

## ABSTRACT

Between 2001 to 2004, the leaching of mineral and organic nitrogen and phosphorus was studied in long-term experiments on two different soil types (sandy loam, clay loam) with different soil cultivation (conventional tillage, minimum tillage), land-use (grassland, arable land) and fertilization (organic and mineral N fertilization).

Passive capillary samplers (PCAPS, fiberglass wick sampler) were chosen to collect seepage water. Pre-studies showed that the hydrological properties (capillarity), as well as the adsorption capacity, are influenced by the pretreatment of the wicks. The fiberglass wicks used in this study showed a cation exchange capacity of  $23 \mu\text{val } 0.5 \text{ m}^{-1}$  ( $= 99 \mu\text{val } 100 \text{ g}^{-1}$ ), but this did not disturb the field survey severely. Water collection efficiency was 37 % on arable land and 76 % on grassland. PCAPS collected 59% of the drainage that was collected by monolith lysimeters.

The highest concentrations of mineral N ( $\text{NO}_3$  and  $\text{NH}_4$ ) were generally detected in the late winter, while mineral P concentrations were highest in late summer. Organic N and P concentrations did not show any clear seasonal trends.

The average share of ammonium-N in total nitrogen was, with 15 %, highest in the seepage waters from the arable land on the sandy loam soil after long-term organic fertilization; while 6 % was found after long-term mineral fertilization, lowest on the clay loam soil (0.8 % for both conventional and minimum tillage), and 2.3 % on grassland. 22 % of the total nitrogen was found as organic N on average during the monitoring period in the drainage from the clay loam (for both conventional and minimum tillage), while it was only 7 % for the sandy loam soil, in both grassland and arable land.

Organic P in the leachates from the sandy loam soil had a share in the total phosphorus of 47 % after long-term mineral fertilization, 27 % after liquid manure application and 15 % on the grassland. For the clay loam; the contribution was 38 % on the conventional tillage plot and 15 % on the conventional tillage plot.

It is noticeable on all experimental sites that in most cases the organic N concentrations in the seepage waters decreased when the organic P concentrations increased, and vice versa. From this observation it is concluded that organic N compounds are leached separately from organic P compounds.

In most cases, a decrease of the nitrate concentration in the drainage was observed parallel to an increase of the  $\text{PO}_4$  concentration. In such situations, a higher contribution of macropore/preferential flow to leaching is assumed. The  $\text{PO}_4/\text{NO}_3$  ratio in the seepage waters was highest on all sites the late summer months, and above average during the wet year 2002. From these results it is concluded that the  $\text{PO}_4/\text{NO}_3$  ratio can be used as an indicator to explain the presence of macropore and/or preferential flow.

## ZUSAMMENFASSUNG

Zwischen 2001 und 2004 wurde die Auswaschung von mineralischem und organischem N und P in Langzeitversuchen auf 2 unterschiedlichen Böden (Sand, Lößlehm) mit unterschiedlicher Bodenbearbeitung (konventionell mit Pflug, Minimalbodenbearbeitung), Bodennutzung (Ackerland, Grünland) und Düngung (ausschließliche Mineraldüngung und organische Düngung) ermittelt.

Zur Beprobung des Sickerwassers wurden passive Glasfaser-Dochtsammler (engl. wick sampler bzw. PCAPS (*Passive Capillary Samplers*)) verwendet. Vorversuche zeigten, dass sich verschiedene Glasfaserkünfte hinsichtlich ihrer hydrologischen Eigenschaften (Kapillarität) als auch ihrem Adsorptionsverhalten unterscheiden und auch die Vorbehandlung hierauf Einflüsse ausübt. Die in dieser Arbeit verwendeten Glasfaserkordeln wiesen eine geringe KAK von  $23 \mu\text{val } 0.5 \text{ m}^{-1}$  ( $= 99 \mu\text{val } 100 \text{ g}^{-1}$ ) auf, was die Konzentrationsverläufe nicht entscheidend verändert haben dürfte.

Die höchsten Konzentrationen an Mineralstickstoff ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) wurden allgemein Ende des Winters ermittelt, während die  $\text{PO}_4$ -Konzentrationen im Spätsommer am höchsten waren. Dagegen wiesen die Konzentrationen an organischem N und P keinen ausgeprägten saisonalen Verlauf auf.

Der durchschnittliche Anteil des Ammonium-N am Gesamt-N war mit 8 % im Sickerwasser des Ackerlands auf dem Sandboden am höchsten (etwa gleich nach mineralischer und organischer Düngung), auf dem Lössboden am niedrigsten (0,8 %, kein Einfluss der Bodenbearbeitung), und im Sickerwasser des Grünlands 2,3 %. Im Mittel des Untersuchungszeitraumes lag auf dem Lössboden in Soest 22 % des Gesamtstickstoffs in Sickerwasser als organisch gebundener Stickstoff vor (sowohl nach konventioneller als auch minimaler Bodenbearbeitung), während es auf dem Sandboden in Braunschweig, sowohl im Ackerland als auch im Grünland, lediglich 7 % waren.

Der Anteil des organischen P am Gesamt-P betrug im Sickerwasser des Ackerbodens auf dem Sandboden 47 % nach Mineraldüngung, 27 % nach Gölledüngung und auf der Grünlandfläche 15 %. Im Sickerwasser des Lößlehms in Soest wurden 38 % (konventionelle Bodenbearbeitung) und 15 % (Minimalbodenbearbeitung) festgestellt.

Auffällig war, dass die Konzentrationen an organischem N i.d.R. immer dann abnahmen, wenn die an organischem P zunahmen. Das deutet darauf hin, dass organische N-Verbindungen unabhängig von organischen P-Verbindungen ausgewaschen werden.

In den meisten Situationen nahm auch die Konzentration an  $\text{NO}_3\text{-N}$  immer dann ab, wenn die  $\text{PO}_4$ -Konzentration zunahm. In diesen Situationen ist ein höherer Beitrag von Makroporen/Preferential Flow am Auswaschungsgeschehen anzunehmen. Das  $\text{PO}_4/\text{NO}_3$ -Verhältnis im Sickerwasser aller Standorte war generell im Spätsommer am höchsten, und überdurchschnittlich hoch im nassen Jahr 2002. Aus diesen Beobachtungen wird geschlossen, dass das  $\text{PO}_4/\text{NO}_3$ -Verhältnis als ein Indikator für einen stärkeren Beitrag von Makroporen und Preferential Flow an der Auswaschung angesehen werden kann.

## 1 INTRODUCTION

### **Nutrient Leaching from Agricultural Soils**

Nitrogen and phosphorus are essential elements for plant growth and are therefore applied as fertilizers on agricultural land to avoid crop nutrient deficiencies and to maintain a high yield level. On the other hand, it is well documented that the entrance of nitrogen and phosphorus to the groundwater might result in the contamination of drinking water resources and cause contamination of surface waters. It has been well researched that a component ration of N and P in the drainage is a limiting factor for the occurrence and the growth of some blue-green algae that can accelerate the eutrophication of fresh water.

#### *Leaching of Nitrogen*

Nitrogen leaching in the soils is a contributor to the  $\text{NO}_3^-$  contamination of drainage. The nitrate ion ( $\text{NO}_3^-$ ) is easily moved down in the soil because it is negatively charged. The leaching of nitrate represents a loss of plant-available N from the soil and enters streams and groundwater. Nitrate movement in soils happens frequently in most temperate regions due to the interaction of soil temperature, pH, moisture, and soil physical properties. Light-textured soils, which have high hydraulic conductivities and low water-holding capacities, lose nitrate by leaching when rainfall exceeds evaporation (White, 1997). In contrast, nitrate leaching in heavy-textured soils is more complex, because water moves through large cracks and channels such as macropores, leaving nitrate behind in the soil aggregates where little water movement occurs (Rowell, 1994).

Unlike a nitrate, the ammonium ion ( $\text{NH}_4^+$ ) is positively charged and can be held by clay and organic colloids that are negatively charged. Immobile ammonium in the soil profile is not leached into groundwater and cannot be denitrified by soil microorganisms (Sommer, 2000).

According to Carpenter *et al.* (1998), N export from agricultural ecosystems to water, as a percent of fertilizer inputs, ranges from 10~40% for loam and clay soils to 25~80% for sandy soils. In 2002, it was estimated that 75 % of the nitrogen pollution of German surface waters are of agricultural origin. The subsurface transport to the ground water and from there to the surface freshwaters is assumed to be the most important. For phosphorus, the contribution of agriculture to the freshwater pollution is estimated to be about 40 % (BMVEL and UBA, 2004).

#### *Leaching of Phosphorus*

Leaching of phosphorus from agricultural soils has not been considered important for a long time because of the high absorption capacity of P by mineral soils (Stamm *et al.*, 1998) and low P concentration in drainage waters (Brookes *et al.*, 1997). Most studies on P losses have focused on soil erosion and surface runoff from agricultural land to water. Dils and Heathwaite (1996) confirmed that great amounts of P are exported by surface runoff during intense, infrequent storm events. P fertilizer applied to the light-textured sandy soil can also be lost by leaching after heavy

rainfall (Steen, 1997). Additionally, in clay soils, dissolved P can be moved through cracks and worm-channels by the preferential flow (Voss and Preusse, 1976; Beauchemin *et al.*, 1997). Delgado and Torrent (2001) reported that the losses of P from soils to fresh and marine waters are probably more related to soil properties (limed acid soils) than to the amounts of total applied P fertilizer. Heckrath *et al.* (1995) found linearly increasing P concentrations (soluble reactive mineral P as well as total P) in the tile drain waters of the silt loam and silt clay soil of Rothamsted on those plots which exceed a soil P level of  $\text{mg l}^{-1}$  (according to the Olsen-method) in the plough layer.

### **Movement of Agrochemicals and Nutrients through Macropores**

Intensive cropping using mineral and organic fertilizers as well as pesticides is widely discussed as one of the dominant sources for ground water pollution and also for the surface waters and marine ecosystems, especially with nitrates, phosphates and pesticides. Moreover, a significant charge with organic nitrogen and phosphorus compounds to surface and ground waters is discussed (Heckrath *et al.*, 1995).

Recharge processes are considered to consist of two or even three components. Boll *et al.* (1992) consider macropore flux through channels and cracks in the soil as preferential flow, and matrix flux through the bulk soil matrix (matrix flux) as the second component. Other scientists consider preferential flow separately from macropore flux, as a flux through soil matrix areas with higher flux rates compared to the surrounding soil, resulting in color tracer experiments in the so-called “fingering”. Contaminants that are usually adsorbed by the soil matrix (e.g.  $\text{PO}_4\text{-P}$ ) or metabolized by soil microorganisms (e.g., some pesticides) are moved to deep soil layers and to groundwater through preferential flow, a process by which the bulk soil is bypassed by some part of the infiltrating water. Here, the adsorption and metabolizing power of the soil matrix also is bypassed. Three mechanisms give rise to preferential flow: fingered flow, funnel flow, and macropore flow (Selker, 1996). Preferential flow affects the displacement of chemicals absorbed in the root zone of soils, and is reducing runoff and transport of chemicals to surface waters (Linden and Trojan, 1995). The downward rate of water movement determined by tracer measurements was about 2.5 times faster than would have been predicted by a traditional water balance-water content approach to miscible displacement. This rapid penetration of downwardly percolating water was apparently due to the presence of preferential flow paths in the soil matrix (Bowman and Rice, 1986).

Macropores are formed as a result of biological activity (soil animals as earthworms) and physical processes like frost, swelling and shrinking of clay, and drying (Li and Ghodrati, 1994). Omoti and Wild (1979) and Ehlers (1975) reported that the number of earthworm channels are spread at a depth of 0.02 m ~ 0.6 m. According to Green and Askew (1965), the activities of ants also make a macropore networks (2~50 mm diameter) at a depth of at least 1 m. Cycles of wetting, freezing, thawing and erosive action of soils, or other physical forces, including fractures, cracks, and fissures, are also major activities forming macropores (Beven and Germann, 1982). In addition, macropores are associated with either live or decayed roots, and with shrinkage or chemical weathering.

These macropores are capable of increasing the infiltration of water and dissolved chemicals (Andreini

and Steenhuis, 1990). And, in heavy soils, macropores act as a pathway for the rapid movement of water and solutes to the rhizospheres of the plant (Hatano and Sakuma, 1990).

Macropore transport is a rather fast transport, and for this reason, its ecological importance can only be evaluated from continuous or short interval sampling strategies. During long-term tile drainage measurements in two northern German watershed areas (SFB 179), Lammel (1990) found that drains that were normally inactive during spring and summer, discharged water immediately after the start of a heavy rainfall or irrigation event (20 ~ 30 mm h<sup>-1</sup>). The soil was very dry at that time and should have had enough water storage capacity to retain all this precipitation water. The tile drain water contained increased concentrations especially of total phosphorus during such a discharge event. The agro-ecological consequence can be evaluated from the results of Hasenpusch *et al.* (1990) and Kücke and Hasenpusch (1996) who collected water samples from the small river system in one of these intensively cropped areas at 20 minutes intervals (February to June). 95 % of the solid and phosphorus load during this five month period was discharged within one day as a consequence of a single heavy rainfall event (37 mm h<sup>-1</sup>). During this event, the concentration of total P in the river water increased up to 6.25 mg P l<sup>-1</sup> (normal average 0.62 mg P l<sup>-1</sup>), while the increase of dissolved mineral phosphate was rather low (max. 0.25, average 0.08 mg P l<sup>-1</sup>). It can be concluded from the fact that the increase in total P was significantly and positively correlated with the C concentration that a large part of this phosphorus discharge was associated with organic compounds and with solids. In the same area, Liess (1993) only found herbicides in tile drain water samples in the first minutes after tile drains discharged water after a heavy rainfall event in the spring on a dry arable soil. These observations can only be explained by macropore transport.

### **Sampling Methods to Measure Leachate in Field Studies**

Two basic information points are essentially needed to measure nutrients leaching in the field: 1) the quantity of water percolating through the soil at a specific soil depth and 2) the concentrations of the chemical components (nitrate, phosphate, pesticides, etc.) in the percolate. Of similar interest is the possibility of short-term interval sampling to receive reliable information about the seasonal dynamics of the nutrient flux. Soil coring, tile drain water recordings, suction ceramic cups and ceramic plates are widely used sampling techniques to measure leaching processes in the field (Table 1). From the overview in Table 1, it can be summarized that most methods do not deliver reliable data in field experiments: Either they do not deliver information about the water flux (soil coring, suction cups), or they deliver unreliable information about the concentration in the mobile water (e.g. soil sampling can deliver concentrations in the total soil water, including the immobile concentrations; ceramic cups interact with chemicals in the water sample by absorption (Brandi-Dohrn *et al.*, 1996)). A lot of sampling techniques disturb or destroy the soil profile during installation (e.g., ceramic plate samplers), so they cannot deliver data on water fluxes in undisturbed soils.

A new technique called “Wick samplers (*Passive CAPillary Samplers*, PCAPS)” has been proposed by Brown *et al.* (1986), and a similar sampler design is used in this project. The PCAPS suck the pore water from unsaturated soils using the capillary potential of fiberglass wick, which acts as a hanging

water column and develops a suction of 0 to 50 cm H<sub>2</sub>O when it is wetted (Holder *et al.*, 1991). PCAPS appear to have essential advantages compared to the other leaching sampling techniques: They collect seepage water from undisturbed soil profiles of a defined area related to water flow dynamics (time and flux proportions) without any artificial suction or vacuum (Boll *et al.*, 1992). Components of the sampler (fiberglass, HDPE plastic) that are in contact with the percolate are assumed to be chemically inert and do not interact with the chemical component (Topp and Smith, 1992).

Samplers work reliable reliably over many years: all 32 samplers installed in a field experiment at the North Willamette Research and Extension Center, Aurora, Oregon, USA, have reportedly worked since 1992 without any disturbances.

Wick samplers are mostly used to study nitrate leaching (Brandi-Dohrn *et al.*, 1996). Biddle *et al.* (1995) successfully investigated clay particle transport, which demonstrates that not only dissolved, but also colloidal components, in leachate can be sampled by the wick sampler technique.

PCAPS can be used not only to measure the variation of concentration of agrochemicals under agricultural field conditions but also to monitor the soil water flux due to management practices.

Table 1 Sampling techniques and their features (modified from Boll *et al.*, 1992)

Sampling technique	Sampling location	Sample size	Matrix potential at sampler-soil interface (cm)	Type of water sampled	Sample information *	Flux information	Location in soil	Sampling time frame	Soil limitations
<b>Soil coring</b>	Vadose zone	Auger size	-	Immobile and mobile	C	None	Disturbed soil	Instantaneous	All stone-free types, until ground water table
<b>Porous cup samplers</b>	Vadose & saturated zone	~ 5 cm radius	Depending on applied vacuum	Mobile	C for NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup>	None	Disturbed soil	With permanent vacuum continuously, otherwise in intervals from days to weeks	Heavy clay soils, Sandy soils
<b>Zero-tention Pan samplers</b>	Vadose zone	Pan size	0	Mobile	C & Q	Macropore flux	Undisturbed soil	Heavy rainfall events	All stone-free types, until ground water table
<b>Wick samplers</b>	Vadose zone	Sampler size	0-50 cm, depending on wick length	Mobile	C & Q	Macropore & preferential & matrix flux	Undisturbed soil	Continuously	
<b>Tile drains</b>	Shallow ground water	Field size	0	Mobile	C & Q	Preferential & macropore flux	Disturbed soil, depending on time after tile drain installation	Month to years for matrix flow, instantaneously for preferential flow	
<b>Ceramic plates, with and without rim</b>	Vadose zone	Plate size	Depending on applied vacuum	Mobile	C & Q, C for NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup>	Matrix flux	Disturbed soil	With permanent vacuum continuously, otherwise in intervals from days to weeks	

\* C = Concentration, Q = Water Quantity