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DETERMINING DIFFERENTIAL WATER MOVEMENT THROUGH ION EXCHANGE RESIN FOR NITRATE LEACHING MEASUREMENTS

H. A. Torbert and C. B. Elkins

Agronomy and Soils Department, Auburn University, Auburn, AL 36849

ABSTRACT The fate of fertilizer N applied to agricultural soils is of growing concern due to the potential for groundwater contamination. The recent development of an exchange resin that specifically absorbs NO_3 has led to the potential for a new technique to measure cumulative NO_3 leaching. The main limitation to the application of the resin technique is the matching of water movement through the resin with that of soil. A soil water movement device was developed to compare water movement through the resin to that of soil. A study was initiated to develop a resin/soil pack with water movement characteristics that closely matches those of natural soils. Three different soil types were used in this study: a Cahaba sandy loam (fine-loamy, siliceous, thermic Typic Hapludult), a Congaree clay loam (fine loamy, mixed, nonacid, thermic Typic Udifluvent), and a Hiwassee clay (clayey, kaolinitic, thermic Typic Rhodudult). Both pure resin and resin mixed with soil were found to have higher water movement characteristics compared to bulk soil. A resin pack method was found which had water movement characteristics that were not significantly different from that of bulk soil for the three different soil types. The resin pack method is described.

INTRODUCTION

The fate of fertilizer nitrogen applied to agricultural soils is of growing concern due to the potential for groundwater contamination and health risks associated with high NO_3 nitrogen levels in groundwater. In addition to the potential environmental problems associated with NO_3 leaching, the economic impact to the farmer is considerable. Therefore, measurement of NO_3 leaching is important for the evaluation of N fertilizer practices. However, quantitative measurements of NO_3 leaching losses in the field are very difficult and often inadequate to fully describe the amount of NO_3 leached.

Several techniques are commonly used for determining soil NO_3 leaching, including chloride balance (1), porous cup soil solution samplers (2), soil sampling below the rooting zone, and vacuum extractors (3). However, there are limitations to all of these techniques which make interpretation of data very difficult (1, 3, 4). Soil samples below the rooting zone can be used to accurately measure NO_3 in the soil at a given point in time, but this is a periodic measurement which may miss much of the total N flux (4).

The recent development of an exchange resin that specifically absorbs NO_3 has the potential for measuring NO_3 leaching by burying it below the rooting zone. The potential advantage of an exchange resin technique for measuring NO_3 leaching is its use to measure cumulative movement of NO_3 without an independent measurement of water flux and without interfering with crop production.

The use of ion exchange resin to measure NO_3 leaching was first proposed by Schnabel (4), who demonstrated that ion exchange resin effectively adsorbed added NO_3 at flow rates expected in soils. However, because the ion exchange resin is commonly in the form of spherical beads, about the size of medium sand grains, it (when placed in the soil for NO_3 measurements) would most likely cause textural discontinuity and alter water flow patterns through the soil (4).

To overcome this limitation, resin systems are needed with similar water movement characteristics as the surrounding soil. The objective of this study, therefore, was to compare water movement of potential ion exchange resin systems to those of soils with widely different textural classes.

MATERIALS AND METHODS

Laboratory experiments were conducted utilizing a soil water movement (SWM) testing device developed to compare the water movement of soil with those of various potential ion exchange resin systems. A 33 x 28 cm polypropylene pan of 14 cm height (Figure 1) was used to hold the soil to be tested. The pan was supported by a stand to allow for space between the pan and the floor. Four polyvinyl chloride (PVC) cylinders of 4.5 cm diameter and 5 cm height were mounted in the bottom of the pan (with 2 cm inside the pan and 2.5 cm below the pan) with silicon sealant. Two of the test cylinders were used as checks for the water flow through bulk soil and the other two test cylinders were used to test various resin systems. Filter paper was placed at the bottom of each test cylinders to hold the soil or resin system inside. After packing the test cylinders with soil and the resin system to be tested, additional soil was place in the SWM device until at least 8 cm of soil covered the PVC test cylinders. The soil under study was sieved through a 2.0 cm sieve and placed in the SWM device in the most uniform manner possible.

The soil was uniformly wetted to near saturation by placing the SWM device in standing water and allowing the soil to absorb water through the test cylinders. After wetting, the SWM device was allowed to drain, with drainage water from each test cylinder being collected in weighing tins filled with dry sand, which was in close contact with the soil and resin systems in the test cylinders to allow for continuity of water movement. At periodic intervals the weighing tins were removed, weighed, and replaced with tins with dry sand. The sand in each tin was then oven dried for use.

Drainage from the SWM was measured at 1/2 hour increments, with the addition of approximately 100 ml of water sprinkled on the soil surface of the SWM device after each time increment. Each run consisted of 6 time intervals. Calculation of the differential water movement was made by subtracting the average water movement through the soil test cylinders from the average water movement through the resin system under study for each run.

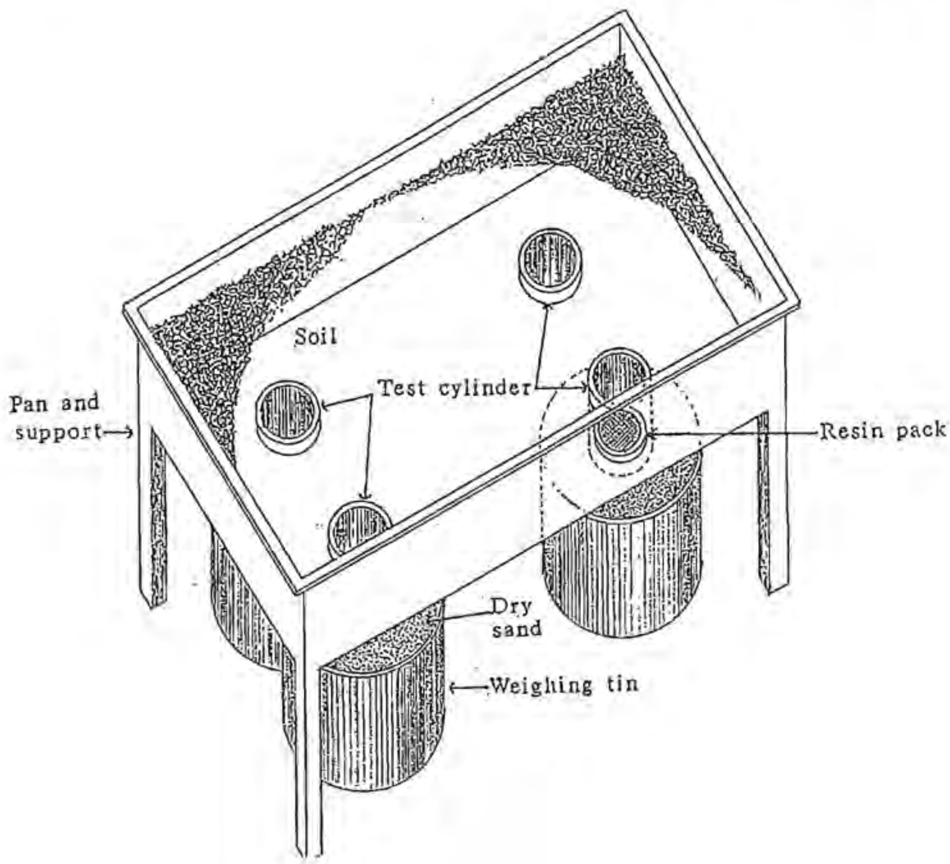

FIGURE 1. Schematic of an Soil Water Movement Testing Device for Comparing Water Movement Through Bulk Soil to that of Ion Exchange Resin.

The NO_3 selective anion ion exchange resin used in this study was Ionac SR-6 (Sybron Chemicals INC.)[1]. This resin (developed for removal of NO_3 from drinking water) has a high selectivity for NO_3 and is resistive to removal of NO_3 by other anions. Properties of the resin are given in Table 1.

1. Trade names and products are mentioned solely for information. No endorsement by the U.S.D.A. is implied.

TABLE 1. Typical Properties of Anion Ion Exchange Resin SR-6 Ionac†.

Typical Properties	Ionac SR-6
Physical	
Form	Spherical beads
Physical size (diameter mm)	0.25 - 0.5
Average hardness (g/bead)	800
Whole bead count (%)	90
Water retention (%)	32 - 36
Density (g/cm^3)‡	0.64 - 0.67
Chemical	
Polymer Structure	Tributyl Quaternary Amine Styrene Divinylbenezene Copolymer
Total Ion Capacity	
	Weight (meq/g) 1.8
	Volume (meq/ml) 0.8
Nitrate selectivity constant§	700
Ionic form‡	Chloride

† Ionac SR-6 is a product of Sybron Chemicals Inc., Birmingham, NJ 08011.
‡ Reported for conditions as shipped.
§ Nitrate selectivity constant is calculated for nitrate vs. sulfate. Normal anion ion exchange resin is equivalent to 1.

Three soil types of varying soil textures were used: a Cahaba sandy loam (fine-loamy, siliceous, thermic Typic Hapludult), a Congaree clay loam (fine loamy, mixed, nonacid, thermic Typic Udifluvent), and a Hiwassee clay (clayey, kaolinitic, thermic Typic Rhodudult) (Table 2). Water movement through bulk soil averaged over the 1/2 hour increment was approximately 4.7, 1.35, and 6.8 cm/hr for Hiwassee c, Congaree cl, and Cahaba sl, respectively.

TABLE 2. Physical Characteristics of Soils.

Soil			%	%	%
Series	Subgroup	Texture	Sand	Silt	Clay
Hiwassee	Typic Rhodudult	clay	23	17	60
Congaree	Typic Udifluvent	clay loam	20	51	29
Cahaba	Typic Hapludult	sandy loam	75	16	9

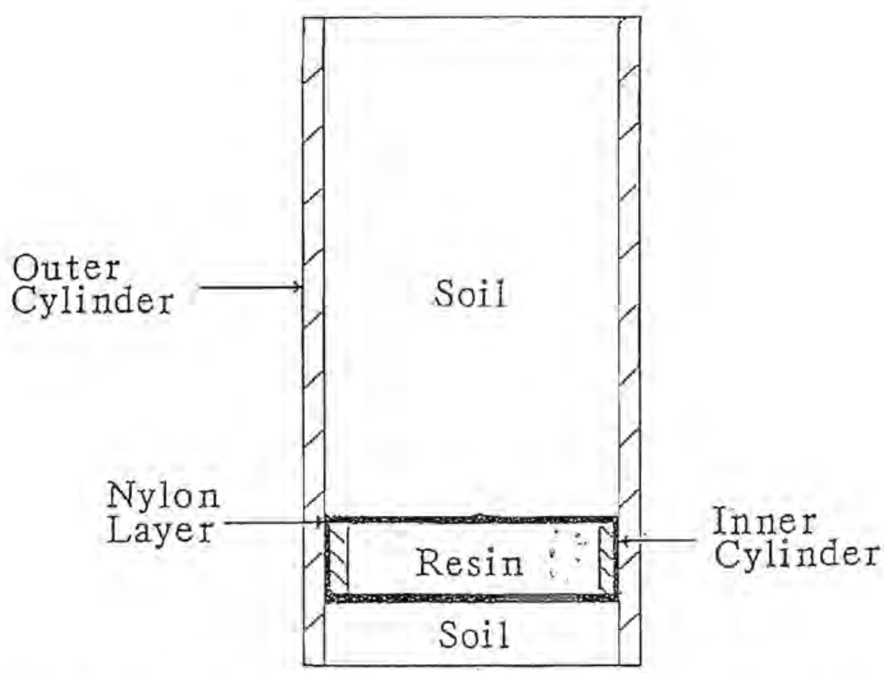

FIGURE 2. Cross Sectional Schematic of an Ion Exchange Resin Pack for Measurement of Nitrate Leaching in Agricultural Soils.

Several resin systems were tested, including a pure resin, a 1/2 resin and 1/2 soil mixture, and a 1/4 resin and 3/4 soil mixture. A system of using the resin in a separate pack was also tested (Figure 2). The resin pack used in this study was designed with consideration that the material used must be both readily available and able to withstand field conditions during the growing season. The resin pack was constructed using rings of 4.3 cm diameter PVC pipe cut into 1.3 cm lengths. These rings were then filled with 18.9 ml of ion exchange resin (total NO_3 adsorption capability approximately 937 mg) and covered with a fine nylon netting (nylon stockings). This material was chosen because it was strong, resistant to biodegradation and fine enough to hold the resin while allowing free movement of water. The resin pack was then placed near the bottom of a second PVC tube of 4.5 cm diameter. The second PVC tube was then filled with the soil under study from both the top and bottom.

In addition, several other systems were tried, including various concentrations of montmorillonite clay mixed with resin or with soil and resin. The resulting data demonstrated the inadequacies of these systems and were abandoned as potential systems (data not shown). Additional resin pack designs were also tested, but were abandoned due to inconsistencies.

The experimental design was a completely randomized design of 3 replications. The SWM device was emptied and repacked with the soil for each replication. Treatment means separation were made using the least significant difference (LSD) procedure ($P = 0.05$) (5).

RESULTS AND DISCUSSION

Results from the SWM device indicate that there is a drastic change in the water movement compared to bulk soil when ion exchange resin is added (Figure 3). Water movement through pure resin was much higher than soil, but it was not a simple additive relationship when added to soil. It was found that mixtures containing smaller proportions of soil had smaller differential water movement in all three soil types. This would indicate that dilution of the resin with more soil

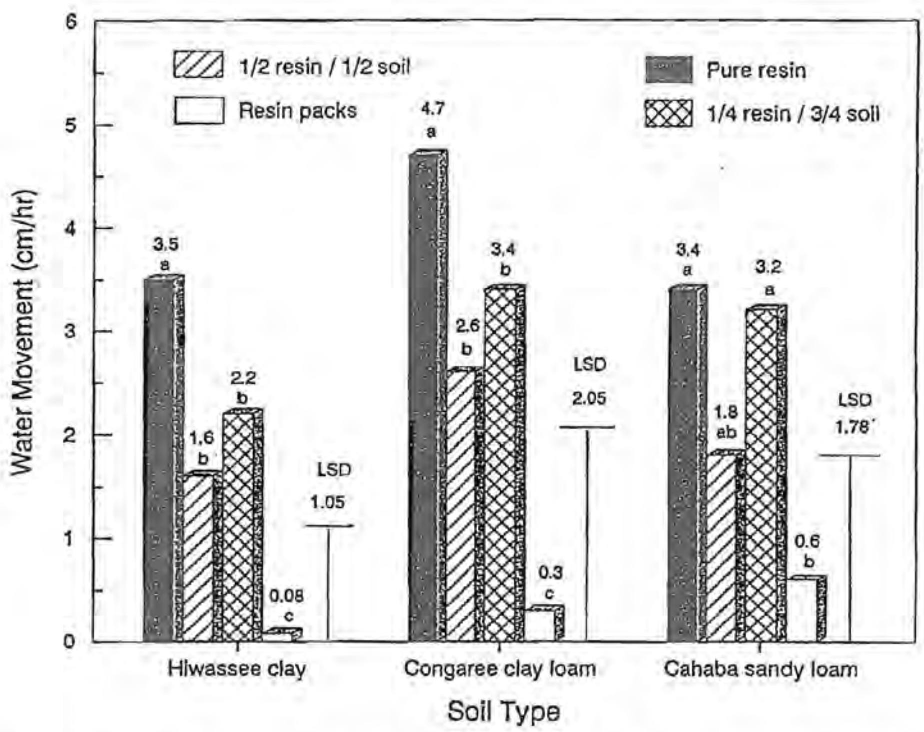

FIGURE 3: Differential Water Movement of Four Ion Exchange Resin Methods in a Hiwassee Clay, a Congaree Clay Loam, and a Cahaba Sandy Loam.

may not be a viable solution to the water movement problem when used in the field. Unlike sand particles, the resin is a porous material that allows intra-aggregate water movement. It is believed that this complicates the water movement characteristics (with water moving both around and through the resin), causing unexpected results when added to soil.

The resin pack was found to have the lowest differential water movement for soil in all three soil types and did not significantly differ from that of bulk soil ($P > 0.05$) (Figure 3). The resin pack was found to increase differential water movement as the clay content of the soil decreased. In the Cahaba sandy loam soil, the resin pack was not significantly different than the 1/4 resin 3/4 soil mixture ($P > 0.05$), although this mixture was different than bulk soil, indicating that caution should be used in applying this technique in very sandy soils.

In addition to more closely matching the water movent of soil, there are additional advantages to using the resin pack approach. The use of some form of resin pack would allow the resin to be used in a form equivalent to a fixed bed for which exchange resins are normally designed to function. The kinetics of an ion exchange resin's removal of anions is a very complicated relationship depending on the flow rate of water, concentration of anion, nature of the equilibrium, particle size, temperature, and bed depth (6). In any exchange resin there is a breakthrough capacity of captured anions which must not be exceeded to prevent leakage. While the relationship is not exactly definable (especially in a system with changing flow rates), there is a minimum bed depth that is dependent on the favorability of the equilibrium (6). The mixing of the resin with soil would most likely interfere with the ability of the resin to capture NO_3, becoming worse as the resin is diluted further with soil. The results from this study indicate that the problem of textural discontinuity in most soils could be overcome with the use of resin pack. It is believed that the use of resin packs would isolate the water moving through the soil and possibly allow the resin to remove NO_3 before returning the soil water to the bulk soil. While further study is needed, it is believed that with further development the ion exchange resin could be a viable method for making NO_3 leaching measurements in agricultural soils.

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