

Exchange resin cores for the estimation of nutrient fluxes in highly permeable tropical soil

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Summary – Zusammenfassung

There is an urgent need to improve the methods to estimate solute fluxes in soil, e.g. cumulative capture of leaching ions by exchange resin cores. We compared the suitability of different resin materials, core sizes, and installation procedures to assess nutrient leaching in a highly permeable, tropical Xanthic Ferralsol. Three different cation and anion resins, respectively, and two combined anion-cation resins were tested in laboratory experiments with respect to their removal and recovery of nutrients (Mg, NH_4^+ , NO_3^-) and total dissolved organic carbon (TOC) from solution. In a field experiment, cores with three different diameters (25, 100, and 200 mm) were installed either vertically from the soil surface or laterally from a soil pit. Cumulative leaching of NO_3^- and NH_4^+ and of applied Sr was determined after 45 days. The combined anion and cation exchange resin (MB 20) showed satisfactory recovery of NO_3^- and NH_4^+ from solution. None of the investigated resins could be used for TOC removal from solution due to high contents of soluble carbon compounds in the resins. Wetting and drying cycles did not affect the removal of solutes from solution or subsequent recovery from the MB 20 resin. Additionally, the combined resin MB 20 was easier to handle than separate anion or cation resins and was therefore used for further field experimentation. The smallest core size (25 mm) was not suitable for nutrient leaching determination due to high preferential flow along the inner core walls. The medium diameter cores (100 mm) showed the lowest variability and the best correlation between NO_3^- and Sr capture. They were easier to install and retrieve than the large diameter cores (200 mm), which posed serious handling problems and soil disturbance. The lateral installation caused significantly lower artificial flow in comparison to a vertical installation, which was shown by the lower Sr loss and slightly lower N capture. Therefore, a lateral installation of medium sized resin cores (100 mm diameter) from a soil pit was superior to the other alternatives tested in this study.

Key words: exchange resin / nitrogen / nutrient leaching / total dissolved organic carbon / strontium

Abschätzung des Nährstoffaustrages aus stark durchlässigen tropischen Böden mit Austauschharz-Zylindern

Es gibt einen dringenden Bedarf zur Weiterentwicklung von Methoden, mit denen Stoffflüsse im Boden abgeschätzt werden können, wie z.B. mit Austauscherharz-Zylindern („exchange resin cores“). Diese Studie befasst sich mit der Eignung verschiedener Austauscherharze zur Bestimmung von kumulativen Nährstoffausträgen aus einem stark durchlässigen tropischen Xanthic Ferralsol. Neben den Sorptionseigenschaften von Anionen- und Kationharzen sowie kombinierten Anionen-Kationharzen für Nährstoffe (Mg, NH_4^+ , NO_3^-) und gelösten organischen Kohlenstoff (TOC) wurden mögliche Durchmesser und zwei verschiedene Techniken zum Einbau der Zylinder in Böden untersucht. In einer Feldstudie wurden Harzzylinder dreier Durchmesser (25, 100 und 200 mm) entweder vertikal von der Bodenoberfläche aus oder lateral von einer Grube aus eingebaut. Die Auswaschung von NO_3^- und NH_4^+ sowie von ausgebrachtem Sr wurde nach 45 Tagen bestimmt. Das kombinierte Anionen-Kationharz (Amberlite MB 20) zeigte gute Sorptionseigenschaften für NO_3^- und NH_4^+ . Aufgrund hoher Gehalte an löslichen organischen Substanzen im Harzmaterial war keines der Harze zur Erfassung von TOC geeignet. Wiederholte Trocknungs- und Befeuchtungszyklen hatten keinen Einfluss auf die Adsorptionseigenschaften des MB 20 Harzes. Wegen der zusätzlich leichteren Handhabbarkeit eines kombinierten Harzes wurde das MB 20 für die anschließenden Feldversuche eingesetzt. Die Harzzylinder mit dem kleinsten Durchmesser (25 mm) waren wegen starker Stoffflüsse entlang der inneren Wandung der Zylinder nicht zur Bestimmung der Nährstoffauswaschung geeignet. Die Harzzylinder mit mittlerem Durchmesser (100 mm) wiesen die geringste Variabilität zwischen den Einzelmessungen auf und waren einfacher zu installieren und auszubauen als die großen Zylinder (200 mm). Ein lateraler Einbau verursachte eine signifikant geringere Bodenstörung als ein vertikaler Einbau von oben, wie die geringere Sr- und N-Auswaschung bewies. Lateraler Einbau der Harzzylinder mit mittlerem Durchmesser (100 mm) zeigte sich gegenüber den anderen getesteten Varianten überlegen.

1 Introduction

In many soils of the tropics the nutrient losses by leaching exceed the inputs by fertilizers as shown for a number of African countries (Stoorvogel et al., 1993). Also in agroecosystems without fertilization, nutrient leaching can be

very high especially after slash-and-burn interventions in humid tropical lowlands (Williams et al., 1997). These losses need to be reduced for sustainable agricultural production. In addition, nitrate (NO_3^-) was frequently reported to exceed threshold values in drinking water wells in many parts of the world (Follet, 1989).

The determination of nutrient fluxes in soil poses considerable technical problems. For quantifying nutrient losses by seepage a variety of techniques was developed,

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Table 1: Physical and chemical properties of the Xanthic Ferralsol on the Terra Firme in Central Amazonia.**Tabelle 1:** Physikalische und chemische Eigenschaften eines Xanthic Ferralsol auf der Terra Firme in Zentralamazonien.

Depth [cm]	Horizon	Bulk density [Mg m ⁻³]	Clay content [g g ⁻¹]	K _s ¹ [m day ⁻¹]	Soil water content [m ³ m ⁻³] at		pH H ₂ O	C ² [g kg ⁻¹]	N ² [g kg ⁻¹]	CEC [mmol _c kg ⁻¹]
					pF 0	pF 4.2				
0–10	Ah	0.82	0.59	12–14	0.61	0.20	4.1	29.1	2.7	7.4
10–50	B1	0.93	0.65	12–14	0.55	0.25	4.1	15.6	1.2	3.3
50–150	B2	0.97	0.72	n.d.	0.54	0.29	4.3	4.5	0.5	2.4

¹ Estimated saturated hydraulic conductivity (Renck, 2000)

² Elemental analyses (CN-Analyzer Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany)

n.d.: not determined

Table 2: Technical details of the resin materials under study.**Tabelle 2:** Technische Einzelheiten der verwendeten Austauschharze.

Resin product	Manufacturer	Adsorption type	Matrix	Particle size [μm]	Functional groups	Capacity [mol _c l ⁻¹]
Amberjet 1200 Na ⁺	Rohm and Haas	cation	styrene-DVB	650	–SO ₃ ⁻	2.0
Amberlite 252 Na ⁺	Rohm and Haas	cation	styrene-DVB	600–800	–SO ₃ ⁻	1.8
Serdolit CS-2 Na ⁺	Serva	cation	styrene-DVB	350–800	–SO ₃ ⁻	1.9
Amberlite IRA 900RF Cl ⁻	Rohm and Haas	anion	styrene-DVB	600–800	–N ⁺ –(CH ₃) ₃	1.0
Amberlite IRA 910 Cl ⁻	Rohm and Haas	anion	styrene-DVB	550–750	–N ⁺ –(CH ₃) ₂ C ₂ H ₄ OH	1.2
DEAE 52-Cellulose Servacel Cl ⁻	Serva	anion	cellulose	100–200	–N ⁺ –(C ₂ H ₄) ₂ C ₂ H ₄ OH	1.1
Amberlite MB 20 Na ⁺ /Cl ⁻	Rohm and Haas	cation/anion	styrene-DVB	300–1200	–SO ₃ ⁻ /–N ⁺ –(CH ₃) ₃	0.6
Amberlite MB 6 Na ⁺ /Cl ⁻	Rohm and Haas	cation/anion	styrene-DVB	300–1200	–SO ₃ ⁻ /–N ⁺ –(CH ₃) ₃	0.3

most of them being very laborious and expensive. Zero-tension lysimeters and suction cup lysimeters are widely used. Zero-tension lysimeters are useful for the determination of rapidly draining soil water in macropores and solutes therein (Meissner et al., 2000). However, they fail to sample soil water moving slowly within smaller pores (Jemison and Fox, 1992; Marques et al., 1996). In contrast, suction cup lysimeters mainly collect water bound by the soil matrix and provide information on the composition of slowly moving and stagnating soil solution. The estimation of solute fluxes from suction cup lysimeters presupposes, however, the calculation of water balances from meteorological and soil physical data. This procedure is complex and requires much expert knowledge and large technical resources. In addition, suction cup lysimeter fail to sample soil water under conditions of preferential flow (Haines et al., 1982; Van Grinsven et al., 1988; Brandi-Dohrn et al., 1996; Marques et al., 1996). Tensiometer-controlled suction plate lysimeters are a means to sample soil solution proportional to soil water fluxes, but this requires sensitive regulation of the applied tension (Van Grinsven et al., 1988).

An inexpensive and simple method for the estimation of solute fluxes is the use of monitoring boxes filled with ion exchange resin (Kaupenjohann and Kukowski, 1995; Skogley and Dobermann, 1996; Bischoff et al., 1999; Lehmann et al., 1999a). Exchange resins have been used to extract plant-available nutrients for many years. The extraction of soil-P with exchange resin is a standard procedure for assessing their P status (Bache and Ireland, 1980; Schoenau and Huang, 1991; Cooperband and Logan, 1994). Methods using exchange resins were developed regarding the assess-

ment of available soil-N as well as N mineralization and leaching (Zou et al., 1992; Schnabel et al., 1993; Kolberg et al., 1997; Lehmann et al., 1999b). The extremely large leaching rates in highly permeable soils of the humid tropics may impose different constraints than when leaching rates are very low, but were not investigated up to now.

The methods applying exchange resins cannot yield information about short-term processes and are not adequate to measure nutrient leaching dynamics. However, in many cases cumulative leaching data are sufficient for answering the questions posed. In addition, the exchange resin cores provide these data at much lower costs than the techniques described above. The low price and the rather low maintenance requirements allow a high number of replicates. This is a prerequisite for representative sampling and characterization of the spatial heterogeneity of nutrient flow patterns. Only few studies are available, however, which compare exchange resins (Bischoff and Kaupenjohann, 1998; Schnabel, 1982) regarding their chemical properties as well as construction, size, or installation of the cores.

This study compared (1) different anion and cation resins with respect to their chemical suitability for nutrient capture from soil solution, (2) the effects of core diameter, and (3) installation procedure on nutrient flux determinations in a highly permeable Xanthic Ferralsol in the humid tropics.

2 Materials and methods

2.1 Study site

The field experiment was carried out at the Embrapa Amazonia Ocidental research station near Manaus in 1998/99. The rainfall distribution is

unimodal with a maximum between December and May and a mean annual precipitation of 2503 mm (1971–1993). The soils are classified as Xanthic Ferralsols (FAO, 1988). They are deeply developed and clayey, strongly aggregated, have high hydraulic conductivity and water holding capacity. The soil-pH is low and the soils have medium organic C and N contents (Table 1). The investigated site was homogeneously covered with *Pueraria phaseoloides* (Roxb.) Benth. within a mixed fruit-tree cropping system as described in Lehmann et al. (2000).

2.2 Comparison of resin materials

Laboratory experiments were carried out to compare the adsorption and recovery of nutrients and dissolved organic matter to different anion and cation exchange resins under several experimental conditions. Three anion and cation exchange resins, respectively, and two combined anion-cation resins (Table 2) were equilibrated with leaf litter extract from European beech (*Fagus sylvatica* L.). The resin materials were used as supplied without any pre-treatment or after thorough washing with demineralized water. In order to remove organic contaminations with low water solubility, the MB 20 resin was additionally tested after pre-washing with acetone followed by demineralized water. Three grams of the resin material were sealed in polyethylene fabric bags and agitated with 50 ml of diluted leaf litter extract for half an hour (equilibration). The beech litter extract contained 1.1 mg NO₃-N l⁻¹, 1.5 mg NH₄-N l⁻¹, 2 mg Mg l⁻¹ and 3.5 mg TOC l⁻¹ (total organic carbon), resembling concentrations typically found for soil solutions of unfertilized soils in the experimental area. In addition, the effects of drying the resins were tested before and after each equilibration with test solutions and between two or five equilibration cycles. Each drying was done at 40°C for one week. After the equilibration, the resins were extracted with 50 ml 1 M KCl for 2 hours on an agitator. Five replicates per resin were used for MB 20, and three for the other resin materials.

2.3 Soil nutrient flux measurements

Resin cores with 25, 100, and 200 mm diameters were constructed from PVC tubes with a length of 100 mm. One volume of a combined cation-anion exchange resin (Amberlite MB 20; Table 2) was mixed with four volumes of acid washed sand. The mixture was well compacted. On 5 to 13 October 1998 at the end of the dry season, 185 resin cores were installed at different depths either vertically from above or laterally from the side as specified in Table 3. The vertical installation was done by removing the overlying soil with a root sampling auger (100-mm diameter) for the 25-mm cores and with a ring auger (250-mm diameter) for the 100-mm cores. The soil columns were cautiously removed from the augers keeping them mostly intact. Subsequently, the volume for the resin cores was removed from the underlying soil by 25 and 100 mm augers, respectively, and the cores were inserted. Thereafter, the intact soil columns were replaced on top of the resin cores and were gently compacted to restore the original soil surface. For the cores installed at 0.45 m depth, several soil columns had to be removed and were placed in the same order after the installation. The lateral installation was done by digging a trench and excavating a hole into the wall fitted to house the resin cores at the respective depth. When installing, the cores were gently pressed into the overlying soil and fixed by filling the volume underneath with sand. The resin cores were arranged in a randomized complete block design with three replicates (2 by 2 m plot), each replicate comprising several cores depending on the core size (see Table 3). After installation, 5 g Sr m⁻² was applied on-site as a SrCl₂-solution. This experiment was designed to compare the flux assessment of nutrients applied to the soil surface in comparison to those of native soil nutrients as affected by core size and installation.

After 45 days, the resin cores were collected and each was cut into three layers, 0–30, 30–70, and 70–100 mm. The total fresh mass was determined

Table 3: Number of installed resin cores, minimum and maximum amount, and percentage of cores with evaluable results and coefficient of within-plot variation of leaching rates after exposure in a Xanthic Ferralsol using two different installation procedures and three different diameters (for all determined substances).

Tabelle 3: Anzahl der eingebauten Harzzylinder, minimale und maximale Anzahl und Anteil an Zylindern mit auswertbaren Ergebnissen sowie Variationskoeffizienten des Stoffaustrages innerhalb einer Parzelle nach Messung des Stoffaustrages aus einem Xanthic Ferralsol mit zwei verschiedenen Einbauverfahren und drei verschiedenen Durchmessern (alle untersuchten Stoffe).

Depth [m]	Core diameter [mm]	Installation	Individual core surface area [cm ²]	Total number of cores	Evaluable cores [%]	CV ¹ of solute fluxes [%]
0.1	25	lateral	20	93	28–66	85–416
0.1	25	vertical	20	46	57–87	60–257
0.1	100	lateral	314	11	73–100	21–82
0.1	100	vertical	314	6	67–100	17–97
0.1	200	lateral	1257	4	100	7–102
0.45	25	lateral	20	15	27–93	32–128
0.45	25	vertical	20	10	80–100	11–80

¹ CV coefficient of variation

and an aliquot (15–25 g) of the resin-sand mixture was extracted with 1 M KCl-solution as described above. Reference resin cores were leached in the laboratory with demineralized water at rates similar to those found in the field. Blank values from the reference cores were at least one order of magnitude lower than the values from the resin cores exposed in the field. The blanks were subtracted from the nutrient fluxes calculated under field conditions. The total solute trapped by the resin was computed from the weight of each layer and the nutrient concentration therein. The element fluxes and the recovery of the applied Sr were calculated using the surface area of the cores and the total amounts of solutes adsorbed in the first two resin layers (Bischoff et al., 1999). Resin cores with lower nutrient concentrations in the top resin layer than the second layer were rejected from further evaluation because of core disturbance during installation or by soil fauna.

2.4 Chemical analyses

NO₃⁻ and NH₄⁺ concentrations were determined photometrically with a continuous flow analyzer (RFA-300, Alpkem Corp., Clackamas, OR and Scan Plus analyzer, Skalar Analytical B.V., Breda, The Netherlands) after reduction with Cd and reaction with salicylate, respectively. Mg and Sr were analyzed with an atomic absorption spectrometer (AA-400, Varian Associates, Inc., Palo Alto, CA). Total organic carbon was measured by elemental analysis (Pt-catalyzed high-temperature (680°C) combustion; TOC-5050, Shimadzu Corp., Tokyo, Japan).

2.5 Statistical analyses

The data was evaluated by analysis of variance (ANOVA) using a randomized complete block design after testing for normal distribution. Due to inhomogeneity of variances, logarithmically transformed data were used for analyzing the fluxes. In case of significant effects or interactions, multiple comparisons of means were computed with the least significant difference method (LSD) at P<0.05. All statistical calculations were done with the software package Statistica 5.0 (StatSoft, Inc., Tulsa, OK).

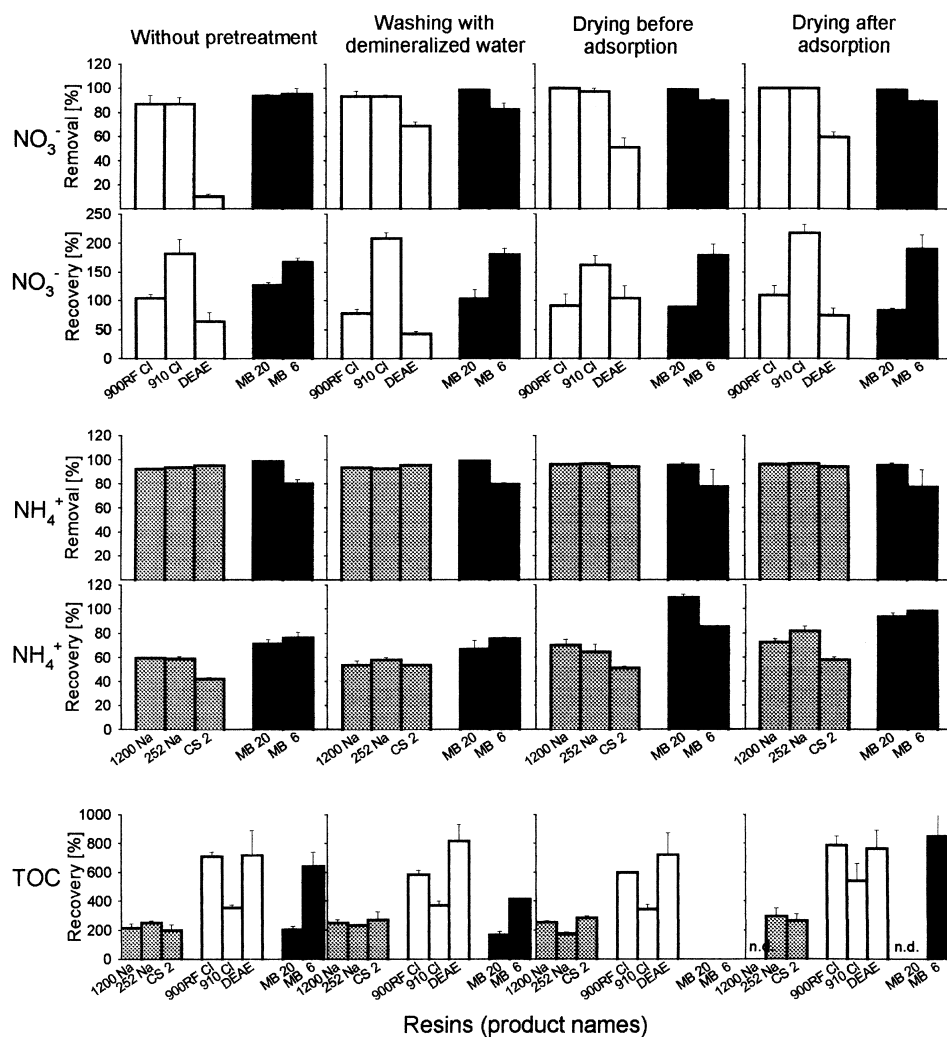


Figure 1: Solute removal from solution by different resins (see Table 2) and recovery from the resins as affected by different pre-treatment, means and standard errors ($n = 3$; $n = 5$ for MB 20). **Abbildung 1:** Stoffentnahme aus einer Lösung durch verschiedene Harze (siehe Tabelle 2) sowie deren Wiederfindung bei Extraktion der Harze, beeinflusst durch unterschiedliche Vorbehandlung, Mittelwerte und Standardfehler ($n = 3$; $n = 5$ für MB 20).

3 Results

3.1 Resin materials and preparation effects

The removal of NO_3^- from the beech litter extract generally approached 100% for all resin materials except the DEAE resin, irrespective of the treatment (Figure 1). Without preparing the resins by washing, the recovery by 1 M KCl-extraction was always higher than the removal of NO_3^- from the solution due to contamination of the resin. If the resins were washed with demineralized water, only the anion exchange resin 900RF Cl and the combined resin MB 20 had a satisfactory recovery, which was independent of drying. Washing the MB 20 resin with acetone prior to the equilibration with the beech litter extract did not improve the removal of Mg and NH_4^+ in comparison to no pre-treatment or washing with demineralized water (data not shown). In contrast, washing with acetone even decreased NO_3^- removal from the solution and NH_4^+ recovery. Regarding NH_4^+ , the resins achieved complete removal from the solution except the MB 6 with less than 80%. The recovery, however, was only 60% or less for the cation exchange resins, and 80% for the combined resins, generally increasing after drying. The Mg removal almost reached

100% except the MB 20-resin, but the recovery was less than 90% for the cation resins, and considerably higher than 100% for the combined resins even after pre-washing with demineralized water. When the resins were dried after equilibration, the 1200 Na and MB 20 resins had recoveries of 80 and 70%, respectively (data not shown). There was no evidence for removal of total organic carbon (TOC) from the solution, which was even enriched after the equilibration (data not shown). All resins released soluble TOC even after pre-cleaning with demineralized water or acetone. The recovery of TOC clearly exceeded 100% and reached up to 800% for the anion resins and MB 6. The lowest TOC release was noted from the MB 20 with a recovery of 160% (Figure 1).

Repeating the equilibration two times followed by drying (data not shown) did not yield different removals of NO_3^- , NH_4^+ , and Mg from the test solution or recovery by the resin. After five repeated exposures, however, the NO_3^- and NH_4^+ removal from solution decreased for DEAE and MB 6 resins (Figure 2). The removal by the other resins remained close to 100%. In contrast to NH_4^+ , the Mg removal by MB 6 did not decrease with repeated exposures (Mg data not shown). Both the NO_3^- and the NH_4^+ recoveries after five exposures were best for the MB 20 resin.

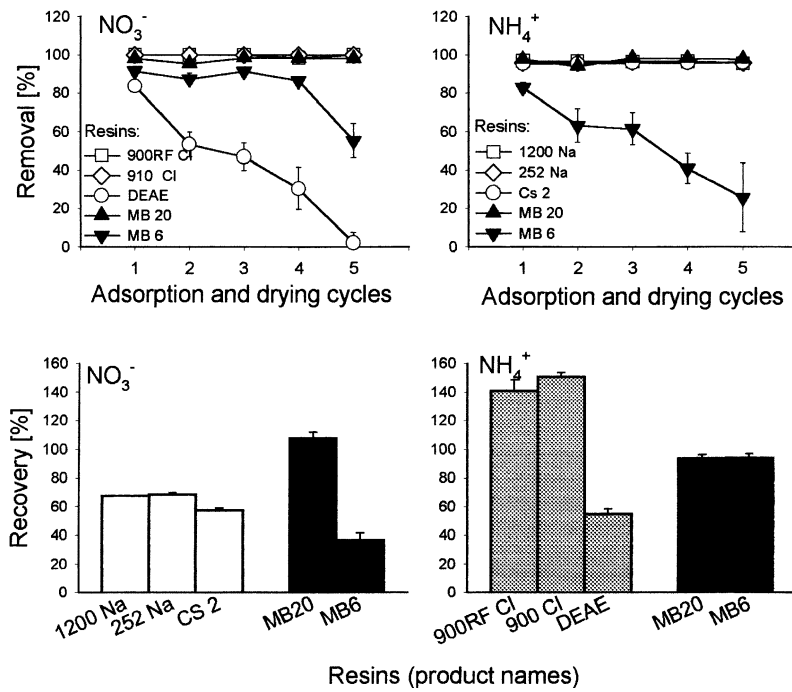


Figure 2: Solute removal from solution by different resins (see Table 2) and recovery from the resins as affected by five sequential adsorption and drying cycles, means and standard errors (n = 3; n = 5 for MB 20).

Abbildung 2: Stoffentnahme aus einer Lösung durch verschiedene Harze (siehe Tabelle 2) sowie deren Wiederfindung bei Extraktion der Harze, beeinflusst durch fünf sequentielle Adsorptions- und Trocknungszyklen, Mittelwerte und Standardfehler (n = 3; n = 5 für MB 20).

3.2 Nutrient trapping by exchange resins under field conditions

The infiltration rate (1.3 m day⁻¹) into 100-mm resin cores (Amberlite MB 20) was not significantly different from the infiltration into undisturbed soil cores of the same dimensions (1.4 m day⁻¹) (P < 0.05; n = 10; data not shown). For reaching the same area for flux assessment with the 25-mm diameter resin cores as one 100- and 200-mm resin core, 15 and 64 more 25-mm-units have to be installed, respectively (Table 3). Only 28 to 66% of the 25-mm resin cores could be used for flux calculations, whereas almost all cores with large diameter were undisturbed during installation and retrieval or by soil fauna. The variability of leaching results within one plot was higher in the smaller cores than in the larger cores (Table 3).

The majority of the captured NO₃⁻ was adsorbed in the upper resin layer of the 25-mm resin cores (P < 0.05; Figure 3). The proportion of the retention at the middle and lower layer increased with increasing diameter of the resin cores. The total amount of NO₃⁻ captured slightly decreased with increasing diameter of the resin core (P = 0.15; n = 3) as shown in Figure 4. The Sr fluxes were significantly lower in 100-mm resin cores than when assessed in 25-mm cores (P < 0.05; Table 5). Results obtained from single resin cores revealed more outlying extreme values from the small than from the large diameter cores (Figure 4).

The NO₃⁻ fluxes were always more than one order of magnitude larger than those of NH₄⁺ (Table 4). The leaching rates for both NO₃⁻ and NH₄⁺ were larger when the resin cores were installed vertically from above than from the side (Table 4; effect of vertical or lateral installation over all treatments P = 0.1). The same behavior was observed with the Sr fluxes (Table 5; P < 0.05). The amount of the captured Sr was not significantly related to the NO₃⁻ leaching in the

25-mm resin cores (r² = 0.005, P < 0.05, n = 25). With larger diameters, the correlation improved (100 mm: r = 0.69, P < 0.05, n = 8; 200 mm: r = 0.36, P > 0.05, n = 4). Whereas neither the NO₃⁻ nor the NH₄⁺ fluxes differed between 0.1 and 0.45 m depth (Table 4), the Sr flow was significantly lower at 0.45 m than at 0.1 m depth (Table 5; P < 0.005). The Sr recovery was 0.5 and 28% for the cores installed at 0.45 and 0.1 m depth, respectively (means of installation procedures).

4 Discussion

4.1 Choice of resin material and pre-treatment

All tested resins originally contained large amounts of NO₃⁻ and have to be pre-washed before use. Washing with deionized water was sufficient and preferable to a pre-

Table 4: Fluxes of inorganic nitrogen determined with exchange resin cores as affected by diameter and installation at two depths under *Pueraria phaseoloides* on a Xanthic Ferralsol, means and standard errors (n = 3).

Tabelle 4: Austräge an anorganischem Stickstoff in Abhängigkeit von Durchmesser, Einbauverfahren und -tiefe der Harzzyklindern in einem Xanthic Ferralsol unter *Pueraria phaseoloides*, Mittelwerte und Standardfehler (n = 3).

Installation	Depth [m]	Core diameter [mm]			
		25		100	
		NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺
		[g m ⁻² (45 days) ⁻¹]			
lateral	0.1	3.95 ± 1.75	0.13 ± 0.06	2.57 ± 1.37	0.21 ± 0.09
vertical	0.1	6.36 ± 3.86	0.29 ± 0.06	3.57 ± 1.01	0.14 ± 0.11
lateral	0.45	2.66 ± 1.24	0.14 ± 0.10	n.d.	n.d.
vertical	0.45	4.20 ± 1.55	0.20 ± 0.09	n.d.	n.d.

n.d.: not determined

Table 5: Tracer fluxes and recovery of applied Sr determined with exchange resin cores as affected by diameter and installation procedures at two depths of a Xanthic Ferralsol, means and standard errors (n = 3).

Tabelle 5: Tracerflüsse und die Wiederfindung ausgebrachter Strontiummengen mit Austauschharz-Zylindern in Abhängigkeit von Durchmesser, Einbauverfahren und -tiefe in einem Xanthic Ferralsol, Mittelwerte und Standardfehler (n = 3).

Depth [m]	Diameter [mm]	Installation	Sr flux rates [mg m ⁻² (45 days) ⁻¹]	Recovery [%]
0.1	25	lateral	427 ± 95	8.5 ± 1.9
0.1	25	vertical	2333 ± 1115	46.7 ± 22.3
0.1	100	lateral	58 ± 21	1.2 ± 0.4
0.1	100	vertical	154 ± 66	3.1 ± 1.3
0.1	200	lateral	203 ± 120	4.1 ± 2.4
0.45	25	lateral	19 ± 6	0.4 ± 0.1
0.45	25	vertical	26 ± 2	0.5 ± 0.0

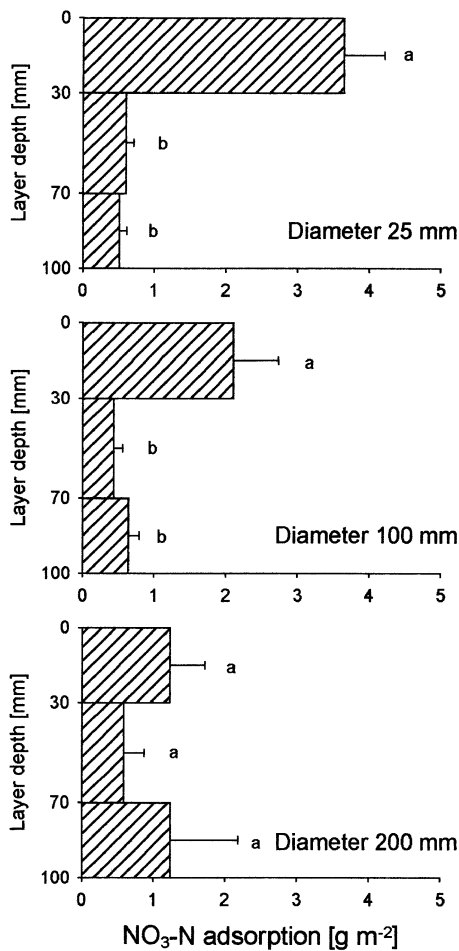


Figure 3: NO₃⁻ adsorption in the three layers of the resin cores as affected by their diameter; bars with the same letter are not significantly different at P < 0.05, means and standard errors (n = 61, 8, and 4 for 25-, 100- and 200-mm core diameter, respectively).

Abbildung 3: NO₃⁻-Adsorption in drei Schichten der Harzzyylinder in Abhängigkeit des Durchmessers; Säulen mit dem gleichen Buchstaben sind nicht signifikant unterschiedlich bei P < 0.05, Mittelwerte und Standardfehler (n = 61, 8 und 4 für Zylinder mit 25, 100 und 200 mm Durchmesser).

treatment with acetone. The anion resin 900RF Cl and the cation resin 1200 Na had satisfactory properties for removing the tested nutrients from solution and subsequent recovery, but they were generally not superior to the combined resin MB 20. Due to easier handling of a combined resin, the MB 20 resin was preferable, when both anions and cations should be determined.

The resins did not show an altered nutrient removal when they were dried out before they came into contact with the solution. This reflects an important property of the resin material, because the resins frequently dry out between rainfall events, especially in topsoils. After repeated drying and wetting, the MB 20 resin showed the best properties for solute trapping among all tested resins. Therefore, only this resin was used in the field studies.

4.2 Effects of core diameter on nutrient flux measurements

The cores of 25-mm diameter did not reveal an advantage for reducing the variability of the results in comparison to the larger cores, even though a higher number of cores was used. The greater number of small-diameter cores gave, however, a better estimate of the heterogeneity of nutrient fluxes in the studied soil than the larger ones. On the contrary, the increasing variability with decreasing core diameter indicated that percolating soil water may flow through small-diameter cores or by-pass them easier than when large-diameter cores were used. A higher amount and better spatial randomization of small cores could not compensate for the larger cross-section surface area of a single large core. Therefore, a higher core diameter averages the fluxes over a larger area. This resulted in a better representation of the fluxes than the actual increase in diameter and therefore sampled area would suggest.

Regarding only the cross-section surface area, one would expect to obtain higher leaching results from large- than small-diameter cores, because soil water may not by-pass around the large-diameter cores so easily. Accordingly, *Jemison and Fox (1992)* demonstrated a higher collection efficiency of zero-tension lysimeters with increasing surface area. However, higher mean leaching values were observed from the cores of 25- than those of 100- and 200-mm diameters in this study. Most likely, preferential flow occurred along the inner walls of the cores and more nutrients were adsorbed by the resin, because the sand-resin mixture may have created larger pores in contact with the core walls. In the highly aggregated Ferralsols of the central Amazon saturated soil water fluxes were very fast during rainfall events (*Renck, 2000*) due to a high proportion of macropores, leading to preferential flow through soil. Therefore, larger pores and possible gaps at the inner side of the cores became important pathways for the percolating soil water after heavy rainfall. The small-diameter cores were more affected by this process, as they have a higher edge-to-surface ratio than the larger diameter cores.

The 100-mm diameter cores appeared to have caused the least soil and water flux disturbance as they showed the best correlation between NO₃⁻ and Sr fluxes. A close correlation

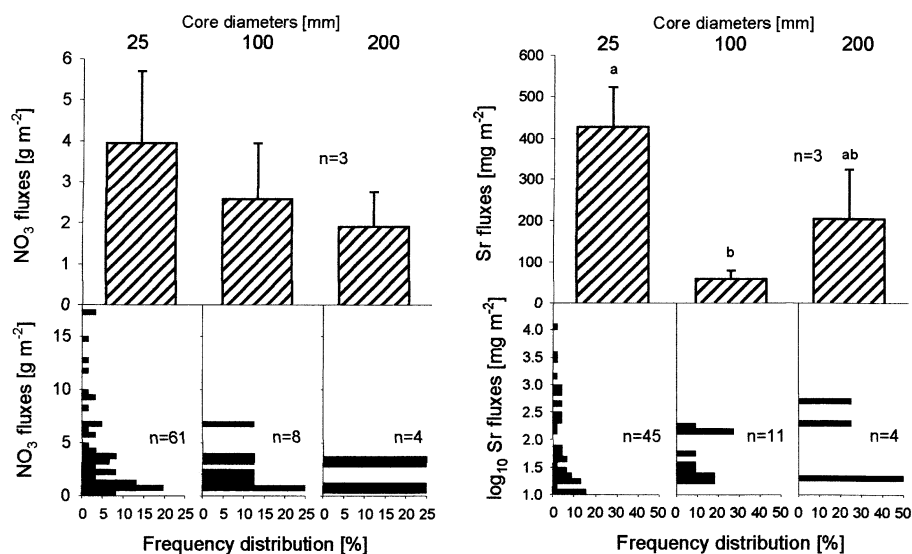


Figure 4: NO₃⁻ and Sr fluxes within 45 days and frequency distribution as affected by diameters of the resin cores; bars with the same letter are not significantly different at $P < 0.05$, means and standard errors.

Abbildung 4: NO₃⁻- und Sr-Flüsse in 45 Tagen und Häufigkeitsverteilung in Abhängigkeit der Durchmesser der Harzzyylinder; Säulen mit dem gleichen Buchstaben sind nicht signifikant unterschiedlich bei $P < 0.05$, Mittelwerte und Standardfehler.

between both indicated that increasing water percolation led to increasing retrieval of added and native soil nutrients in the same way. This indicates that preferential flow through macropores as well as matrix fluxes were captured in the cores. Preferential or impeded pathways in the soil above the cores will lead to larger or lower leaching estimates, respectively, with increasing leaching for an added than a native soil nutrient. The 200-mm cores were extremely difficult to install and the contact with the overlying soil was only achieved by filling sand into the space above the core. Also the excavation disturbed the soil proportionally more than for the smaller cores.

4.3 Installation effects on nutrient flux results

With a vertical installation of the exchange resin cores from above, nutrient leaching can be seriously overestimated as shown by the tracer study. The fluxes of Sr seemed to bypass the replaced soil columns and the Sr was captured in the resin cores beneath. However, the determined leaching rates in case of a vertical installation represented well approximated estimates with respect to the overlying soil, if the source can be attributed to the soil just above the core like in N mineralization studies (Kolberg et al., 1997; Lehmann et al., 1999b). This was shown by the closely matching NO₃⁻ leaching rates in both installation procedures in contrast to the Sr leaching rates. These results also suggest that an installation from the side could achieve a firm contact between the resin-sand mixture and the overlying soil as the NO₃⁻ capture was similar to an installation from above.

4.4 Exchange resin cores for soils with high infiltration rates

The leaching rates from exchange resin cores had a similar variability than those commonly found using other methods such as zero-tension or tension lysimeters (e.g., Barbee and Brown, 1986; Lord and Shepherd, 1993; Marques et al.,

1996). In addition, the variability of soil water fluxes is a well-known soil property which requires quantification (Bischoff et al., 1999). Being less expensive and easier to handle, the resin core technique may be an alternative to the other ones mentioned above considering that a large number of cores can be installed and a time integral is already obtained. Resin traps were also used for tension-free lysimeters to obtain cumulative leaching rates (Sakadevan et al., 1994), but the tension-free lysimeters may not adequately sample solution from unsaturated soil (Haines et al., 1982; Jemison and Fox, 1992; Webster et al., 1993).

In the humid tropical climate most of the nutrients were leached during heavy rainfall, which led to rapid infiltration under saturated or nearly saturated soil water condition and subsequent rapid flow through soil (Renck, 2000). For these conditions, differences of the soil water suction or unsaturated water conductivity between the resin-sand mixture and the surrounding soil may not be important (Arnold, 1996). The hydraulic conductivity near saturation will then determine whether the water flow through the soil is similar to the one through the resin core. This difference was demonstrated to be rather small in the studied Ferralsols.

5 Conclusions

Exchange resin cores are a new technique to quantify nutrient leaching in soil. Based on detailed studies of different resin materials, core diameters and installation procedures we recommend:

- (1) the combined anion-cation resin MB 20 because of best nutrient removal and recovery after extraction, as well as easy handling,
- (2) a lateral installation of 100-mm cores because of minimal soil disturbance and preferential flow along the sides of the replaced soil columns,
- (3) continued search for resin materials that enable simultaneous collection and investigation of nutrients and dissolved organic matter.

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