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ASSESSMENT OF SOIL POTASSIUM AND ITS UPTAKE BY RYEGRASS

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Potassium concentrations in soil solutions isolated by a centrifugal method, equilibrium K-activity ratios, K extracted with NH_4+Cl^- ion exchange resin and K extracted in conventional 1.OM ammonium acetate solutions were compared. A total of 44 Scottish soils representing five soil series and a Sri Lankan acid tea soil from St. Coombs were used.

The ability of ammonium N-fertilizer to mobilise soil potassium was demonstrated by substantial changes in soil solution K concentrations and resin extractable K, by small changes in ammonium acetate exchangeable K,but not by equilibrium K-activity ratios which were unchanged following nitrogen fertilizer addition to a granitic till soil under a ryegrass/clover sward.

K extracted with NH_4+Cl^- ion exchange resin and in 1.OM NH_4 oAc^- solution from 41 Scottish soils representing three soil series correlated well ($P < 0.001$) with K-uptake by ryegrass grown in the glasshouse. A greater amount of K was extracted by the resin compared with NH_4 oAc^- solution. Nitrification of NH_4 + -ion exchange resin was not significant during the 16 h equilibration of two Scottish soils and a Sri Lankan acid tea soil.

INTRODUCTION

Potassium is usually the most abundant of the plant nutrient elements found in soils. However, only a small fraction of the soil K is available for plant uptake.

Soil K occurs notionally in four different forms that are in equilibrium with each other, but differ in their availability to plants.

$$\underset{}{\text{Mineral K}} \underset{(a)}{\rightleftharpoons} \underset{}{\text{Non-exchangeable K}} \underset{(b)}{\rightleftharpoons} \underset{}{\text{Exchangeable K}} \underset{(c)}{\rightleftharpoons} \text{Soil solution-K}$$

Potassium release to plants in a single growing season is dominated by equilibrium (*a*), whereas (*b*) and (*c*) affect the long-term availability (Sinclair, 1979 a). Plants obtain their nutrients largely if not exclusively by soil solution (Adams *et al.*, 1980). Ions in the soil solution are in equilibrium with those adsorbed on the soil solid phases. Therefore an assessment of the nature of the soil solution K together with soil solid

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phase is required to understand the principles that govern soil-plant-K interactions. However, little attention has been paid to the seasonal variations in K concentrations in the soil solution and its replenishment from the soil solid phases. There are various reasons for this. Soil solution has been regarded as difficult to obtain in a form likely to relate closely to that present in undisturbed soil. Numerous methods have been proposed either to isolate soil solution, such as liquid displacement and lysimeters or to estimate potassium in soil solution, such as electro-ultrafiltration (EUF) and Quantity/Intensity measurements, but none has proved entirely satisfactory (Adams *et al.*, 1980; Sinclair, 1982; Ghorayshi and Lotse, 1986).

In this paper we describe a modified centrifugal method to isolate soil solution and the behaviour of K^+ in soil solution within the major root zone of a ryegrass/clover sward in the field.

The replenishment of soil solution K is affected predominantly by the concurrent release of non-exchangeable K together with exchangeable K during the growing season. Various methods have been used to estimate this non-exchangeble K, such as H^+ ion exchange resins, H^+ ion exchange resin + 1M NH_4 oAc, Quantity/Intensity measurements, EUF and Ca^{2+} ion exchange resins (Salomon and Smith, 1957; Arnold 1958; Talibudeen *et al.*, 1978; Sinclair, 1982). In this paper a novel method involving NH_4^+ – ion exchange resin has been used to study the chemistry of soil K dynamics and the results have been compared with standard methods.

MATERIALS AND METHODS

Soils

A total of 44 Scottish cultivated soils representing five soil series were selected to give a range of parent materials, texture and clay mineralogy. One Sri Lankan acid tea soil from St. Coombs Estate, Talawakele was used . Forty - one soils were used earlier (Sinclair, 1982). Two of the other three Scottish soils were derived from granitic tills of the Countesswells Association and the remaining soil was derived from slates and schists of the Foudland Association (Glentworth and Muir, 1963).

Soil solution

Soil solutions were isolated by centrifugation of 300 g field moist soil at 2000 x g for 1 h in a two component cell (diameter 9 cm and total height 10 cm) separated by a perforated disc (Linehan and Sinclair, 1985) and disposable polythene bags were used to reduce the possible contamination of the soil solution. The solution collected in the lower part of the cell was separated and re-filtered through a Whatman no. 42 filter paper to avoid contamination due to fine clay material. Potassium concentrations were determined by flame photometry.

When the samples were too dry to allow collection of enough solution for chemical analyses, samples were re-moistened by adding de-ionised water up to 90% of the field capacity. Re-moistened soil samples were stored in the cold room for 3-4 days and thoroughly mixed. Forty-eight soil samples can be centrifuged per day provided that the centrifuge has a 6-component head with appropriate dimensions equivalent to the cell.

Mixed NH_4^+ - cation exchange and Cl^- - anion exchange resin preparation

Four g of Duolite 225 H - resin (BDH; particle size of 0.50 - 1.18 mm) and 4.0 g of Amberlite Cl-resin ((BDH;IRA-400 particle size of 0.30 - 1.18 mm) were introduced into a nylon netting bag (3.5 x 6.5 cm) with mesh size of 0.2 mm. The oblong and tetrahedron shaped bags were sealed by means of an electric sealer (Sibbesson, 1977). These mixed-resin bags were equilibrated with excess 1M NH_4 Cl and 0.01M HCl (1:1) solution either in an orbital shaker or a vertical column. After the equilibration the pH of the solution/leachate was measured and a fresh solution of 1M NH_4 Cl and 0.01M HCl was introduced. This procedure was repeated until the pH was constant. The excess ions' were washed free in the same vessel with de-ionised water until the chloride ion concentration dropped to minimum. The final resin material contained NH_4^+ and Cl^- ions. Resin bags were stored under de-ionised water in order to avoid breakdown of resin beads.

Soil K extraction with $NH_4^+Cl^-$ ion exchange resin

Air-dried soil, equivalent to 5.0 g oven- dried soil, which had been passed through a 2 mm sieve was equilibrated with 100 ml of de-ionised water and a mixed ion exchange resin bag in a wide mouth polypropylene bottle for 16 h (overnight) in an end-over end shaker (40 r .p.m.). After the equilibration, the ion exchange resin bags were removed from the soil/water suspension and washed thoroughly with de-ionised water. The resin bags were eluted with 100 ml of 1M NH_4Cl and 0.01M HCl (1:1) solution in a wide mouth polypropylene bottle for half-an-hour in the same end -over end shaker. Potassium concentration was measured by flame photometry.

Nitrification of NH_4^+ ion exchange resin

The possibility of nitrification of NH_4^+ ion exchange resin material during the 16 h equilibration with soil/water suspension was studied by using "Nitrapyrin" [2-Chloro-6- (trichloromethyl) pyridine] as a nitrification inhibitor (Powell and Prosser, 1986). Five g of Sri Lankan acid tea soils and Scottish soils having three different pH values (4.0, 4.8 and 5.5) were equilibrated with 4.0 g of the NH_4^+ cation exchange resin and 100 ml of de-ionised water for 16 h with and without 15 $\mu g\ ml^{-1}$ "Nitrapyrin". A control set of soils were equilibrated without resin bags. After the equilibration, the soil suspensions were filtered through Whatman no. 42 filter paper. The nitrate concentration in the filtrate was measured colorimetrically after reduction to nitrite with hydrazine (Industrial method no. 333-86E Technicon).

Exchangeable K

Exchangeable K (K_{ex}) was determined by equilibrating air-dried and 2 mm sieved soils equivalent to 10.0 g oven - dried soils with 50 ml of 1.O M ammonium acetate (pH=7.0) in a 110 ml polypropylene tube for half-an-hour in a mechanical shaker. After the equilibration soil suspension was centrifuged at 1600 g for 15 min and supernatant was filtered through Whatman no. 42 filter paper. Potassium concentration was measured by flame photometry.

Equilibrium K-Activity Ratio (AR_o)

Quantity/intensity isotherms were determined for moist samples (<6.4 mm). The samples were equilibrated at 20±2°C for half-an-hour with 0.01M $CaCl_2$ solution containing KCl from 0.005 to 0.0035M, using the equivalent of 5.0 g oven-dry soil to 50 ml solution and with 0.01M $CaCl_2$ containing no K at soil: solution ratios from 1:10 to 1:250 in an end-over-end shaker (40 r.p.m.). After the equilibration, resulting suspensions were centrifuged at 1600 *g* for 15 min and filtered through Whatman no. 42 filter paper to avoid contamination from fine clay material. The K concentration of the clear supernatant solutions and the unreacted solutions were determined by flame photometry, and the change in soil K, Δ K meq kg^{-1} oven dry soil, was calculated.

Calcium and Magnesium ($Ca^{2+} + Mg^{2+}$) concentration in the clear supernatant was determined titrametrically with 0.02N Na_2 EDTA solution, calmagite indicator and triethanolamine. The gain or loss of K by the soil during the equilibration (ΔK) was plotted against the final activity ratio, $AR^K \times 10^3$ (Ml^{-1}), where,

$$AR^K = \frac{aK}{\sqrt{a(Ca^{2+}+Mg^{2+})}} = \frac{CK^+}{\sqrt{c(Ca^{2+}+Mg^{2+})}} \cdot \frac{r\,K^+}{\sqrt{r\,(Ca^{2+}+Mg^{2+})}}$$

and a = activity (mol dm^{-3})
c = concentration (mol dm^{-3})
r = activity coefficient

The ratio $rK \Big/ \sqrt{(Ca^{2+}+Mg^{2+}}$ was taken as 1.18 because the value varied little from this within the range of K and (Ca+Mg) concentrations found. The values of AR^K at Δ K = 0(AR_o) were obtained by interpolation (Fig. 1).

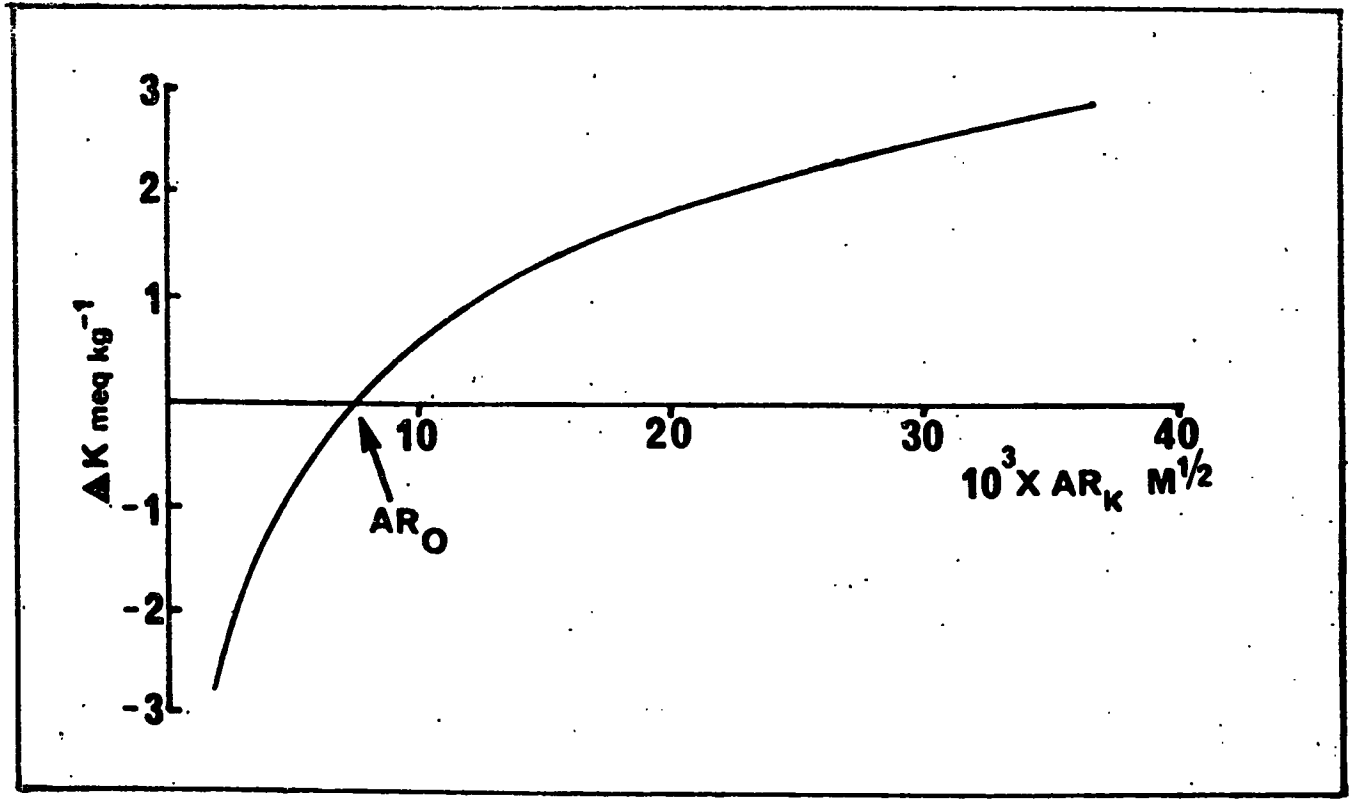

Fig. 1 — Diagrammatic Quantity/Intensity Isotherm

RESULTS AND DISCUSSION

Soil Solution K

A ryegrass/clover field experiment (Countesswells Association) with and without fertilizer K was selected to monitor the concentration of K in soil solutions within the major root zone soil. Soil solution K levels through the season were in the range of 0.20 to 1.26 ppm in the zero K applied plots and 0.50 to 4.38 ppm in the plots receiving 70 kg K/ha/cut as potassium chloride. The nitrogen addition to all plots was 110 kg N/ha/cut as ammonium nitrate. Soil samples were collected at 2-week intervals except immediately after fertilizer application when sampling was at 2-day intervals.

Figure 2 gives the variation of soil solution K level in the non-potassium fertilizer plots. "C" indicates when the sward was cut and "F" the timing of ammonium nitrate application. The increase in soil solution K concentration following N fertilizer alone is attributed to displacement of K^+ from exchange sites by fertilizer NH_4^+ ions. A similar effect was found in the soil solutions of winter barley (Linehan and Sinclair, 1988). This soil solution K variation was compared with K_{ex} (exchangeable K), K_r (NH_4^+ Cl^- ion exchange resin extractable K) and AR_o (equilibrium K-activity ratio). Because surfaces of most soils hold negative charges, the solution concentrations of K are altered by soil:solution ratios and initial salt concentration in the soil solution. The only way to obtain a constant number for K is to express its intensity relative to that of a reference ion. Calcium, with magnesium often included, is chosen as the reference ion because it is the dominant cation in most agricultural soils. In very acid soils, the choice of Al as reference ion is more suitable. The K_r values show a similar variation to soil solution K changes compared to K_{ex} . This could be due to some loosely held non-exchangeable K, which is not extracted by conventional 1M NH_4 oAc solution, but becomes extractable with NH_4^+ Cl^- ion exchange resins, following ammonium fertilizer application. These findings have implications in fertilizer use.

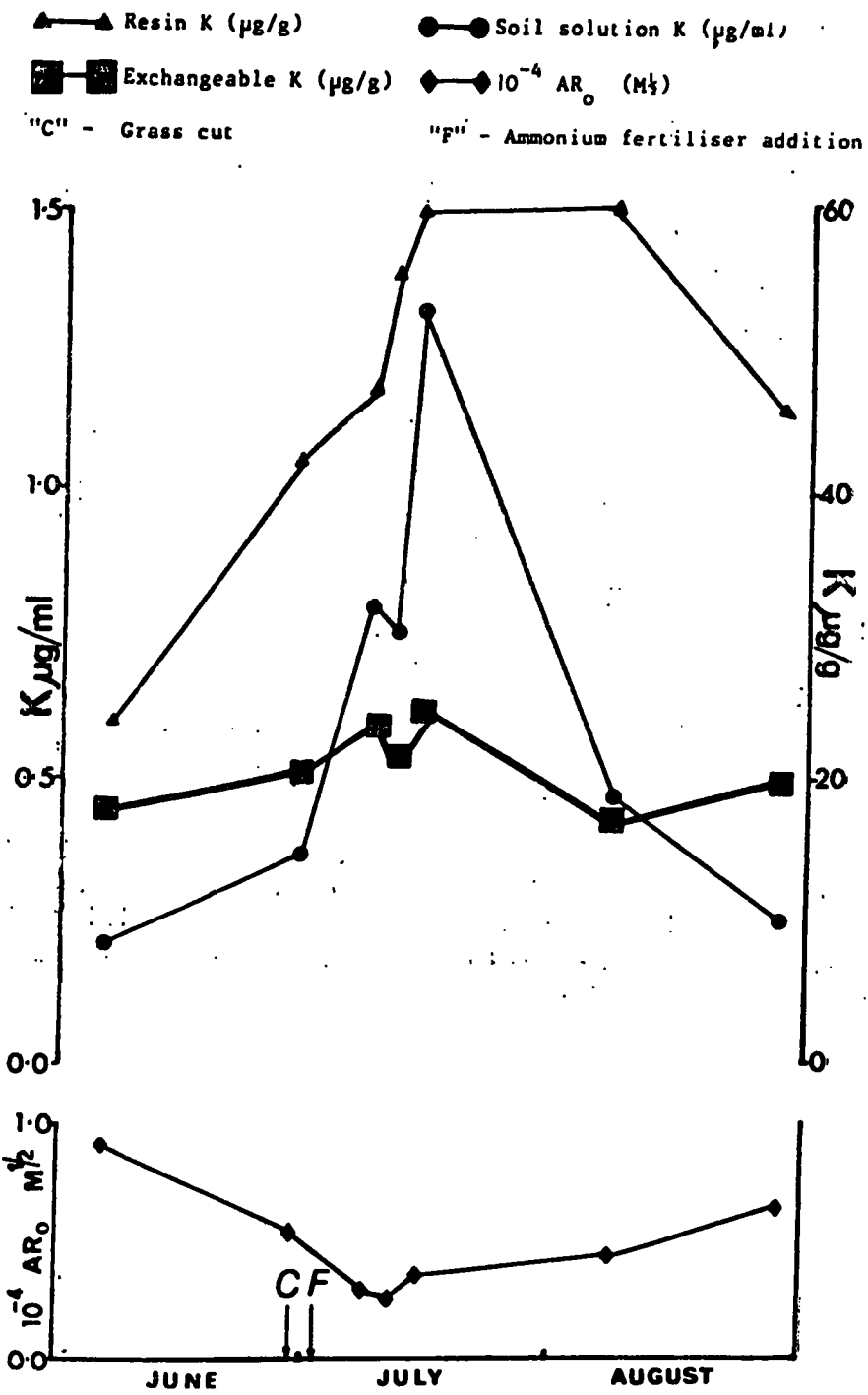

Fig. 2 — Variation of soil solution K level in the non - potassium fertilizer plots.

Mixed NH_4^+ Cl^- ion exchange resin K

Potassium was extracted from 41 soil samples with the mixed $NH_4^+Cl^-$ ion exchange resin (Kr) and the results (Table 1) compared with dry matter yield and crop K uptake from these soils by ryegrass grown in pots, and with K extracted by the conventional method using 1M NH_4 oAc solution at pH 7.0 (K_{ex}) (Sinclair, 1982; Wimaladasa and Sinclair, 1988).

TABLE 1— *Correlation coefficients of linear regressions of exchangeable and resin extractable soil K on cumulative K uptake and quadratic regressions on yield of ryegrass at different cropping stages.*

K measurements	*K uptake at cut no.*			*Yield at cut no.*		
	1	1+2	1+2+3	1	1+2	1+2+3
1M NH_4 oAc (K_{ex})	0.928	0.981	0.981	0.682	0.869	0.934
NH_4^+ Cl^- ion exchange resin (Kr)	0.943	0.982	0.980	0.642	0.845	0.917

(all $P<0.001$)

The Kr results in Table 1 shows similar correlations between soil test values and K uptake by ryegrass compared with conventional K_{ex}. An additional advantage of the mixed NH_4^+ Cl^- ion exchange resin is its ability to extract available soil phosphorus (Anon. 1987). Loosely held non-exchangeable K, K int, is not extracted by 1M NH_4 oAc solution, but becomes available to ryegrass. A close correlation between K_{int} and K_{ex} has been shown (Sinclair, 1979 b), which helps explain the observed close correlations betwen K_{ex} and ryegrass data. However, the mixed $NH_4^+Cl^-$ ion exchange resin does extract part of the non-exchangeable K. This ability to extract part of the non-exchangeable K is demonstrated by the relationship

$$Kr = 0.674\ K_{ex} + 0.935,\ r = 0.986\ (P < 0.001)$$

The equation shows that the greatest proportion of non-exchangeable K, compared to exchangeable K, is extracted by the ion exchange resin from soils of low exchangeable K. The rate of release of this non-exchangeable K is being investigated in the laboratory by means of sequential ion exchange resin extractors.

A quadratic relationship was found between the yield of ryegrass and soil K values (Table 1).

Nitrification of NH_4^+-ion exchange resin

The nitrate concentrations in Table 2 indicate that nitrification of NH_4^+ ion exchange resin was not significant during the 16 h equilibration.

TABLE 2 — *Nitrate-N concentrations (ppm) in aqueous extracts of soil with and without the presence of NH_4^+- ion exchange resin and "nitrapyrin".*

Extractant	*Soil pH*		
	4.0	4.8	5.5
Soil/water	0.52	0.91	2.25
Soil/water /NH_4^+ - ion exchange resin	0.55	0.86	1.60
Soil/water /NH_4^+ - ion exchange resin/nitrapyrin	0.54	0.72	1.53

Standard error of means $= \pm$ 0.047

CONCLUSIONS

The ability of ammonium N-fertilizer to mobilise potassium into soil solutions was demonstrated by a centrifugal method for isolating the soil solutions. These increases in plant-available K were also found in $NH_4^+Cl^-$- ion exchange resin extractions of soil. The K extracted with the ion exchange resin was greater than with the conventional ammonium acetate method and was correlated closely ($P < 0.001$) with K uptake by ryegrass grown in the glasshouse.

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