

Assessing plant-available potassium in soil using cation exchange membrane burial

P. Qian¹, J. J. Schoenau¹, K. J. Greer¹, and Z. Liu²

¹Department of Soil Science, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0; ²Soil and Fertilizer Institute, Shandong Academy of Agricultural Sciences, Jinan, Shandong, 250100, P. R. China. Received 7 April 1994, accepted 17 November 1995.

Qian, P., Schoenau, J. J., Greer, K. J. and Liu, Z. 1996. **Assessing plant-available potassium in soil using cation exchange membrane burial.** *Can. J. Soil Sci.* **76**: 191–194. We assessed a method for extraction of plant-available potassium using a **cation exchange membrane (CEM)** burial technique. The study compared the amounts of K extracted by CEM burial with three reference chemical-based extractants for 19 soil samples representing a wide range of soil types in Saskatchewan, Canada and the People's Republic of China. The three reference extractants were (1) 1 M NH₄OAc, (2) a mixed solution of 0.01 M EDTA, 0.25 M NaHCO₃ and 0.01 M NH₄F and (3) 1 M HNO₃. Potassium extractable by 1 M NH₄OAc ranged from 37 mg kg⁻¹ to 1889 mg kg⁻¹ among the 19 soils. The K availability as predicted by CEM was significantly correlated with the reference methods with the strongest relationship ($r^2 = 0.94$, $P < 0.001$) with the EDTA-NH₄F test. To evaluate the relative ability of CEM and the conventional tests to predict K availability to plants, canola and wheat were grown on the 19 soils in the growth chamber and plant K uptake was compared with test-predicted K availability. All test methods revealed a similar ability to predict K availability with good correlation ($r^2 \approx 0.70$, $P < 0.001$) with plant uptake. However, the CEM method showed its advantages in predicting plant availability in a variety of soil types with large coefficients of determination in both acidic and neutral to alkaline soil groupings. The CEM burial technique could be readily adopted in soil K availability analysis because of low cost and simplicity as well as its consistency over a wide range of soil types.

Key words: Cation exchange membrane, burial technique, extraction, plant K availability, plant K uptake, soil test

Qian, P., Schoenau, J. J., Greer, K. J. et Liu, Z. 1996. **Évaluation de la teneur en potassium assimilable du sol par enterrage d'une membrane d'échange cationique.** *Can. J. Soil Sci.* **76**: 191–194. Nous avons évalué une méthode d'analyse de la teneur en K assimilable du sol par enfouissement d'une membrane d'échange cationique (MEC). Nous comparions les quantités de K extraites par cette méthode avec celles obtenues au moyen de trois méthodes d'extraction chimique. L'étude portait sur 19 prélèvements de sol recouvrant un large éventail de types de sol de la Saskatchewan au Canada et de la République populaire de Chine. Les trois extractifs de référence étaient 1) 1 M NH₄OAc, 2) une solution mixte de EDTA 0,01M-NH₄F 0,01M NH₄F et 3) une solution 1M HNO₃. Les quantités de K extractible par NH₄OAc 1M fluctuaient, selon les 19 sols, de 37 à 1,889 mg kg⁻¹. Les quantités de K assimilables prédites par MEC étaient significativement corrélées avec celles obtenues par les méthodes de comparaison, en particulier le test EDTA-NH₄F. Pour évaluer l'efficacité relative de MEC et des tests classiques à prédire la biodisponibilité de K pour les végétaux, des plantes de colza canola et de blé étaient cultivées en chambre de croissance sur chacun de ces sols et l'absorption de K était comparée à la biodisponibilité prédite. Toutes les méthodes d'analyse démontraient une égale efficacité ainsi qu'une bonne corrélation ($r^2 \approx 0,70$, $P < 0,001$) avec les valeurs d'absorption réelles de K par les plantes. La méthode MEC l'emportait cependant par son efficacité de prédiction dans divers types de sol, comme l'attestent les coefficients de détermination élevés obtenus, autant dans les sols acides que dans les sols neutres à alcalins. La technique d'enfouissement de MEC pourrait facilement s'inscrire dans le protocole d'analyse du K assimilable, en raison de son faible coût et de sa simplicité d'exécution, en plus de la stabilité de ses prédictions dans un large éventail de types de sol.

Mots clés: Membrane d'échange cationique, technique d'enfouissement, extraction, assimilabilité de K, absorption de K, analyse du sol

A variety of extracting solutions are used to assess plant-available K in different parts of the world (Knudsen et al. 1982). These soil extraction methods usually require numerous steps which include pretreatment of soil, extraction with some type of extracting solution and filtration of soil suspensions before instrumental measurement. Increased complexity of the procedure can reflect on the accuracy of results and the cost of handling large numbers of samples. However, a major disadvantage is that none of the chemical extracting solutions is well related mechanistically to factors controlling K availability to plants in the field.

Ion exchange resins have been used to measure the K release in soil (Pratt 1951; Arnold 1958; Havlin and

Westfall 1985; Heming and Rowell 1985). This method, used as a batch extraction, gives an improved correlation with plant uptake when compared with other single extracting solution methods (Arnold 1958). Batch resin extraction in soil suspensions can improve K extraction compared with chemical extraction, but still does not account for phenomena affecting plant availability and uptake in the field, such as diffusion (Yang et al. 1991). Thus, direct burial of ion exchange resin in the soil may be attractive not only due to its convenience, but also because of its ability to better account for factors affecting plant uptake (Schoenau et al. 1993). The objective of this study was to evaluate the potential for using direct burial of CEM in soil as a new approach

for assessment of plant available K over a wide range of soil types.

MATERIALS AND METHODS

Soils

A total of 19 soils (0–15 cm depth) were selected for this study. Among the 19 soil samples, 17 were from across the agricultural region of Saskatchewan, representing a wide range of soil types and soil properties, and two were from China. The samples were air-dried and ground to pass a 2-mm sieve prior to analysis. Texture was estimated by hand. The clay minerals found in Saskatchewan soils are typically smectite, illite and vermiculite, with illite and vermiculite containing significant quantities of non-exchangeable K (Huang and Lee 1969). **Electrical conductivity (EC)** and pH were measured using a 1:1 soil:water suspension. Organic C was measured using a Leco carbon analyzer. The selected soil properties are summarized in Table 1.

Soil K Extraction and Determination

The new technique to extract K from the soil is based on burial of cation exchange resin membrane directly in the soil. The cation exchange membrane used consisted of a divinyl benzene base with sulfonate functional groups on the surface, giving the membrane surface cation exchange properties. The CEM is fixed to a plastic applicator to permit easy insertion and retrieval (Western Ag Innovations, Saskatoon, SK). Before use, the membrane is converted to the NH_4^+ or Na^+ form by soaking in either 0.5 M NH_4HCO_3 or 0.5 M NaHCO_3 overnight. The new technique is practised by inserting CEM directly into the soil. Water is then added to bring the soil around the membrane surface to field capacity. After 1 h, the CEM is retrieved from the soil and washed free of adhering soil with deionized water. Ions sorbed on the membrane during 1 h burial are then eluted using 0.5 M HCl (Qian et al. 1992). The K concentration in HCl solution was determined using both conventional flame emission spectrometry and a hand-held **ion selective electrode (ISE)**; (Horiba Cardy K Meter). In the determination of K using ISE, a drop of eluent solution to which CaCO_3 has been added to neutralized the acidity, is placed on the sensor and the K^+ concentration directly read from the meter. The amount of K sorbed during a resin membrane burial is expressed as $\mu\text{g K } 10 \text{ cm}^{-2}$ of membrane surface area.

The reference methods used to extract K in soil include 1 M NH_4OAc extraction (Chapman and Kelly 1930), boiling 1 M HNO_3 extraction (Wood and DeTurk 1941) and the extraction using a mixed solution of 0.25 M NaHCO_3 , 0.01 M EDTA, and 0.01 M NH_4F (Hunter 1984). The reasons the above three methods were chosen as the comparison methods are: (1) the NH_4OAc method is probably the most widely used extractant of all methods for measuring plant-available K and it is considered a “standard” method for available K, (2) the boiling HNO_3 method can extract some non-exchangeable K as well as exchangeable and soluble K (Knudsen et al. 1982), and (3) the EDTA- NH_4F mixed solution is commonly used in more highly weathered soils, including southern states in the United States, and has

Table 1. Ranges, averages and coefficient of variation of selected soil properties (n = 19)

Variable	Range		Mean	CV
	Min.	Max.		
pH	3.6	8.1	6.2	26.0
EC (ms cm^{-1})	0.1	0.5	0.2	60.7
Organic C (%)	0.5	39.0	5.5	158.6
Exchangeable K^z (mg kg^{-1})	37.0	1,889.0	423.3	104.5

^z1 M NH_4OAc extractable.

been widely used in China (13 of 29 provinces) since the mid-1980s (Jin and Porth 1991). The K concentration in the extracts for the three reference methods was determined using flame emission spectrometry.

Growth Chamber Study

All 19 soil samples were used in the growth chamber study. One kilogram of air-dried soil was measured into each pot. The test crops used were canola (*Brassica campestris* ‘Profit’) and wheat (*Triticum aestivum* ‘Biggar’). Before seeding, a nutrient solution was applied to each pot, providing N, P and S at rates of 100, 30 and 50 mg kg^{-1} of soil. All soils were also given a blanket micronutrient treatment of Cu, Zn, Mo and B at rates of 0.6, 4.0, 0.6 and 1.5 mg kg^{-1} , respectively.

Approximately 10 seeds of each crop were sown into each pot. The pots were transferred to a growth chamber with the temperature kept at 26°C daytime (16 h) and 12°C at night (8 h). All pots were watered twice daily to keep soil moisture at 90% of field capacity. After emergence, the pots were thinned to three plants for both canola and wheat. The pots were completely randomized and rotated every week. After 4 wk, additional N and S were applied in solution to each of the pots at rates of 100 mg N kg^{-1} and 50 mg S kg^{-1} to ensure that deficiency did not limit growth.

The plants were harvested at 7 wk for canola (blooming) and 8 wk for wheat (heading), dried at 60°C and weighed. Plant samples were then ground through a 1-mm stainless steel screen and stored for chemical analyses. Total plant K was measured by digesting plant tissue in sulfuric acid-peroxide using a temperature-controlled digestion block (Thomas et al. 1967), followed by flame emission spectrometry using a Perkin Elmer model 3100 AA/FE instrument.

RESULTS AND DISCUSSION

Effect of Different Counter-ion Forms on CEM Potassium Extraction

The trend in K extracted during burial in the 19 soils was similar ($r^2 = 0.90$, $P < 0.001$) regardless of whether Na^+ or NH_4^+ was used as the counter-ion on the membrane. According to the relative absorption affinity order for selected ions on cation exchangers, NH_4^+ is more strongly held than Na^+ (Walton and Rocklin 1989), but the amount of K extracted by the membrane in NH_4^+ form was 1.4 times

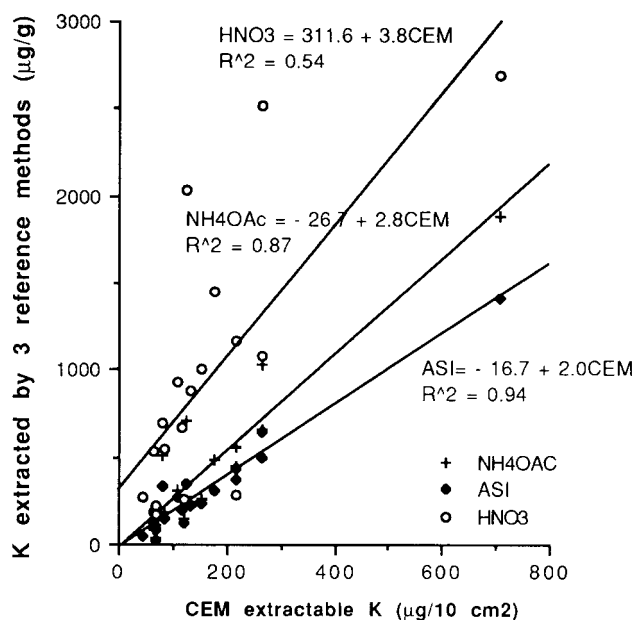


Fig. 1. Relationships of K extracted by CEM with K extracted by the three reference methods.

more than that extracted by the Na⁺ form. As NH₄⁺ and K⁺ ions have a similar hydrated ionic radius, the NH₄⁺ will have a better chance to exchange with interlayer K in 2:1 clay minerals, which are the main clay mineral forms in Saskatchewan soils.

Relationship Between K Extracted by CEM and Conventional Soil Tests

Potassium extracted by 1 h CEM burial was significantly related to the K extracted by three reference methods ($P < 0.001$; Fig. 1). The strongest relationship ($r^2 = 0.94$), using either a linear model or polynomial model, was observed between K extracted by CEM burial and K extracted by the EDTA-NH₄F method. The weaker correlation between K extracted by CEM burial and K extracted by the HNO₃ method (linear model, $r^2 = 0.54$; polynomial model, $r^2 = 0.58$) may reflect the fact that the HNO₃ method includes much more non-exchangeable interlayer K than the CEM burial. Boiling 1 M HNO₃ has been used successfully by a number of investigators as an index of K release from non-exchangeable forms (McLean and Watson 1985) since it was first introduced by Wood and DeTurk (1941). Pratt (1951) measured the K release in soil using ion exchange resin (bead form) and found that the amount of K released from non-exchangeable form to the resin was surprisingly similar in magnitude to that released with 1 M boiling HNO₃. In the study by Pratt (1951), however, 5 g of resin beads were equilibrated with 5 g of soil paste for up to 60 d. In our study, the CEM is buried in soil only for 1 h.

In the CEM technique, the r^2 of the relationship between K in HCl eluent measured by flame emission and K measured by portable ISE was 0.997 with probability level less than 0.001 ($n = 47$), and the amounts of K in the HCl eluent determined by the two methods were nearly identical. The

Table 2. Coefficients of determination (r^2) for relationship between total uptake of K by canola and wheat and K extracted in the K availability assessment techniques

Crop	Availability assessment technique			
	CEM	NH ₄ OAc	ASI	HNO ₃
Canola	0.65***	0.62***	0.68***	0.45**
Wheat	0.68***	0.73***	0.74***	0.70***

, *Significant at 0.01 and 0.001 levels.

Table 3. Coefficients of determination (r^2) for relationships between total uptake of K by canola and wheat and K extracted in soils grouped into different pH ranges

Crop	Soil pH group	Sample nos.	Soil tests			
			CEM (NH ₄ ⁺ form)	NH ₄ OAc	EDTA/NH ₄ F	HNO ₃
Canola	3.6 - 5.4	9	0.71**	0.17	0.35	0.72**
	6.7 - 8.1	10	0.69**	0.69**	0.75**	0.24
Wheat	3.6 - 5.4	9	0.66**	0.40*	0.53**	0.83**
	6.7 - 8.1	10	0.73**	0.79**	0.82**	0.56**

*, ** Significant at 0.05 and 0.01 levels.

hand-held ion selective electrode appears accurate enough to determine K content in the HCl eluent and would be highly suitable when used in conjunction with direct in-field burial of CEM to provide K availability assessments on site.

Ability of CEM to Predict K Availability to Canola and Wheat

The correlations between K uptake by canola and wheat and the predicted relative K availability among the soils as given by the CEM and reference methods are provided in Table 2. All the relationships were highly significant. Overall, all availability assessment methods showed a similar ability to predict K availability, with the exception of HNO₃ extraction. The weaker correlation between HNO₃ extractable K and plant K uptake for canola may reflect a limited ability of canola roots to use non-exchangeable K compared to wheat roots.

When the 19 soils were divided into two groups according to soil pH and correlations were conducted separately for each group, the coefficients of determination (r^2) for the relationships between K extracted by the NH₄OAc, EDTA-NH₄F and HNO₃ methods and plant K uptake were inconsistent. In general, the NH₄OAc and EDTA-NH₄F methods performed poorly in the acidic pH range. However, the CEM method performed equally well in the two pH groups (Table 3), implying that it functions well as an indication of relative availability in the different soil types we used.

CONCLUSION

Direct in-soil burial of cation exchange membrane is a suitable approach to assess K availability in a soil. The CEM burial method was equally well correlated with plant uptake as methods based on extraction of a soil sample using an extracting solution. Furthermore, the CEM technique appears to work well as an availability index in a variety of

soil types. Because of its simplicity in use, convenience and efficiency, CEM burial is particularly well suited to in-field K availability assessments, especially when combined with a portable ion selective electrode meter such as the Horiba Cardy meter to measure K concentration.

ACKNOWLEDGMENTS

The financial support of the Potash and Phosphate Institute of Canada (PPIC) is gratefully acknowledged.

Arnold, P. W. 1958. Potassium uptake by cation-exchange resins from soils and minerals. *Nature* **182**: 1594–1595.

Chapman, H. D. and Kelly, W. P. 1930. The determination of replaceable bases and base exchange capacity of soils. *Soil Sci.* **30**: 391–406.

Havlin, J. L. and Westfall, D. G. 1985. Potassium release kinetics and plant responses in calcareous soils. *Soil Sci. Soc. Am. J.* **49**: 366–370.

Heming, S. D. and Rowell, D. L. 1985. Soil structure and potassium supply. I. The release of potassium from soil aggregates to Ca-resin. *J. Soil Sci.* **36**: 45–60.

Huang, P. M. and Lee, S. Y. 1969. Effect of drainage on weathering transformations of mineral colloids of some Canadian Prairie soils. *Proc. Int. Clay Conf., Tokyo*. **1**: 541–551.

Hunter, A. H. 1984. Soil fertility analytical services in Bangladesh. A Consultancy Report, Bangladesh Agricultural Research Council, Dhaka, Bangladesh.

Jin, J. and Portch, S. 1991. Summary of greenhouse plant nutrient survey studies of Chinese soils. Pages 209–215 in *Int. Symp., Role of Sulfur, Magnesium and Micronutrients in Balanced Plant Nutrient*. Soil and Fertilizer Inst., Chinese Academy of Agricultural Science, Beijing, P. R. China.

Knudsen, D., Peterson, G. A. and Pratt, P. F. 1982. Lithium, sodium and potassium. Pages 225–246 in A. L. Page et al., eds. *Methods of soil analysis, Part 2*. American Society of Agronomy, Madison, WI.

McLean, E. O. and Watson, M. E. 1985. Soil measurements of plant-available potassium. Pages 227–308 in R. D. Munson et al., eds. *Potassium in agriculture*. American Society of Agronomy, Madison, WI.

Pratt, P. F. 1951. Potassium removal from Iowa soils by greenhouse and laboratory procedures. *Soil Sci.* **72**: 107–118.

Qian, P., Schoenau, J. J. and Huang, W. Z. 1992. Use of ion exchange membranes in routine soil testing. *Commun. Soil Sci. Plant Anal.* **23**: 1791–1804.

Schoenau, J. J., Qian, P. and Huang, W. Z. 1993. Assessing sulphur availability in soil using ion exchange resins. *Sulphur in Agriculture* **17**: 13–17.

Thomas, R. L., Sheard, R. W. and Moyer, J. P. 1967. Comparison of conventional and automated procedures for nitrogen, phosphorus and potassium analysis of plant material using a single digest. *Agron. J.* **99**: 240–243.

Walton, H. F. and Rocklin, R. D. (eds.). 1989. Ion exchange in analytical chemistry. CRC Press, Boston, MA.

Wood, L. K. and DeTurk, E. E. 1941. The adsorption of potassium in soil in non-replaceable forms. *Soil Sci. Soc. Am. Proc.* **5**: 152–161.

Yang, J. E., Skogley, E. O., Georgitis, S. J., Schaff, B. E. and Ferguson, A. H. 1991. The phytoavailability soil test: development and verification of theory. *Soil Sci. Soc. Am. J.* **55**: 1358–1365.