2 Quantification of Nitrate Leaching in Soils using an Adsorber Method

Abstract

Several methods and techniques have been applied so far to quantify diffuse leaching losses under agricultural fields each of them bearing its limitations. The Self Integrating Accumulator (SIA) method is proposed to overcome some of these limitations. Basically SIA is an infinite-sink based method which integrates the solute fluxes over time of installation in the soil. To test the suitability of the SIA I followed three different approaches: I. With a chloride mass balance experiment on 6 agricultural fields with 5 replicates I determined accuracy and precision of the method. II. To examine the capability to intercept preferential flow paths I used 3 qualitative approaches: IIa. A dye tracer experiment to mark the flow paths in the soil and around the SIA. IIb. An experiment with a strongly sorbing solute (tributyltin), which presumably is transported only preferentially. IIc. Nitrate leaching during a very dry summer, where matric flow is very unlikely. III. In a plausibility experiment I measured the mean nitrate losses under different land uses: forest, long term fallow and agriculture. These were compared with published results. With 30 replicates 92 % of the validation value from the mass balance were recovered (Exp. I). The variation is such that 10 replicates would estimate the true mean within an error of less than 20 %. From II. it could be shown that SIA intercept and sample from preferential flow paths. Mean values for N-losses were 7, 5, 21 kg ha^{-1} for forest, fallow and agriculture respectively (Exp. III). I conclude that the Self Integrating Accumulator (SIA) Method is valid to measure leaching losses of nitrate on a mass per area basis in our experiments and is a promising method also for preferentially transported solutes.

2.1 Introduction

The loss of nutrients like nitrate and phosphate is not only an economic problem for farmers, but it also causes eutrophication of rivers, lakes and coastal regions. In Germany, close to 50 % of the nitrate input into surface water is due to influx of groundwater previously loaded under agricultural fields. Nitrate is still the greatest problem for German drinking water quality (Umweltbundesamt 2002) and of major concern in many other countries, e.g. the USA (Nolan et al. 1998). Besides, diffuse contamination by agriculture has been recognised as a major problem in the European Community and is tackled on a legislatory level (EU-Wasserrahmenrichtlinie 2000; Soil framework directive (proposal) 2006).

It is therefore desirable to monitor leaching losses on a field scale under practical farming and natural boundary conditions to estimate the effectiveness of management practices, which are introduced to reduce the groundwater pollution by diffuse pollutants. However, quantitative information on leaching losses of nitrate and other diffuse pollutants to groundwater is only available at great costs and with several limitations to the applied methods so far. This has been shown for tile drains (Elliott et al. 1998; Kladivko et al. 1999; Pampolino, Urushiyama, and Hatano 2000; Kladivko et al. 2004), lysimeters (Jemison and Fox 1992; Jene 1998; Pampolino, Urushiyam, and Hatano 2000), suction plates (Dressel 2002; Siemens 2003; Kosugi and Katsuyama 2004), suction cups (Kung 1990; Selker et al. 1992; Pampolino, Urushiyama and Hatano 2000; Elliott et al. 1998; Grossmann and Udluft 1991; Netto 1999) and soil coring (Pampolino, Urushiyama and Hatano 2000; Netto 1999).

The work and cost problem is mainly related to the repeated sampling and analysis necessities. For lysimeters high investment and maintenance costs add to the limited applicability. The technical limitations are mostly due to the heterogeneity of solute transport in the field and the transfer of soil solution concentrations into mass fluxes.

Infinte-sink methods seem appropriate to avoid frequent sampling. (Skogley 1992) developed a method, in which ion exchange resin is packed tightly into plastic nets with small grid spacing. This allows for diffusive movement of exchangeable ions to the resin, which acts as an infinite sink. This method also captures a part of the solute transported through convection. The two processes can not be separated, however, so that the amount of leached N or plant available diffusive N can not be calculated. Still, in comparison to suction cups the ion-exchange method was more appropriate to detect fast spontaneous movement of bromide under intermittent unsaturated flow conditions (Yang and Skogley 1992; Li, Skogley, and Ferguson 1993).

I took up the idea of ion-exchange resin to capture solutes, but wanted a method to measure the absolute leaching losses on a [mass area^{-1} time^{-1}] basis, which closes the mass balance for the soil - groundwater path. Therefore, it was necessary to differentiate between convective and diffusive transport to the resins. In addition, the water and solute flux had to be representative for a defined cross sectional area of the soil under a range of relevant environmental conditions.

The objectives of this paper are (i) to present the method developed which I call SIA (Self Integrating Accumulator) and (ii) to demonstarte potentials and limitation of the method. Fore the latter objective I tested the following hypothesis: (I) The method collects the flux of conservative ionic solutes quantitatively. (II) The method collects solutes transported mainly through preferential flow. (III) The method yields reasonable solute-flux data under field conditions.

2.2 Materials and Methods

In order to test the hypothesis I conducted the following experiments:

I estimated accuracy and precision of the method with a chloride mass balance experiment on 6 agricultural fields with 5 replicates.

To examine the capability to intercept preferential flow paths I used 3 qualitative approaches: IIa. A dye tracer experiment to mark the flow paths in the soil and around the SIA. IIb. An experiment with a strongly sorbing solute (tributyltin), which presumably is transported only preferentially. IIc. Nitrate leaching during a very dry summer, where matric flow is very unlikely.

I measured the mean nitrate losses under different land uses: forest, long term fallow and agriculture.

2.2.1 Self Integrating Accumulators (SIA)

The Self Integrating Accumulators (SIA) consist of a cylinder (10 cm height; 10 cm diameter) with a fine net on the bottom side filled with a mixture of quartz sand, quartz silt and an anion-exchange resin (Figure 2-1; right side) or a hydrophobic adsorbent for tributyltin. All materials were provided by TerrAquat, Stuttgart. The mixture develops its own suction under drying soil conditions, so that leaching in unsaturated soils is also intercepted.

The soil water containing the target solutes enters the open top of the SIA, passes through and flows out at the lower end. During the passage the solute is sorbed to the adsorber and immobilised. In this way, all transported target substances are accumulated inside the SIA. Therefore, the SIA yields an integrated total value of the leached amount for a defined cross sectional area of the soil during the measurement period. This would allow for a projection to larger areas, if the measured values are representative for the same cross sectional area of the soil as of the SIA. This is to be tested in experiment I.

It should be stressed that I do not measure residual concentrations or masses in the soil, but only *solutes transported by convection* through the cross section of the top of the SIA and that I *do not* intend to *get information on how much water carried the solutes* that are captured.

The SIA are installed such that the soil on top of them is undisturbed (Figure 2-1, left side). Hence the pore system, which is crucial for solute transport under natural conditions, is preserved.

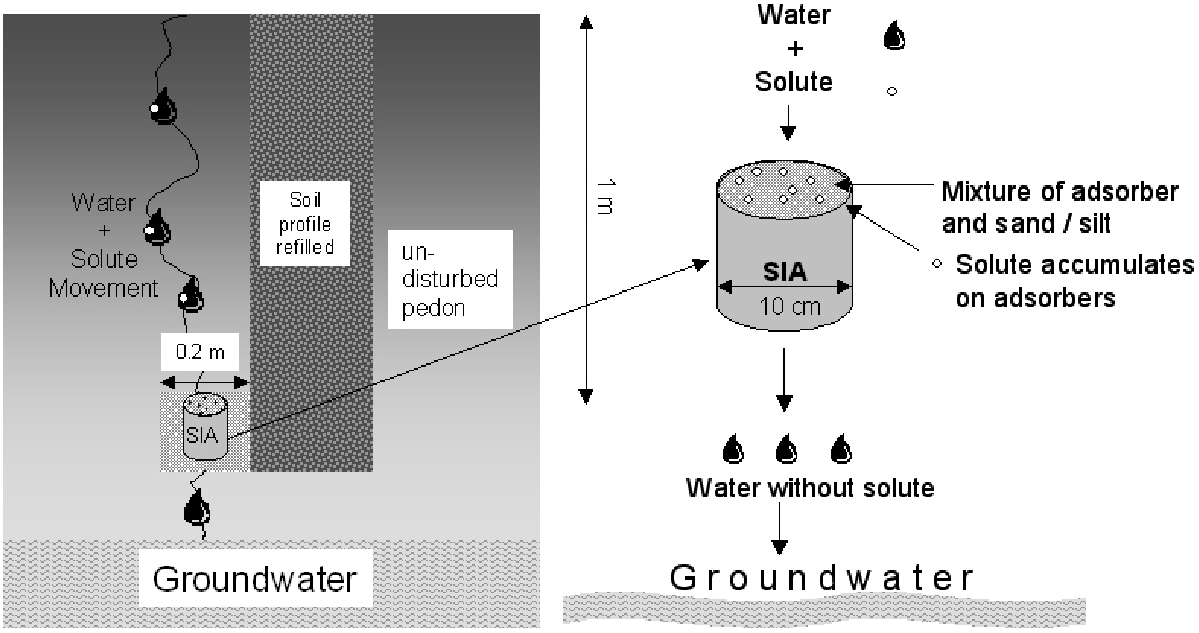

Figure 2-1: Installation and functional principle of the Self Integrating Accumulator (SIA): The SIA is located below the undisturbed soil and surrounded by material with the same hydraulic properties. Solutes are extracted out of the water by (specific) sorption, while water passes through.

To that end soil profiles are dug to 20 cm below the envisaged installation depth. From the wall of the profile side tunnels are dug under the undisturbed soil, in which the SIA is installed afterwards. The side tunnel and the profile are closed after installation. Thus, after installation soil management like ploughing, sowing, harvesting etc. can be done without limitation, because no continous sampling of solution is necessary. The installation under an undisturbed soil led to the idea that the mass flux by preferential flow (like in earthworm holes, fissures) may also be sampled successfully, because these structures simply end on the SIA-surface. A qualitative answer shall be given by the experiments II a,b,c.

The installation time of the SIA may typically be 6 months or a vegetation period. After this, the SIA are recovered and the resin-substrate mixture within the cylinders is then split into 3 fractions, the upper 5 cm, middle 1 cm and bottom 4 cm. The upper and middle layer fractions are analysed (see experimental sections) separately. The bottom fraction normally is discarded. Only the upper 5 cm are used for the interpretation of mass flow from above. The middle fraction is used as a control whether the exchange capacity of the top layer was sufficient and no target substance travelled deeper than 5 cm from the top. The lowest layer is discarded, because its use is as a barrier for a mixture of possible upward fluxes like diffusion or capillary rise, which should not be mingled with the downward flow.

2.2.2 Experiment I: Chloride tracer mass balance under field conditions

The tracer application took place in October 1999 on six fields owned by local farmers and previously used for vegetable cultivation. Some of the fields were already tilled; on others the plant residues from the previous crop were still visible. None of the fields contained vegetation during the measuring period. Therefore, chloride uptake by plants can be excluded.

At these six field sites between 20 and 250 km apart in SW-Germany with varying soil management and soil properties I installed 5 SIA per site and applied the chloride tracer. The idea was – given the limited resources – an experiment on several sites with fewer replicates would be more meaningful than the same experiment on only one site with more replications. Statistically, if we include more heterogeneity (different fields) and still get a sensible tracer recovery, we have more information on the validity of the method than with limited heterogeneity (one field).

2.2.2.1 Soils and site description

Site Karlsruhe is situated on the lower terrace of the river Rhine and developed on sandy alluvial material. All other sites are influenced by loess deposits to some degree, which is most typical for arable land in South West Germany and large parts of Central Germany.

The average temperature is between 7 - 8.5°C and the mean annual precipitation varies from 700 to 800 mm. During winter approximately 150 – 250 mm of water are leached from the unsaturated zone towards groundwater. The sites are between 80 m and 350 m above sea level and the inclination of all experimental fields did not exceed 2° (Table 2-1).

Table 2-1: Selected soil properties of the tracer experiment sites

Site	Soil type (FAO)	Texture (USDA) A-horizon / B-horizon	pH (0.01 $CaCl_2$) A-horizon / B-horizon	CEC_{pot} [$mmol_c$/kg] A-horizon / B-horizon
Bad Wimpfen	Stagnic Luvisol	Silty clay loam / Silty clay	6.4/ 6.1	245/ 295
Ulm	Calcic Luvisol	Silt loam / Silty clay loam	5.5/ 5.7	185/ 243
Tuebingen	Haplic Luvisol	Silt loam / Silt loam	6.6/ 7.2	300/ 290
Stuttgart	Stagnic Luvisol	Silty clay loam/ Silty clay loam	6.5/ 6.0	210/ 220
Ludwigsburg	Eutric Regosol	Silt Loam/ Silt Loam	6.7/ 6.8	158/ 145
Karlsruhe	Eutric Cambisol	Loamy sand/ Loamy sand	5.3/ 5.5	77/ 65

2.2.2.2 Experimental

At these six field sites I installed 5 SIA per site in 60 cm depth in a transect of 150 cm length.

On top of these plots I applied 1 kg of NaCl on an area of 2 m * 1.5 m (5.7 Mol*m^{-2}) evenly through a fine net. The tracer was then dissolved with an evenly distributed irrigation of 2.5 mm.

Before the application of the tracer I collected soil samples from 0 - 15; 15 - 30; 30 - 50; 50 - 60 cm soil depth at each site, which were analysed for chloride background concentrations.

The field sites were then left untreated for six months to allow leaching of chloride by the winter rains.

At the end of March 2000 the soil body on top of the installed SIA was sampled on all sites at depth of 0 - 15; 15 - 30; 30 - 50; 50 - 60 cm to allow for chloride residue analysis. This was done by collecting 3 soil core samplers (100 m^3) and about 1 kg of loose soil material at every depth. I sampled vertically at the profile wall and horizontally on plains at several depths to avoid singularities at the profile wall. In addition, large undisturbed samples (~ 10 kg / site) were taken from the top 15 cm of the soils, because the largest residual amounts and largest bulk density heterogeneities were expected in this soil depth. I also took samples from the disturbed area in the refilled pit and from undisturbed soil close by to account for anomalies or later chloride application.

At the same time the SIA were collected for analysis. The resin-substrate mixture within was sampled in three layers (Top 5 cm; Middle 1 cm; Bottom 4 cm). Top and middle layer were analysed for chloride after a 0.5 M H_2SO_4 extraction at a water-solid mass ratio of 4:1.

Soil cores were analysed for bulk density and water content. All soil samples were analysed for chloride content of homogenised samples in 2 replicates to control homogenisation. Laboratory analysis was performed with a chloride selective electrode against a Pt reference electrode (WTW, Weilheim) in a range of 10^{-1} to 10^{-6} mg Cl*L^{-1}.

2.2.2.3 Calculations

Performance of the SIA was calculated as:

Recovery [%] = (Recovered amount SIA [mol * m^{-2}] /(Total amount applied [mol * m^{-2}] – Residual amount in top 60 cm of soil profile [mol * m^{-2}])) * 100 %

The residual amount is given by:

Residual amount [mol * m^{-2}] = Σ_i {Concentration [g_{Cl} * L^{-1}] * sample weight^{-1} [L * g_{soil}^{-1}] * layer$_i$ [m] *bulk density$_i$ [g_{soil} * m^{-3}]*molar mass^{-1} [mol * g_{Cl}^{-1}]} for each soil layer i from 0 – 60 cm.

2.2.2.4 Statistics

The data were normally distributed for the whole set (Kolmogorov-Smirnov-Test). Therefore, an analysis of variance was performed to distinguish between experimental sites.

I planned the design to cover a wide range of external factors like management, microclimate, soil etc. and were mainly interested in the general applicability of the SIA method regardless of sites. Therefore, it was interesting to treat the whole data set as one experiment. This is also justified statistically by the fact that the analysis of variance did not yield significant differences between the experimental sites.

I used combinatorial analysis to calculate the error of estimate for all numbers of replications. Combination mathematics deals with the question: How many possibilities are there to draw at random distinguishable pieces (e.g. single measurements) from a given number of pieces (e.g. a data set) without putting them back. Probabilities can then be calculated by dividing the chance (number of possible draws) to draw a certain subset or a number of subsets by the total possible combinations.

The results can then be used for statistical interpretation. For example, if an experimentator chooses to measure leaching triplicate with SIA, what would be the mean error and how would this improve, if he chose to replicate his measurements 15 times with this method?

To calculate e.g. triplicate replication I drew every possible combination of 3 measurements from our data set of 30, which makes 30 * 29 * 28 or 30! / 27! = 24,360 possible combinations. To calculate this for all sensible replications (2 – 29) about 1 billion calculations were necessary. All results were then grouped in 1 % steps to get cumulative frequencies of tracer recovery with the mean experimental recovery set as 100 %. The experimental mean was set as 100 % instead of the real mean, because we can not know a priori, whether we will approach 100 % of the real value with more replicates due to possible systematic errors of the method. These cumulative frequencies were then used to see how many combinations fall into a certain recovery range, e.g. between 80 % and 120 %, and how many do not.

The advantage of this method is that confidence levels can be obtained directly from the data of the validation experiment without any statistical assumption on the data distribution.

2.2.3 Experiments II a), II b) and II c): Sampling of preferential flow paths

2.2.3.1 Experiment II a): Brilliant Blue tracer experiment for the identification of preferential flow paths

I wanted to test qualitatively, whether SIA are able to intercept preferential flow paths in the soil. Therefore, I used the dye Brilliant Blue in two experiments at Muenster, NW-Germany, and Bern, Switzerland. In Muenster I installed SIA at 35 and 60 cm depth on a Fimic Anthrosol with a loamy sand texture and applied an irrigation of 30 mm on a 3* 2 m² plot on top of the SIA. The irrigation water contained approximately 1 $g*L^{-1}$ of the dye Brilliant Blue, which colours the actual flow paths, through which it is moving.

After 2 hours I dug to the SIA and evaluated optically the presence of Brilliant Blue in the soil profile and on top of the SIA.

A similar experiment was performed on a site near Bern (Inforama Rütti, Zollikofen). The soil was an Eutric Cambisol derived from a heterogeneous morainic silt loam to clay loam material with < 5 % of stones. Here, the installation depths of the SIA were 15, 30 and 60 cm.

2.2.3.2 Experiment II b): Mass flux experiment with the sorbing solute tributyltin

In a field experiment of 4 months (April 2000 – July 2000) I applied sewage sludge containing a known amount of tributyltin on 2 agricultural fields afterwards sown with carrots.

Soils and Sites

Both sites had an inclination < 1^0. Site Forcheim is situated on the lower terrace of the river Rhine and developed on sandy alluvial material. Its elevation is 116 m above sea level, the mean annual temperature is 9.5^0C and the mean annual precipitation is 650 mm. Site Rottenburg is situated on an elevation of 440 m above sea level SW of

Stuttgart and developed on loess deposits. Its mean annual temperature and precipitation are 8^0C and 750 mm (Table 2-2).

Table 2-2: Selected soil properties of the tributyltin experimental sites

Site	Soil type (FAO)	Texture (USDA) A-horizon / B-horizon	pH (0.01 $CaCl_2$) A-horizon / B-horizon	CEC_{pot} [$mmol_c$/kg] A-horizon / B-horizon
Forchheim	Dystric Cambisol	Sandy loam / Loamy sand	5.1/ 5.5	48/ 14
Rottenburg	Calcic Luvisol	Silty clay loam /Silt loam	7.3/ 7.1	243/ 196

Experimental

At both sites SIA were installed in two plots (100 m²) at a depth of 80 cm. The SIA were distributed evenly in 5 pits containing 2 SIA (10 replicates) at each plot. Wet sewage sludge equivalent to 5 t ha^{-1} dry substance was applied at one plot at each site. The other plot received no sewage sludge and served as a control. Carots (Daucus carota ssp. Sativa ‘Nantaise’) were sown and harvested 3 months later. After the harvest, SIA were recovered and taken to separate analysis.

Analysis

Tributyltin was analysed by the Wave Ltd. Laboratory (Stuttgart) in a modified DIN 38 407-13 procedure with a hexane extraction, derivatisation with ethylborate and measurement with GC-MS using tripropyltin as an internal standard.

2.2.3.3 Experiment II c): Mass fluxes of nitrate during a dry vegetation period

General

Nitrate leaching loss mass fluxes were measured in a 3-year field experiment at 9 sites and 2 fertilizer treatment plots per site. 10 SIA per plot (180 total) were used to monitor continuously nitrate leaching losses during vegetation (March to September) and winter period (October to February). I present the results from the vegetation period 2003 because of its unusual weather conditions.

Soils and sites

All nine sites are situated in a hilly region of shell-limestone underlying weathered loess deposits. The loess loam cover averages 60 cm. The site inclination ranges between < 1^0 to 4^0. The mean annual precipitation is 650 mm and mean annual temperature is 7^0C.

The soils are mostly Calcic Luvisols (FAO) or similar. The pH is in the range of 6.3 – 7 for the top and subsoils. The CEC is in the range of 200 – 350 $mmol_c\ kg^{-1}$. The texture is silty loam to silty clay loam.

Experimental

Each site was treated with two fertilizers with exactly the same content of N. CULTAN (Controlled Uptake Long Term Ammonia Nutrition) is a concentrated Ammonium-Nitrate-Urea solution fertilizer, which was placed in thin lines close to the seeds, whereas KAS (Calcareous NH_4NO_3) is a granulate, which was spread evenly over the field.

Each site has the same basic 3-year crop rotation of winter rape (Brassica napus L. var. napus) - winter wheat (Triticum aestivum L.) – phacelia intercrop (Phacelia tanacetifolia Benth.) - summer barley (Hordeum vulgare L.). In each of the 3 experimental years each crop was represented by 3 sites, so that after the experiment each site had the same rotation, but with a different starting crop.

The nitrate leaching losses were monitored with 10 replicate SIA in 60 cm depth (average loess cover depth) on each site and treatment (180 total). The SIA on all fields were exchanged within 3 - 4 consecutive days in March and September.

Basic weather data (Precipitation and temperatures) were collected at two sites within the experimental area.

Analysis

Each SIA was split into 3 layers (see above) and the top and middle layers were analysed separately. The samples were homogenized and an aliquot of 15 g was extracted with 60 mL of a 1 M NaCl solution. The measurement was performed on a N rapid flow analyser (SANplus, Skalar, Breda, The Netherlands).

2.2.4 Experiment III: Nitrate losses under different land uses

General

A four year monitoring experiment was performed to highlight the possible contributions of different land uses to the high nitrate loads in an aquifer in central Germany. Three agricultural fields with regional crops, a long term fallow and a forest site were monitored for nitrate losses with SIA.

Soil and site description

The sites are situated on an upper terrace of the river Main (Central Germany) covered with coarse to medium sized sandy eolian deposits (flat dunes) with a depth of 1 – 2 m. The soils are Dystric Cambisols with a pH of 5 (forest) to 6.5 (agriculture) in the top soil. All sites have an inclination of < 1 °. The elevation is 130 m above sea level, the mean annual temperature is 9°C and the mean annual precipitation is 680 mm.

Experimental

At all 5 sites SIA were installed at a depth of 90 cm. The SIA were distributed diagonally across the fields (3 crops and fallow) in three pits containing 10 SIA and a transect of 4 pits within the forest, also containing 10 replicates. SIA were changed at the end of September and in April from Sept. 1998 to Sept. 2002.

Analysis

Analysis was the same as in 2.2.3.

2.3 Results and Discussion

2.3.1 Experiment I: Tracer Recovery

Precision

The chloride tracer recovery with the SIA method ranged between a mean of 63 % with a standard deviation (Std. dev.) of 44 % for site Stuttgart and a mean of 128 % (Std. dev.: 15 %) for Karlsruhe with an overall mean of 92 % (Std. dev.: 39 %) for all 30 replicates. The mean recoveries were 66 % for Tübingen, 89 % for Bad Wimpfen, 104 % for Ulm and 104 % for Ludwigsburg. This is a better recovery for all sites than in the reported examples for other methods, where chloride or bromide were used as a tracer. Dressel (2002) overestimated by 30-40 % with suction plates, Jemison and

Fox (1992) recovered 45 -58 %, but Boll, Selker and Nijssen (1991) only 6.5 % in pan lysimeters. Jene (1998) recovered 48 % with a suction cup grid and 77 % in a monolith lysimeter. Passive capillary or wick samplers (Boll, Selker, and Nijssen 1991; Brandi-Dohrn et al. 1996) recovered between 29 – 63 % of a bromide tracer. Only Siemens (2003) got similarly good results (118 % recovery) with tension controlled suction plates in a sandy soil, but his experiment was limited to a 2-day irrigation experiment.

Therefore, the SIA method with a total mean of 92 % is more efficient in measuring chloride leaching losses in a long term leaching experiment than any other reported field method.

Chloride and bromide have been used to evaluate conservative solute transport and to serve as a good approximation for water movement (e.g. Wang et al. 2003; Brown et al. 2000; Brandi-Dohrn et al. 1996; Li, Skogley, and Ferguson 1993). It has been shown that both are equally suitable as tracers (Saffigna 1977), even though anion exclusion may be responsible for a slightly faster movement compared to tritium tracer studies (Logsdon, Keller, and Moorman 2002).

Therefore, our understanding is that chloride as a conservative tracer with insignificant adsorption in the investigated soils is a good indicator for the water flux in the soil. If the chloride mass balance is correct, the water balance is supposed to be correct as well. I conclude that I did not only measure solute flux within an error of 10 %, but also the water flux through the SIA was represented within the same range of error.

This is important to decide whether the method may also be suitable for sorbing and/or non-conservative tracers. The effectiveness of the method with these substances depends on the validity of the water balance and suitable adsorber materials.

Accuracy

From the statistical evaluation of the samples from 6 field sites (Figure 2-2) one can calculate the amount of replications necessary to obtain a certain accuracy of the estimated mean.

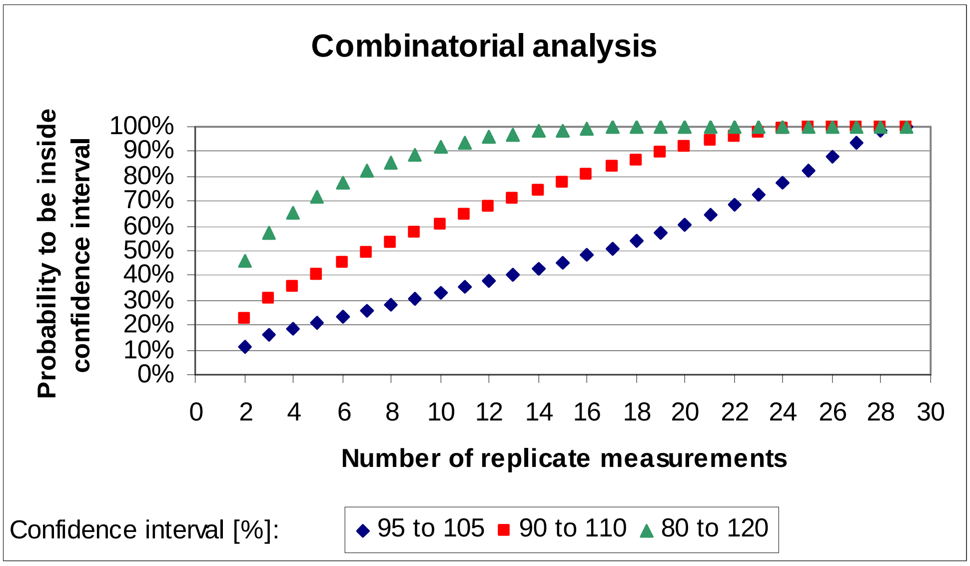

Figure 2-2: Results of an exact combinatorial analysis. Relation between SIA method precision and number of replications. At least 10 replicates are needed to achieve 20 % accuracy with a probability of > 90 %.

According to combinatorial analysis two replicates estimate the overall mean within an error of 20 % in less than 50 % of the six month measurements, whereas 10 replicates yield a value within the 20 % confidence interval in more than 90 % of the measurements. A high accuracy of the mean (e.g. +/- 5 % estimates) can only be obtained with high replication numbers > 27.

It also has to be considered that I compare relative precision to the overall mean of 92 % recovery of the true value. The method may be able to approach 100 % recovery with higher replications. In this case, the prediction from our analysis may be wrong for n close to 30 and therefore also for high accuracies.

Brandi-Dohrn et al. (1996) calculated that 25 passive capillary (wick) samplers or 37 suction cups were required to estimate the mean within an error of 30 % for a 0.05 confidence interval. This compares with 12 SIA replicates for an error of 20 % at the 0.05 confidence interval and 10 replicates at the 0.10 confidence interval. This difference to our results may be due to the wider suction range of the SIA compared to wick samplers and the better defined sampling area compared to the suction cups.

All discussed methods need high replication numbers due to the heterogeneity even within one ‘homogeneous’ soil unit. For example, Netto (1999) showed in a field study that for none of the tracers bromide, nitrate and bentazon a distance dependent autocorrelation existed, which is a clear indicator of inherent heterogeneity.

Thus, the SIA shows a favourable precision and spread to measure the flow of the non-sorbing tracer chloride and I deduce that the water flux through the SIA is approximately representative for the flux through the same cross sectional area in the soil.

2.3.2 Experiments II a, b, c: Qualitative evidence for sampling of preferential flow

It is a priori clear that every measurement disturbs the very system it tries to describe. Thus, it is crucial to know, whether certain main processes are excluded or included in the measurement. It is quite common to differentiate solute transport into normal/matric/Richards/capillary and fast/preferential/macropore flow, even though the concepts to discern them differ.

Therefore, I needed to test, if the flow captured by the SIA method includes part or all of possible preferential flows. Unfortunately, the reasons and circumstances for preferential flow are manifold. Therefore, I picked 3 different situations, where preferential flow supposedly is the main explanation for solute transport.

2.3.2.1 Experiment II a): Brilliant Blue tracer experiment for the identification of preferential flow paths

Figure 2-3 is taken from the dye tracer experiment in Bern, Switzerland. Black and dark shades represent regions with visible Brilliant Blue dye. Squares show the locations of the side tunnels in the profile, which are still closed.

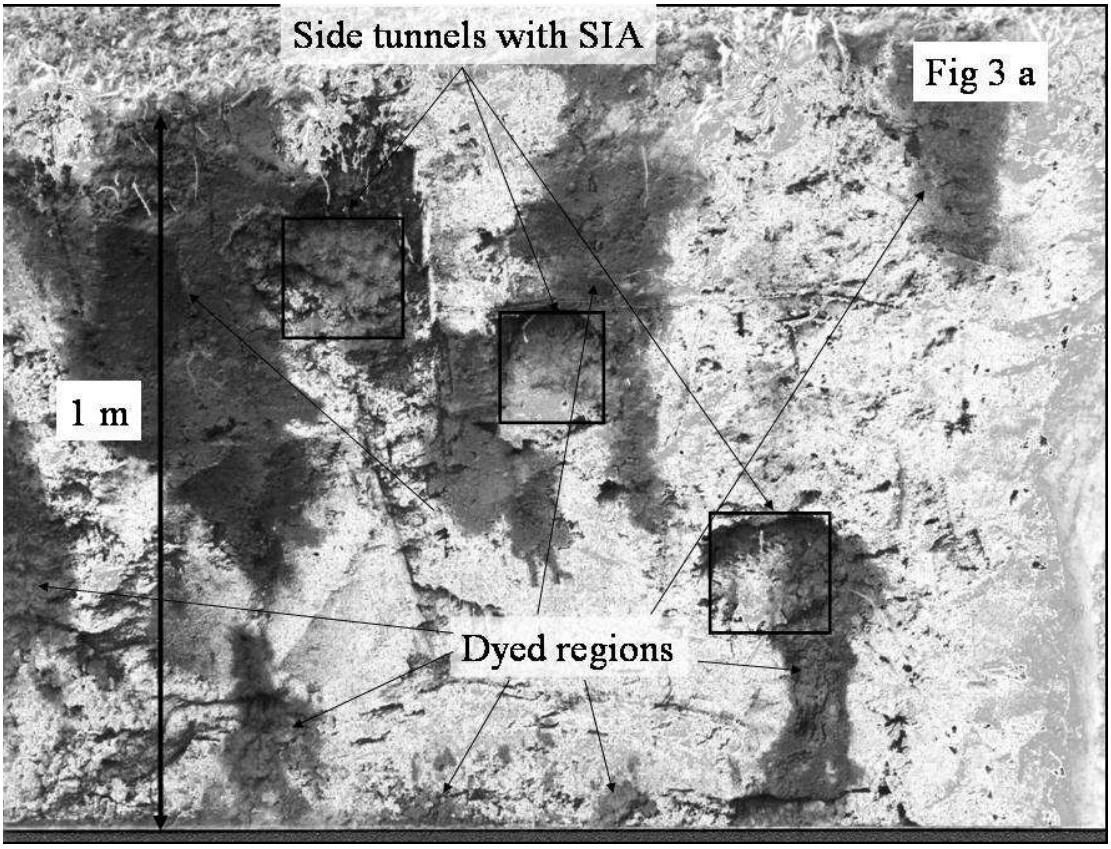

Figure 2-3: Soil Profile (Bern) after a Brilliant Blue dye tracer experiment. Black and dark grey show presence of dye. Squares show the closed entrances of the side tunnels under the undisturbed soil in 15, 30 and 60 cm depth, where the SIA are installed.

It can be seen that in this short term experiment the colour of the dye is not only distributed over the soil profile, but also flows out of the side tunnels, where the SIA are installed. Therefore, the SIA and refilling of the tunnel did not pose an obstacle to the applied water flow. The lowest SIA (60 cm depth) also intercepted a preferential flow path, which is not visible in the upper part of the profile, but lies deeper in the body of the soil. Here, only the right side of the tunnel is coloured indicating a smaller flow path than for the upper SIA at 15 and 30 cm depth.

Figure 2-4 is taken from the dye tracer experiment in Muenster, Germany. Black and dark shades represent regions with visible Brilliant Blue dye. The plain on top of a SIA, which stuck in a side tunnel during the experiment, is prepared, but the SIA only partly uncovered. About one quarter of the SIA is visible. The casing is marked as thick black line. The rest is covered under the undisturbed soil marked as the shaded and striped region on the upper and right hand side. The lower and left hand side show formerly undisturbed soil and filling material of the tunnel in the same plain outside the SIA. The dye is found inside and outside the SIA and the pattern is continuous, e.g. ‘south’ of the border between the shaded area and the prepared plain Figure 2-4.

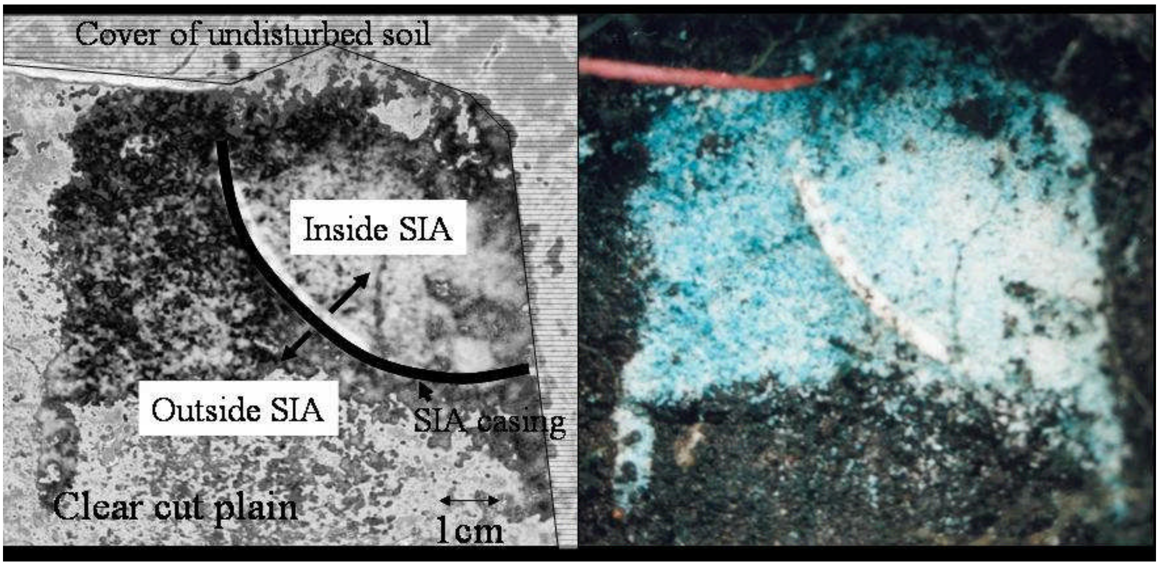

Figure 2-4: SIA in 60 cm depth after a Brilliant Blue dye tracer experiment (Muenster), partly excavated. Left: Black and white conceptual picture. Right: Color Picture. Black and dark grey (left) or blue (right) show presence of dye. Shaded area (up and right) is not yet excavated. Black quarter circle is the casing of the SIA and separates outside and inside.

Dye tracers have been used extensively to mark preferential flow paths (e.g. (Wang et al. 2003; Ghodrati and Jury 1990; Roth et al. 1991). In both of our experiments dye could be found in the SIA. Thus, the SIA intercept preferential flow at least qualitatively in short term dye experiments.

2.3.2.2 Experiment II b): Mass flux experiment with the sorbing solute tributyltin

Tributyltin is a sorbing substance with a reported K_{OW} of 251 (O'Loughlin, Traina, and Chin 2000) and a very high affinity to Aldrich Humic Acids with a K_{OC} of $10^{6.1}$. It is thought to be little mobile in a K_{OW} - classification for pesticides by (Wilson, Duarte-Daidson, and Jones 1996) grouping pesticides in 4 classes between very mobile and little mobile and highly sorptive to humic substance.

On site Forchheim (sandy loam over loamy sand) 0.5 % of the applied tributyltin were leached out of the rooting zone into the SIA. Only one out of ten SIA contained a detectable amount of tributyltin. In Rottenburg (silty clay loam over silt loam), 2.2 % of the applied amount was lost by leaching. Four out of ten SIA contained detectable amounts of tributyltin. The SIA at both control plots contained no tributyltin.

In the experiment, microbial degradation and other dissipation processes could not be quantified and residues in the soil, if any, were below the detection limit of 1 $\mu g*kg_{soil}^{-1}$. Therefore, the experiment gives no quantitative information on the performance of the SIA method. The experiment was performed in late spring and summer, a period when the soil becomes dry in Germany and leaching of water is related to heavy rains. The chemical properties of tributyltin can be compared to those of pesticides, for which preferential flow is thought to be the main transport mechanism (Flury 1996; Elliott et al. 1998).

Preferential transport is the most likely process for the detection of any tributyltin mass flux and that the SIA were capable to detect it. Furthermore, the experiment shows that by accumulation in the SIA tributyltin was detectable, whereas no residues could be found in the soil probably due to the lower detection limit.

2.3.2.3 Experiment II c): Mass fluxes of nitrate during a dry vegetation period

The measurement from March to September 2003 took place under extremely dry conditions in the study area. The precipitation sum during that period was 237 mm compared to an average of 400 mm in the years 1977 to 1995. It was a period, when potential evapotranspiration always exceeded the precipitation. Still, some rainstorm events at the end of July or a wetter period in May (Figure 2-5) may have induced preferential flow.

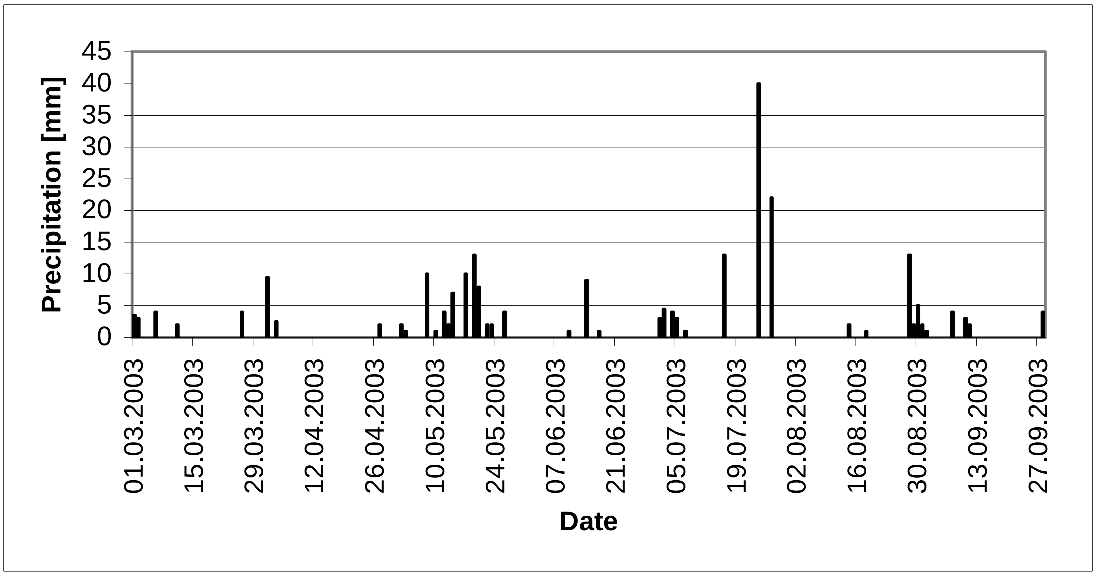

Figure 2-5: Daily precipitation during a field experiment for the leaching of nitrate on nine farm fields with two fertilizer treatments. Marked rainstorm events at the end of July.

The N leaching data (Figure 2-6) from 180 SIA show that in 56 % of the SIA N-transport was not detectable, but for several measurement points in space, leaching losses were considerable. Three SIA (1.8 %) received N-losses of more than 10 kg N/ha during the installation period. About 20 % of the SIA received more than 1 kg N/ha. Each of the nine fields had at least two out of 20 SIA with detectable N-losses. On one field with notably higher clay content due to a mixing of the loess with shell limestone residual clay every SIA contained detectable amounts of nitrate, which I attribute to the higher frequency of shrinkage cracks visible at the end of the measurement period. Field heterogeneity leading to heterogeneous flux has also been reported by Netto et al. (1999), who showed that no autocorrelation existed between adjacent nitrate solution measurements which were repeated during a summer period in SE France.

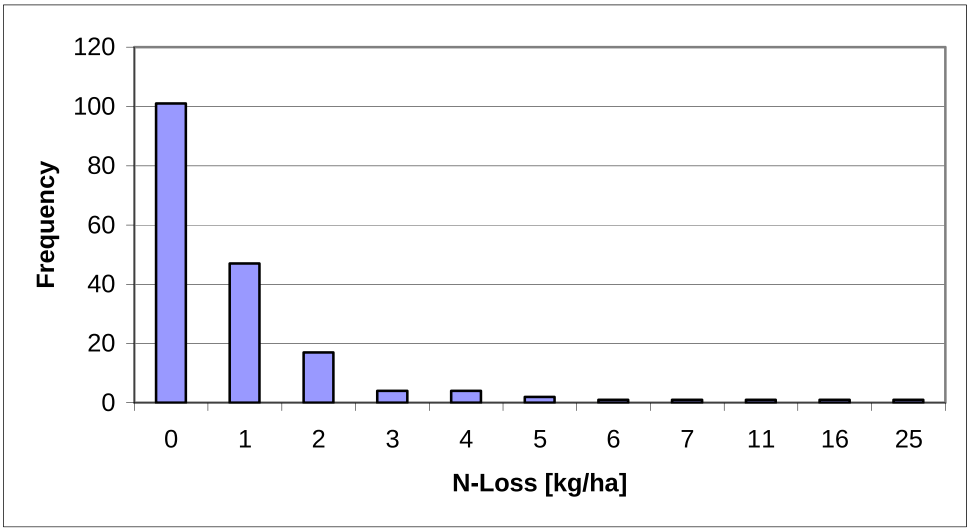

Figure 2-6: N-Leaching (60 cm below surface) under dry conditions. Higher N-losses in a small number of SIA may be explained by the sampling of preferential flow. (Total N = 180)

Preferential flow in only a few points in space, probably induced by scattered rainstorm events is the most likely explanation for our data. Again, we see this as qualitative evidence for the capability of the SIA to sample preferential flow paths. In this case, the sampling took place under very dry soil conditions, where e.g. suction cups would not detect anything.

2.3.3 Experiment III: Plausibility comparison of different land uses

It is well known that different land uses contribute differently to nitrate or other solute leaching from the root zone. This should be reflected by the SIA measurement.

In the average of a 4-year measurement, forest looses 7 kg N ha^{-1} (Std. error: 3 kg N ha^{-1}), a long term fallow 5 kg N ha^{-1} (Std. error: 1 kg N ha^{-1}) and three agricultural fields 21 kg N ha^{-1} per year (Std. Error: 3 kg N ha^{-1}, Figure 2-7).

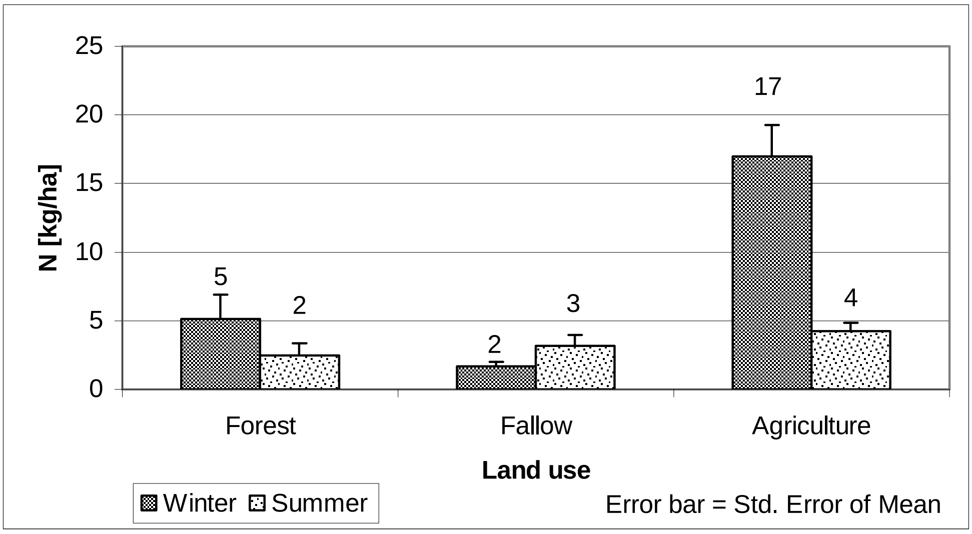

Figure 2-7: Average N-Losses by leaching under different land uses. Data from 7 sites (5 crop fields; 1 long term fallow; 1 forest) and 3 years of continuous measurement (Summer: N=219; Winter: N=191).

The area has rather poor soils for the farmers. The limiting factor is the small water retention capacity of the sandy soils. The farmers therefore apply lower N-amounts (e.g. 100 kg N*ha^{-1} for winter wheat) than in other areas (Winter wheat: 120 – 160 kg N*ha^{-1}). The N-losses of ~ 20 kg N*ha^{-1}*year^{-1} are in good agreement with long term experiments in Eastern Germany on a Haplic Phaeozem with sandy loam texture (Graz et al., 1997). In these, leaching losses were calculated as the difference between long term inputs and removal by the harvest in a one hundred year rye (Secale cereale) experiment. For several treatments of N, P, K fertilizers the surplus is in the range of 18 - 36 kg N ha^{-1} year^{-1}. Atmospheric N-deposition or potential denitrification were not considered in this case.

Zhu, Fox and Toth (2003) report average N-losses of 17, 39 and 112 kg N ha^{-1} year^{-1} with N-fertilizer treatments of 0, 100 and 200 kg N ha^{-1} year^{-1} respectively. These studies show that with comparable N-inputs comparable losses occur under agricultural fields in the long run. Cavero, Beltran and Aragues(2003) state that in two watersheds in the Ebro valley (Spain) under high quality irrigation management N-losses ranged between 8 and 22 % of the N-inputs, which is in the percent range of our data.

The groundwater recharge in this region is about 200 mm year^{-1} and the groundwater wells produce water with nitrate concentrations of 40 – 60 mg L^{-1} in areas where the recharge is predominantly from agricultural land. An extrapolation of our measured mean to a whole recharge area would yield a concentration of 50 mg L^{-1} for the leaching water, which builds up the groundwater. Other measurements (own data, unpublished) show that denitrification can be neglected at least for some wells, so that a direct comparison is possible.

Thus the data produced in this 4-year experiment are plausible on the background of other literature and the hydrological data in the study area.

2.4 Conclusions

A new method (Self-Integrating Accumulators, SIA) has been suggested to measure directly the total leaching losses of solutes. It combines the adjustment to the soil matric potential with the accumulation of a range of solutes onto suitable adsorbers. The SIA method lowers labour and analysis costs compared to soil solution sampling, but it has no time resolution during the installation period.

The validation of the SIA with a tracer mass balance experiment has shown that the method is capable of measuring the long term leaching losses of solutes under field conditions. The error of the measurement is < 10 % with 30 replicates. No less than 10 replications per ‘homogeneous’ field are recommended to hit the mean +/- 20 % with > 90 % probability.

Evidence from a short term dye tracer experiment at two sites, a 6-month field experiment with nitrate under dry soil conditions and a 4-month field experiment with tributyltin leads to the conclusion that the SIA method is capable of measuring solute transport by preferential flow. However, the evidence is qualitative, because all experiments lacked a proper mass balance. Therefore, it cannot be decided as yet, whether and with how many replications the SIA capture preferential flow quantitatively.

An applied groundwater catchment study with nitrate has shown the ability of the SIA to get plausible information on the relative contributions of different land uses to the groundwater pollution.

I conclude that the method may be an alternative to existing field methods, if the main objective is the quantification of a mass $area^{-1}$ solute flux.

Literature

Boll, J., J. Selker, and B.M. Nijssen. 1991. Water quality sampling under preferential flow conditions. Paper read at Int. Symposium on lysimetry.

Brandi-Dohrn, F.M., R.P. Dick, M. Hess, and J.S. Selker. 1996 a. Field evaluation of passive capillary samplers. *Soil Sci. Soc. Am. J.* 60:1705-1713.

Brandi-Dohrn, F.M., R.P. Dick, M. Hess, and J.S. Selker. 1996 b. Suction cup sampler bias in leaching characterization of an undisturbed field soil. *Water Resources Research* 32, No. 5:1173-1182.

Brown, C.D., J.M. Hollis, R.J. Bettinson, and A.; Walker. 2000. Leaching of pesticides and a bromide tracer through lysimeters from five contrasting soils. *Pest Management Science* 56:83-93.

Cavero, J., A. Beltran, and R. Aragues. 2003. Nitrate exported in drainage waters of two sprinkler-irrigated watersheds. *Journal of Environmental Quality* 32 (3):916-926.

Directive establishing a framework for the protection of soil. *Directive 2004/35/EC* (Proposal).

Dressel, J. 2002. Transport von Ethidimuron und Methabenzthiazuron in einer Parabraunerde - Experimente und Modellierung, Institute for Chemistry and Dynamics of the Geosphere, University of Bonn, Jülich.

Elliott, J.A, A.J. Cessna, K.B. Best, W. Nicholaichuk, and L.C. Tollefson. 1998. Soil processes and chemical transport: Leaching and preferential flow of clopyralid under irrigation: Field observations and simulation modeling. *J. Environ. Qual.* 27:124-131.

Flury, M. 1996. Experimental Evidence ofTransport of Pesticides through Field Soils - A review. *J. Environ. Qual.* 25:25-45.

Ghodrati, M., and W.A. Jury. 1990. A field study using dyes to characterize Preferential flow of water. *Soil Sci. Soc. Am. J.* 54:1558-1563.

Grossmann, J., and P. Udluft. 1991. The extraction of soil water by the suction cup method: A review. *J. Soil Sci.* 42:83-93.

Jemison, J.M., and R.H. Fox. 1992. Estimation of zero tension pan lysimeter collection efficiency. *Soil Science* 154:85-94.

Jene, B. 1998. Transport of Bromide and Benazolin in Lysimeters and a field plot with grid suction bases in a sandy soil, Institute of Soil Science, Hohenheim, Stuttgart.

Kladivko, E. J., J. R. Frankenberger, D. B. Jaynes, D. W. Meek, B. J. Jenkinson, and N. R. Fausey. 2004. Nitrate leaching to subsurface drains as affected by drain spacing and changes in crop production system. *Journal of Environmental Quality* 33 (5):1803-1813.

Kladivko, E.J., J. Grochulska, R.F. Turco, G.E. Van Scoyoc, and J.D. Eigel. 1999. Pesticide and nitrate transport into subsurface tile drains of different spacings. *J. Environ. Qual.* 28:997-1004.

Kosugi, K., and M. Katsuyama. 2004. Controlled-suction period lysimeter for measuring vertical water flux and convective chemical fluxes. *Soil Science Society of America Journal* 68 (2):371-382.

Kung, K.-J.S. 1990. Preferential Flow in a sandy vadose zone: 1.Field Observation. *Geoderma* 46:51-58.

Li, Z.M., E.O. Skogley, and A.H.; Ferguson. 1993. Resin adsorption for describing bromide transport in soil under continuous or intermittent unsaturated water flow. *J. Environ. Qual.* 22:715-722.

Logsdon, S.D., K.E. Keller, and T.B.; Moorman. 2002. Measured and predicted solute leaching from multiple undisturbed soil columns. *Soil Sci. Soc. Am. J.* 66:686-695.

Netto, A.M.; Pieritz, R.A.; Gaudet, J.P. 1999. Field study on the local variability of soil water content and solute concentration. *Journal of Hydrology* 215:23-37.

Nolan, B.T., B.C. Ruddy, K.J. Hitt, and D.R. Helsel. 1998. A national look at nitrate contamination of groundwater. *Issue of Water Conditioning and purification* 39 (12):76-79.

O'Loughlin, E.J., S.J. Traina, and Y. Chin. 2000. Association of organotin compounds with aquatic and terrestrial humic substances. *Environmental Toxicology and Chemistry* 19 (8):2015-2021.

Pampolino, M.F., T. Urushiyama, and R.; Hatano. 2000. Detection of nitrate leaching through bypass flow using pan lysimeter, suction cup, and resin capsule. *Soil Science and Plant Nutrition* 46 (3):703-711.

Richtlinie 2000/60/EG zur Schaffung eines Ordnungsrahmens für Maßnahmen der Gemeinschaft im Bereich der Wasserpolitik. 23.10.2000.

Roth, K., W.A. Jury, H. Flühler, and W. Attinger. 1991. Transport of chloride through an unsaturated field soil. *Water Resources Research* 27:2533-2541.

Saffigna, P.G.; Keeney, D.R.; Tanner, C.B. 1977. Lysimeter and Field Measurements of Chloride and Bromide Leaching in an Uncultivated Loamy Sand. *Soil Sci. Soc. Am. J.* 41:478-483.

Selker, J., P. LeClerq, J.-Y. Parlange, and T. Steenhuis. 1992. Fingered Flow in two Dimensions: 1. Measurement of matric potential. *Water Resources Research* 28:2513-2521.

Siemens, J. 2003. Controls of carbon, nitrogen, and phosphorus fluxes in vadose zone and groudwater of protected watersheds in Münster (Germany). Dissertation, Fakultaet VII - Architektur, Umwelt, Gesellschaft-, Technische Universität Berlin, Berlin.

Skogley, E.O. 1992. The universial bioavailability environment/soiltest: Unibest. *Communications in Soil Science and Plant Analysis* 23:2225-2246.

Umweltbundesamt. 2002. Umweltdaten Deutschland 2002.43, 48, 52.

Wang, Z., L. Wu, T. Harter, J. Lu, and W.A. Jury. 2003. A field study unstable preferential flow during soil water redistribution. *Water Resources Research* 39 (4):1075-1089.

Wilson, S.C., R. Duarte-Daidson, and K.C. Jones. 1996. Screening the environmental fate of organic contaminants in sewage sludges applied to agricultural soils: 1. The potential for downward movement to groundwaters. *The Science of the Total Environment* 185:45-57.

Yang, J.E., and E.O. Skogley. 1992. Diffusion kinetics of multinutrient accumulation by mixed-bed ion-exchange resins. *Soil Sci. Soc. Am. J.* 56:408-414.

Zhu, Y., R. H. Fox, and J. D. Toth. 2003. Tillage effects on nitrate leaching measured by pan and wick lysimeters. *Soil Science Society of America Journal* 67 (5):1517-1523.