, where \( \alpha \) and \( \lambda \) are the 'Van Genuchten' parameters, Equation 7-3, \( K_s \) is the saturated hydraulic conductivity, Equation 7-4 and subscripts '1' and '2' refer to the depth strata 0-12 cm and 12-52 cm, respectively. Optimised parameter values for Cl⁻ were similar (not shown). See Table 7-2 for optimised MACRO parameter values.
Table 7.2: Parameters values used in the macro simulations. See text for details.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Single-domain mode</th>
<th>Two-domain mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excluded water content</td>
<td>Initially wet</td>
<td>Initially dry</td>
</tr>
<tr>
<td>Boundary hydraulic conductivity</td>
<td>0.1 cm/y</td>
<td>0.1 cm/y</td>
</tr>
<tr>
<td>Mixing depth</td>
<td>1.3 m</td>
<td>1.3 m</td>
</tr>
<tr>
<td>Dispersion</td>
<td>0.05 m</td>
<td>0.05 m</td>
</tr>
<tr>
<td>Effective diffusion pathlength</td>
<td>0.05 m</td>
<td>0.05 m</td>
</tr>
<tr>
<td>Tortuosity factor in micropores</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Poresizedistribution</td>
<td>Initially dry</td>
<td>Initially dry</td>
</tr>
</tbody>
</table>

*Assumed constant (see text) According to Shackelford (1989).

Boundary hydraulic conductivity, 0-12 cm K = cm h⁻¹, 12-32 cm K = cm h⁻¹. Mixed depth, cm. Diffusion coefficient (x10⁶) cm² h⁻¹.
The estimated values for four of the unknown nine parameters listed in Table 7-2, i.e. the dispersivity ($\varepsilon$), the effective diffusion pathlength ($d$), the tortuosity factor of micropores ($n$; see Equation 7-4) and the depth of homogenous solute mixing in the uppermost soil layer ($z_d$), were similar to each other or did not strongly affect the model outputs. Further, the estimated diffusion coefficient ($D_0 = 8.5 \times 10^{-10}$ m$^2$ s$^{-1}$) was considered to be too small, and the water content excluded from anion transport ($\theta_{cx} = 0.225$) was considered to be too large. In a second round of inverse modelling, the parameters least sensitive or those considered to have unreasonable values were set to fixed values (Table 7-2). The diffusion coefficients for Br$^-$ and Cl$^-$ in a Ca solution were set to $1.3 \times 10^{-9}$ m$^2$ s$^{-1}$, following Shackelford (1989), and $\theta_{cx}$ was set to 0.055 (Table 7-2). The three parameters left, i.e. the hydraulic conductivity of micropores at 0-12 (K$_{h1}$) and 12-52 cm depth (K$_{h2}$) and the macropore distribution parameter ($n^*$), were estimated in a third round (Table 7-2). Again, good agreement between simulated and measured elution curves was obtained.

Theoretically, the differences between parameter values obtained from the two tracer curves for the same column should have been within the range of estimation uncertainty, as they represent the same physical reality. Thus, we tried to find a combination of the three parameters $K_{h1}$, $K_{h2}$ and $n^*$ (see Table 7-2) resulting in the smallest possible goal value, i.e. a reasonable fit to both Br$^-$ and Cl$^-$ elution within one soil column. For the initially wet column, this was in fact successful, and we found a set of parameter values that gave good descriptions for both tracer elution curves (Figure 7-4; Table 7-2).

For the initially dry column, we failed to find any common set of parameters for Br$^-$ and Cl$^-$ that resulted in a reasonable fit to both Br$^-$ and Cl$^-$ elution curves. In the model, the exchange between micro- and macropores was more pronounced in Dry than in Wet. The applied water was mixed with the bromide in the ‘mixing depth’, Equation 7-14, which then was transported to deeper layers via macropores. There, the bromide was transferred into the micropore region because of the large gradients in water content, Equation 7-2, and in concentration between micro- and macropores, Equation 7-12. When the hydraulic conductivity of the micropore region was set to a small value, there was little vertical transport of Br$^-$ within the saturated micropore domain, and this resulted in a long tail to the elution curve as for Cl$^-$ in Dry. Consequently, to fit the measured breakthrough of Br$^-$ in Dry, $K_{h2}$ had to be large (Table 7-2). On the other hand, conductivity had to be sufficiently small for Cl$^-$ to generate an initially large solute flux from micro- to macropores but at the same time also to limit vertical solute flux within the micropore region necessary to produce the observed long-tailed leaching curve.
As a further step in the analysis, we transformed the set of parameters estimated for Br\(^-\) and Cl\(^-\) in Wet (see ‘Br\(^-\) & Cl\(^-\)’ in Table 7-2) to the dry column by calculating the hydraulic conductivities in Wet at the pressure head values corresponding to \(\psi_h\) in Dry at the four depths (see Table 7-1) using Equations 7-6 and 7-8. Thus, the resulting parameter set was equivalent to ‘Br\(^-\) & Cl\(^-\)’ (Table 7-2). When applying this parameter set to the initially dry column, simulations fitted the Cl\(^-\) elution curve well but not the Br\(^-\) elution curve (Figure 7-4).

The transport of Br\(^-\) in the initially dry column was highly sensitive to the initial water content in the uppermost 5 cm. Since (in the simulations) almost all water (including the tracers) infiltrating during the first few hours was transferred from the macropores into the micropores from which it was only slowly lost, preferential flow was retarded until the micropores were saturated. This effect was stronger for Br\(^-\) than for Cl\(^-\) since the soil was driest in the upper 5 cm, and Br\(^-\) concentrations in the infiltrating water were large. We did a simulation in which the initial water content was set to the boundary water content, i.e. micropores were saturated and macropores were empty. The resulting peak of the simulated Br\(^-\) elution curve arrived much earlier than in the original ‘Br\(^-\) & Cl\(^-\)’ parameterization and coincided with the measured (Figure 7-4).
Figure 7-4. Measured and simulated Br$^-$ and Cl$^-$ elution from the initially dry and wet columns using the ‘Br$^-$ & Cl$^-$’ calibration of MACRO (Table 7-2).
Chapter 7

7.6 Model Validation

7.6.1 Depth profiles of resident bromide and chloride

For the initially wet column, the ‘Br⁻ & Cl⁻’ parameter sets (Table 7-2) resulted in a good agreement between concentrations of Br⁻ and Cl⁻ measured in small samples extracted from the soil solution and simulated tracer concentrations, \( c = (\theta_{m1}c_{m1} + \theta_{ma}c_{ma})/\theta \), in the three lower layers (Figure 7-5). At 6 cm depth, the dynamics of resident Br⁻ was reasonably well described by the simulations, whereas the simulated decline of Cl⁻ concentration was faster than measured. However, the large value for Cl⁻ measured after 9 hours at 6 cm may have been an outlier. The mean value for concentration (=45 mg Cl⁻ dm⁻³) was calculated from two values (14 and 76 mg dm⁻³). Although this is one of the most extreme examples of the differences in recorded measurements at the same depth, it demonstrates the variation often observed in soil samples taken within a few centimetres apart (Dekker et al., 1999; Hance, 1976; Shipitalo & Edwards, 1996; Harvey, 1993).

For the initially dry column, Cl⁻ concentrations at 6, 21 and 36 cm depths were not well predicted by the simulation (Figure 7-5), though the simulated Cl⁻ elution in Dry fitted the measured values reasonably well (Figure 7-4). The relatively large Cl⁻ concentrations at 21 and 36 cm 2 hours after the start of the experiment indicate that a fraction of the applied Cl⁻ was displaced more rapidly than in the initially wet column. This agrees with the fact that the peak of the Cl⁻ elution curve of the initially dry column occurred several hours earlier than in the initially wet column. The same was true for Br⁻, but displacement reached only 21 cm depth after 2 hours. Also, the electrical conductivity measured at the four depths (TDR) and in the leachate pointed to a more rapid displacement of solute in the initially dry column. Within 2 hours after the start of the experiment, the electrical conductivity increased to twice that in Dry in Wet in the leachate and five times more in the soil solution at 21 and 36 cm depth in the column. Thus, preferential flow was underestimated within the profile in Dry, but this did not affect Cl⁻ elution. Probably, the preferential flow paths were not continuous throughout the profile.
Figure 7-5. Measured and simulated resident Br\(^-\) and Cl\(^-\) concentrations at four depths in the soil profile in the initially dry and wet column (mg dm\(^{-3}\) soil). For all simulations, the ‘Br\(^-\) & Cl\(^-\)’ parameter set was used (cf. Table 7-2).
The simulated water content in the soil affected the calculation of mass transport. According to the simulations, the water content increased sharply within 1 hour after the start of the irrigation, whereas the measurements showed only small increases, especially in the uppermost layer in Dry (Figure 7-6). This phenomenon could partly explain the overestimation of Cl⁻ at 6 cm.

![Figure 7-6. Measured and simulated soil water content (m³ m⁻³) at 6 cm in the initially dry column.](image)

### 7.6.2 Deuterium breakthrough

The parameter set ‘Br⁻ & Cl⁻’ was then used to simulate the breakthrough curve of deuterium. Since both bromide and deuterium were applied at the soil surface, the simulation was not expected to fit the deuterium breakthrough curve in Dry after simulations had failed to predict the Br⁻ elution curve. However, the results contradicted this. In the initially dry column, deuterium concentrations in the discharge were almost perfectly predicted by the ‘Br⁻ & Cl⁻’ parameter set (Figure 7-7). Also in Wet, simulations agreed reasonably well with the measurements (Figure 7-7). The breakthrough curves for deuterium also supported the observed differences between Dry and Wet as discussed above, i.e. a more rapid increase in relative concentrations after the start of the experiment indicating greater preferential flow in Dry than in Wet.
7.6.3 Nitrate and sulphate transport

The parameter set ‘Br’ & Cl’ was used to simulate resident and eluted nitrate and sulphate in Dry and Wet during the experiment. Only the diffusion coefficients were changed: $D_0$ was increased from 1.3 to $1.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, a value proposed by Shackelford (1989) for small nitrate concentrations, although this affected NO$_3^-$ fluxes by less than 5%. Likewise, decreasing $D_0$ to $1.06 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, as suggested for SO$_4^{2-}$ (Shackelford, 1989), only marginally affected the simulated transport of sulphate. Nitrogen and sulphur transformations during the breakthrough experiment were neglected. As Figures 7-8 and 7-9 show, NO$_3^-$ and SO$_4^{2-}$ elution and concentrations of resident tracer in the profile were reasonably well predicted by the model with this parameterization. Differences between measurements and simulations were due mainly to uncertainties in the initial values, which were based on sample measurements at four depths (as described above) and extrapolated to the whole soil profile.
Figure 7-8. Measured and simulated NO$_3^-$ and SO$_4^{2-}$ elution in the initially dry and wet column. For all simulations, the ‘Br & Cl’ parameter set was used (cf. Table 7-2).
Figure 7-9. Measured (symbols) and simulated (lines) resident $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ in the initially dry (open symbols; dashed lines) and wet (closed symbols; whole line) columns. For all simulations, the ‘Br’ & Cl’ parameter set was used (cf. Table 7-2)
Chapter 7

7.7 General discussion and concluding remarks

Our results support the findings by Shipitalo & Edwards (1996), who found larger concentrations of leached pesticides in a lysimeter study after the first rain storm following the application when the pesticides were applied to dry soil than when they were applied to wet soil. Although total amounts of percolating water are usually greater from a wet soil, greater total leaching losses were reported when solutes were applied to dry soil than when applied to wetter soil (White et al., 1986). Thus, greater variation in precipitation resulting in alternating soil drying and wetting will probably increase total leaching losses of solutes applied at the soil surface but not of those contained within the soil matrix.

Despite the different shapes of the elution curves, the transport of all tracers was reasonably well described by MACRO (two pore domains) by a single set parameters, except for bromide in the initially dry column. The deuterium-labelled irrigation water arrived earlier in the discharge in Dry than in Wet. This clearly showed that solutes applied at the surface of dry soil are initially more rapidly displaced than when applied to an initially wet soil of this type. It was also shown that the differences between simulated and measured Br$^-$ elution in Dry were related mainly to the initial moisture conditions and to the way the model treated infiltration and solute exchange between micro- and macropores in dry soil.

In our experiment, $\theta$ increased only slowly in the uppermost layer during wetting, and did not reach $\theta_s$ throughout the experiment (Figure 7-6). This could have been because the matrix repelled water. Water repellent soils are difficult to wet when drier than some critical soil moisture content and flow in them is often preferential (Ritsema & Dekker, 1998). Drying increases hydrophobicity and by enhanced air entrapment during wetting contributes to a decrease of hydraulic conductivity (Kutilek & Nielsen, 1994).

The simplified description of first-order mass exchange between micro- and macropores in MACRO did not account for this delay in wetting of the initially dry soil. The transfer of water and Br$^-$ from macro- to micropores was too rapid in the simulations, and the performance of MACRO under dry conditions would thus probably improve by introducing a delay in the wetting of initially dry soil.
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7.9 References


Synthesis

As expected, mineralisation of organic matter proved to be a major source of soil mineral nitrogen in the humus-rich soils of the Furttal test area. In addition to the stabilised soil-incorporated organic N pool, fast decomposing constituents of crop residues, manure and sewage sludge applications were important inputs to the mobile N pool of the topsoil, whereas mineralisation of organic matter in the subsoil was of minor importance.

The problem of N leaching was not restricted to the non-growing season. During the 6-month period from May through October a substantial amount (20-60%) of the annual N load was leached via drainage into the Furtbach creek. Mineral N accumulated mainly in spring before plant uptake became effective, creating an increased risk of N leaching at the beginning of the growing season.

In a companion study Kohler (in preparation) showed that preferential flow was a dominant mechanism of nitrate leaching in the soils under study. He estimated that about three quarters of the nitrate exported with drainage discharge was leached to the drains through preferential pathways.

Although subject to a high degree of estimation uncertainty, net N mineralisation and plant N uptake were found to be the most important N fluxes. Losses via drain were small in comparison to the rates of N turnover by soil microbial processes and plant uptake. However, they were not negligible for the water quality of the Furtbach. The discrepancy between the magnitude of these losses and the turnover and transfer rates in the soil-plant system indicates that it will not be possible to control leaching losses by fine-tuning of agricultural management practices without reducing the intensity of agriculture.

Determining parameters by inverse modelling, we were able to describe the water and mineral N dynamics of the investigated field soil successfully using the model LEACHM (Hutson and Wagenet, 1992). Because of practical limitations, as well as time and financial constraints, inverse modelling has in recent years become an increasingly attractive alternative to direct methods of parameter estimation. Our results
suggest that this approach may be a promising tool not only for modelling well-controlled lab experiments, but also for field ecosystems. Addressing the inherent modelling uncertainties, we introduced the concept of ‘conditioned parameter distributions’ as a more appropriate alternative to ‘best-fit’ parameters.

Using net N mineralisation rates determined in ex situ incubations of undisturbed subsoil cores in combination with an empirical moisture and temperature response function provided a good description of the observed fluctuations of mineral N in the field. To describe net N mineralisation in the subsoil (below the plough layer) it was sufficient to assume a single “humus” pool, whereas modelling of the topsoil required the assumption of different types of organic matter. Partitioning the organic matter conceptionally into two separate pools, that is a fast decomposing “litter” and a slowly decomposing “humus” pool, resulted in a fair description of the overall net N mineralisation in 0-40 cm depth, but did not honour the observed dynamics in the topsoil dominated by litter turnover. We conclude that the sequential in situ coring technique used in this study to estimate net N mineralisation in the field has its limitations due to possible upward movement of capillary water. Evaporation occurring at the soil surface and, thus, leading to nitrate accumulation in the uppermost soil layer, may superimpose N mineralisation. Therefore, the inadequate modelling of N turnover processes in the topsoil may be improved by the inclusion of upward N transport. In addition, more differentiation of fast decomposing organic matter pools and factors affecting decomposition rates in the surface layer may be needed.

Our findings corroborate the hypothesis that the risk of N leaching depends mainly on the accumulation of a mobile N pool and its exposure to infiltrating water as well as on the travel time through the soil, where plant uptake and denitrification may taken place. In initially dry soils solutes at the surface were displaced much faster than in wet soils or when resident in the soil matrix, suggesting that solute transport under initially dry conditions was governed by preferential flow of the infiltrating water through macropores, by-passing the matrix. In field situations this leads to a higher risk of mineral N leaching after the application of N fertiliser at the surface or from decomposed plant residues which have not been incorporated into the soil. However, if biological activities such as nitrification are concentrated along preferential flow paths, as suggested by findings of Hagedorn (1999) and Bundt (2000), also N mineralised within the soil may be subject to a high risk of leaching by preferential flow.

The results of this study suggest that estimations of N losses by leaching from soil tend to be biased due to taking inadequate account of transient phenomena such as preferential flow, upward movement of nitrate by capillary water and mineralisation of fast
decomposing constituents of plant residues in the topsoil. As net N mineralisation and plant N uptake were the most important N fluxes controlling the pool of mobile nitrogen in soil, prediction of N leaching requires a better modelling accuracy of the dynamics of these processes.

References


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