ION EXCHANGE RESIN STRIPS AS PLANT ROOT SIMULATORS

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ABSTRACT

Ion exchange resin strips have the potential to closely mimic the manner in which a plant root removes nutrient ions from the surrounding soil. A method was developed involving burial of resin strips in soil, followed by a deionized water and dilute HCl wash of the strips. In approximately 200 soil samples obtained from across Saskatchewan, the plant availability of nitrate, ammonium, phosphate, potassium and sulphate as predicted by resin strip burial was significantly correlated with the plant availability predicted by conventional chemical - based soil extractions. Growth chamber experiments were set up in which canola plants were grown on the soils and actual plant nutrient uptake compared to test - predicted availability. The ability of the resin strip burial to predict differences in availability of N and P to canola was similar to the conventional soil extractants, but for K and S the strip burial appeared to be a better predictor of observed differences in plant uptake.

INTRODUCTION

Extraction of plant nutrient ions from soil with ion exchange resin has long been considered to provide the most reliable index of plant availability (Bowman et al., 1978; Sibbesen, 1983; Yang and Jacobsen, 1990; Schoenau and Huang, 1991a, Qian et al., 1992). This is the result of ion exchange resins closely simulating or mimicking the action of plant roots, as plant roots remove soil nutrients by ion exchange.

Anion exchange resins contain positively charged surface functional groups which attract anions by electrostatic attraction, including phosphate, sulphate, and nitrate. Cation exchange resins contain negatively charged surface groups which attract cations such as potassium to their surface. Thus, exchange resins will act as a sink for ions when placed in a suspension of soil and water (Schoenau et al., 1992). Exchange resins in bead form have been widely used to extract soil phosphate from soil - water suspensions since the 1950's (Amer et al., 1955). Until recently, most of the reported work has involved the use of loose beads in extraction, mainly in research applications to estimate the bioavailability of phosphorus. A problem with using loose beads has been separating the beads from the soil following the extraction. Several recent studies have reported on the use of resin beads sown up in nylon net mesh bags. Skogley et al. (1990) report on such a method in which resin beads in a bag were placed for 2-3 days in saturated paste soil samples and used to determine plant available K and S.

Ion exchange resins in the form of strips or membranes have recently been developed for the extraction of nutrient ions from soil - water suspensions (Saggar et al., 1990; Schoenau and Huang 1991ab; Schoenau et al., 1992; Qian et al., 1992). Qian et al. (1992) have recently reported better correlations with plant nutrient uptake for resin strip extractions than for conventional chemical - based soil tests. Anion exchange resins in membrane form also offer potential advantages in ease of use over loose beads or beads in a bag in soil extractions. Saggar et al.

(1990) compared resin membranes to resin bags and observed that the bag procedure suffered from the disadvantage that resin bags often trap fine root and soil particles which can only be removed by washing under pressure, as well as problems with wear and tear on the sealed edges of the bags.

While resin strips have been occasionally used for removing bioavailable ions in soil - water suspensions in the laboratory, there have been no reported uses of resin strips for direct in - soil burial applications. We felt that a direct in - soil burial of ion exchange resin strips could offer additional advantages in that the resin strips will more closely resemble a plant root in its natural environment than when the strip is placed in a soil - water suspension and shaken. Some additional operational efficiencies though avoidance of soil weighing and handling may also be realized. The objective of this study was to develop and evaluate the direct burial of ion exchange resin strips in soil to act as a plant root simulator.

MATERIALS AND METHODS

Soils

Approximately 200 soil samples were selected from across the soil zones of Saskatchewan to represent the range of soil properties and nutrient availability typically encountered in Western Canadian soils. All soils were measured for N,P,K,S availability using a 1 hour resin strip burial, and conventional chemical extraction. Sixty five of the soils were selected for use in a growth chamber experiment with a 1 hour burial time, while thirty nine of the soils were selected for a growth chamber experiment with a 24 hour resin strip burial time.

Procedure

Resin Strip Burial

Sheets of anion and cation exchange membrane (BDH product no. 55164, 55165) were cut into 20 x 65 mm strips. The resin strips were then washed in 0.5M $NaHCO_3$ or 0.5M HCl and stored in deionized water prior to use. Then one anion exchange and one cation exchange resin strip was inserted directly into approximately 200 g of soil. After burial, deionized water was added to the surface of the soil to ensure that the soil in the vicinity of the strip was at or near field capacity. After the burial period, the strips were removed, washed free of adhering soil with a few squirts of deionized water, and then placed into a flask containing 20 mL of 0.5M HCl to elute (displace) the ions from the resin. All nutrient ions absorbed from the soil by the strips are displaced into solution by the dilute HCl. After 15 minutes, the strips were removed and nutrient concentration in the HCl eluent determined using Technicon automated colorimetry for nitrate and phosphate, a flame emission spectrometer for potassium, and ICP emission for sulphate. The resin strips are made ready for re-use by washing in 0.5M $NaHCO_3$ or 0.5M HCl. We have used the same strips for hundreds of short - term extractions with no apparent physical deterioration or loss of effectiveness. A technique similar to that described above was used for burial directly in the field. Nutrient removal is expressed as micrograms of nutrient per square centimeter of strip surface.

Chemical Extraction

In the determination of $NaHCO_3$ - extractable P (Olsen P) and K, a 3 cm^3 scoop of soil was shaken with 60 mL of 0.5M $NaHCO_3$ for 30 minutes on a reciprocating shaker. Then the suspension was filtered, and the phosphate in the extract determined by automated colorimetry and K determined by flame emission analysis. Another chemical extraction for P and K, known as the modified Kelowna method (Qian et al., 1991), was performed. The modified Kelowna extracting solution is comprised of 0.25N HOAc and 0.015N NH_4F as well as 0.25N NH_4OAc. Soluble NO_3-N and SO_4-S were determined by shaking a 25cm^3 scoop of soil with 50 mL of 0.001M $CaCl_2$ for 30 minutes. Samples were then filtered and the nitrate and sulphate concentrations determined colorimetrically.

Growth Chamber Study

Two separate growth chamber experiments were conducted using canola as the test crop for which actual plant uptake was measured and related to availability as predicted by the resin strips and chemical extractions. One of the growth chamber studies used 39 soils selected from the 200 soil samples on hand and a 24 hour strip burial time, and the other used 65 selected soils and a 1 hour burial time. In each pot, three canola plants (var. Profit) were grown to the late flowering stage, harvested, and the tissue dried for analysis. Total N,P and K in the plant tissue was determined by a sulfuric acid - peroxide digestion at 360 degrees followed by determination of the ion concentrations in the digest. Total S in the plant tissue was determined by sodium hypobromite oxidation (260^oC) to sulphate as per the method of Tabatabai and Bremner (1970), followed by determination of the sulphate in the digest using inductively coupled plasma emission spectrometry.

RESULTS AND DISCUSSION

Effect of Burial Time on Amount of Nutrient Extracted

Comparison between 24 hour and 1 hour resin strip burial for 5 selected soils showed lower amounts of nutrient removed in the 1 hour burial period (Table 1). This trend was particularly pronounced for N and S, while P and K were less affected. The greater effect of short versus long burial times on nitrate and sulphate removal may be explained in part by the additional contributions to nitrate and sulphate from organic matter mineralization over longer burial times such as 24 hours. As well, contact exchange is likely a more significant ion removal process for P and K as compared to nitrate and sulphate where diffusion is of greater relative importance. The diffusion would be affected more by burial time than the contact exchange. Differences observed between the soils may be explained on the basis of differences in mineralization potential as well as differences in soil texture, structure and density which would affect the relative impact of diffusion and contact exchange.

Table 1. Nutrient removal by resin strips buried for 24 hr and 1 hr in five Saskatchewan soils.

Soil	Nitrate		Phosphate		Potassium		Sulphate	
	$\mu g / cm^2$							
	24hr	1hr	24hr	1hr	24hr	1hr	24hr	1hr
1	142.9	20.9	1.60	0.66	72.0	35.5	15.5	3.6
2	84.1	4.7	0.23	0.07	28.3	17.6	106.6	10.1
3	167.9	28.7	0.40	0.23	12.7	18.1	15.4	3.9
4	21.6	5.9	0.25	0.14	30.6	20.9	5.4	2.3
5	28.9	8.6	1.21	0.30	17.5	27.5	8.3	2.5

Values are means of three replicate analyses.

Comparison of 15 minute and 1 hour burial times revealed a lower amount of nutrient extracted over 15 minutes, although the amount removed over 15 minutes still exceeded 70 percent of that removed over 1 hour. Burial times shorter than 15 minutes using a single strip of the size indicated above, along with the above indicated eluent volume resulted in phosphate concentrations in the eluent that were approaching the detection limit of the autoanalyzer equipment. This may be overcome by using larger strips, or else through burial of two or more strips which are then placed into the same eluent. If two or more strips are buried, this gives the additional advantage that the concentration of nutrient expressed per unit area of strip surface represents an average of the amounts removed by the two strips, similar to a bulked soil sample.

We compared nitrate removed by resin strip burial for times shorter than 15 minutes for four Gray Luvisolic soils. In this case, two strips were buried in 120 g samples of the 4 soils for 1, 5, 10 and 15 minutes. The shorter burial times resulted in lower removal of nitrate N from the soil. However, even for only a 1 minute burial the amounts of nitrate removed were well within the detection limits of our autoanalyzer. For another 16 soils in a comparison of 1 minute and 15 minute burials (Fig. 1), the amounts of nitrate removed in 1 minute were strongly correlated with nitrate removed over 15 minutes ($r^2 = 0.97^{***}$).

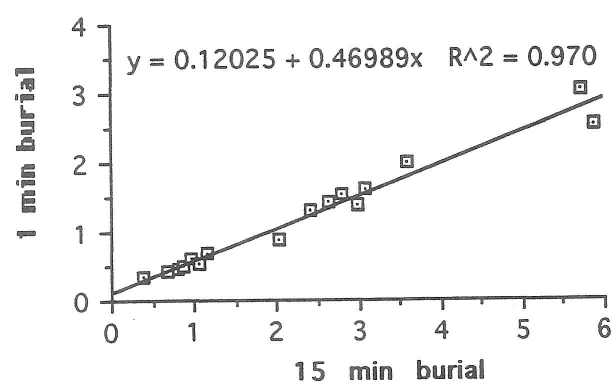

Figure 1. Relationship between nitrate removed by resin strips buried for 15 minutes and 1 minute.

Effect of Temperature

The amounts of N, P, K and S removed by buried resin strips was evaluated at four temperatures: 30,20,10 and 4 °C. The overall trend was found to be a slight decrease in the amount of nutrient extracted as soil temperature decreased, although in many cases the decreases were not significant. In most instances, 10°C temperature differences did not have a significant effect on amount extracted ($p = 0.05$), especially between 20°C and 10°C. The greatest incidence of significant decreases was observed over the 10°C to 4°C range. This effect was mainly observed for N and S over short (15 minute) burial times. The trend towards decreasing amounts removed with decreasing temperature likely reflects the direct effect that temperature has on ion diffusion, as well as an additional effect of increasing viscosity of water near and at temperatures of 4°C. This may not be viewed as a limitation since plant roots absorbing nutrient ions from soil in the field under similar temperature conditions would experience the same effect on nutrient diffusion to the root.

Effect of Moisture

The amount of nitrate, phosphate, potassium and sulphate removed from four soils at five soil moisture contents (saturated, field capacity, and 70, 45, and 15% of field capacity) was evaluated. In all cases, a similar trend was observed. As soil moisture content decreased, the amount of ion absorbed by the resin strips decreased significantly. Data are presented for two of the soils in Table 2.

Table 2. Nutrient ion removed by 1 hour resin strip burial in two soils at five soil moisture contents.

	Soil 1				Soil 2			
	N	P	K	S	N	P	K	S
	$\mu g / cm^2$							
Moisture								
Saturated	17.5	0.41	47.9	69.5	28.2	0.45	21.8	5.0
100% F.C.	10.9	0.33	39.1	50.8	20.0	0.27	18.1	3.9
70% F.C.	7.4	0.20	28.2	30.8	19.6	0.14	15.5	3.7
45% F.C.	4.2	0.13	20.2	16.7	11.3	0.09	9.3	2.6
15% F.C.	0.7	0.04	10.0	1.9	2.4	0.03	4.8	1.2

values are means of three replicate analyses.

The largest changes in amounts removed were associated with changes in moisture contents below about 70% of field capacity. The decrease in ion removed with decreasing soil moisture content, especially at low soil moisture contents, reflects the relationship between soil moisture content and diffusive flux of nutrient ions. As the soil becomes drier, the diffusion path becomes longer and more tortuous, as the large pores are no longer filled with soil solution. This is the same limitation on diffusive flux that plant roots encounter as the soil dries out. However, moisture contents in the field are highly variable and most nutrient uptake occurs when the plant is actively growing under moist soil conditions. For this reason, the recommended method of use for the resin strip burial as a root simulator is to add water after burial to ensure that the soil in the vicinity of the strip is at or near field capacity.

Relationship Between Nutrient Extracted by Strip Burial and Chemical Extractants

In over 200 soil samples, resin strips were buried for 1 hour and the amounts of N,P,K, and S extracted were compared to conventional chemical extractants (Table 3). For all nutrients, the amounts removed by the resin strip burial were significantly correlated with the conventional chemical extractants ($p = 0.0001$).

Table 3. Coefficients of determination (r^2) for regressions between nutrient extracted by resin strip burial (1 hour) and chemical extractants.

Nutrient	No. of samples	r^2
N	255	0.69***
P	244	0.57***
K	205	0.33***
S	232	0.73***

*** significant at P= 0.0001

As well, in a small field study in southwestern Saskatchewan, resin strips were buried directly in the field for 1 hour in 10 different soils with contrasting slope position, management, and cropping history. The amounts removed were compared to conventional extractions conducted on a sample of soil taken from beside each burial site and analyzed in the laboratory. For N,P,K and S, the amounts removed by the two methods were strongly and significantly correlated. Shown in Fig. 2 are the relationships for P and K.

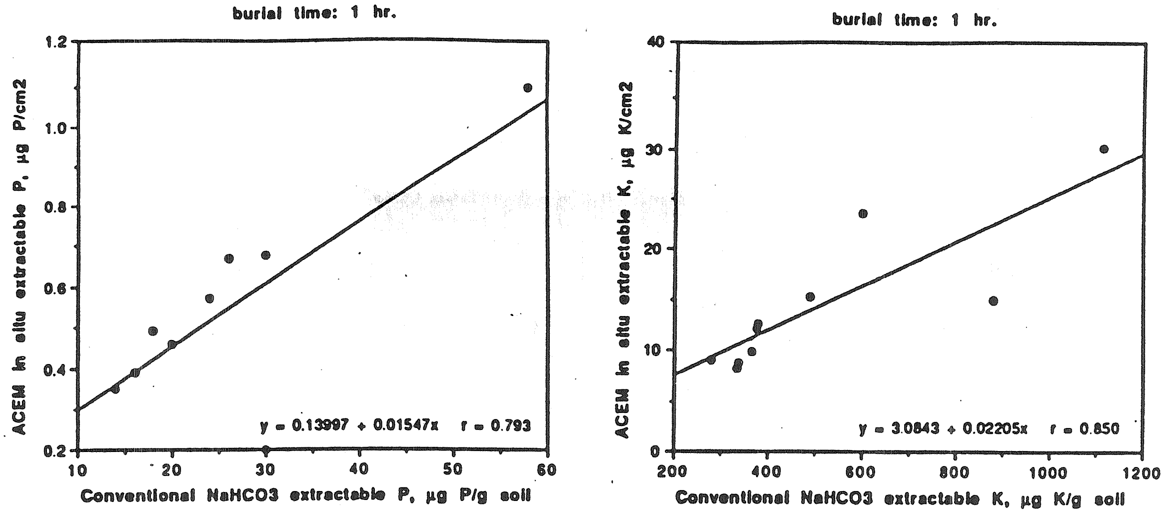

Figure 2. Relationships between amount of P and K removed by 1 hour in situ field burial of resin strips and P and K removed by $NaHCO_3$ extraction in the lab.

Relationships with Canola Nutrient Uptake

Two separate growth chamber experiments were conducted, one using 65 soils and a 1 hour strip burial period, and the other using 39 soils and a 24 hour strip burial period. For the 1 hour burial experiment, the Kelowna extracting solution was used as the chemical extractant for P and K. In the 24 hour burial experiment, the sodium bicarbonate (Olsen) extraction was used for P and K. In the two growth chamber experiments, both the resin strip burial and the conventional chemical extractions were highly and significantly correlated with actual measured plant uptake of the nutrients (Table 4).

Table 4. Coefficients of determination for relationships between soil nutrient extraction and nutrient uptake by canola.

Nutrient	Extraction	r^2 Experiment 1 (1hr, n=65)	r^2 Experiment 2 (24 hr, n=39)
Nitrogen	Resin Strip	0.55^{***}	0.62^{***}
	$CaCl_2$	0.60^{***}	0.57^{***}
Phosphorus	Resin Strip	0.71^{***}	0.72^{***}
	$NaHCO_3$	-	0.70^{***}
	Kelowna	0.76^{***}	-
Potassium	Resin Strip	0.46^{***}	0.52^{***}
	$NaHCO_3$	-	0.37^{***}
	Kelowna	0.40^{***}	-
Sulfur	Resin Strip	0.80^{***}	0.96^{***}
	$CaCl_2$	0.75^{***}	0.61^{***}

significant at p=0.0001.

Both the resin strip burial and chemical extractions were good predictors of plant nutrient uptake patterns among the soils. There appears to be little difference in the ability of the resin and the conventional chemical extractions to predict nitrogen and phosphorus availability to canola grown on the soil samples tested. However, the resin strip burial may offer somewhat better predictive ability for S and K availability. In the case of predicting K availability, the resin may be able to distinguish between K ions held onto soil colloids with differing degrees of affinity and therefore plant availability. Since ground and dried soil samples were used for the resin strip burials, any effects that soil structure has on nutrient availability to plants growing in the field is not accounted for in either of these tests. This would be expected to be most important for nutrients like potassium and phosphorus, where soil structure as it affects the nature of the pores and the diffusion path will greatly affect the ability of the nutrient to move to the root. Direct in field burial of resin strips may have an advantage in being able to account for this.

CONCLUSIONS

Burial of ion exchange resin strips offers considerable potential as a means of simulating the removal of nutrient ions from the soil by plant roots. In this study the technique proved to be well correlated with conventional methods of assessment and with measured plant uptake. The use of buried resin strips as plant root simulators may have practical applications in assessing soil nutrient availability as well as a research tool in the study of soil nutrient dynamics.

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