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Potassium reserves in British soils

I. The Rothamsted Classical Experiments

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SUMMARY

Thirty-four soils from the Rothamsted Experiments were exhaustively cropped with ryegrass in the glasshouse. The concentration and yield of potassium in ryegrass tops and the potassium intensity in the soil were measured every 4 weeks, after harvesting the grass.

The change in K-intensity of soils, rich in potassium, with exhaustion differed from that of 'poor' soils. This change was related to the rate of change of the cumulative K-yield. The rate of change of soil K-intensity demarcated periods of intense and limited exhaustion and partial recovery of the soil during cropping.

The cumulative K-yield of ryegrass was very significantly related to the K-intensity of the uncropped soil; the '16-week' yield was slightly better related than the '60-week' yield. For Park Grass soils, the relationship was improved by allowing for variations in soil pH.

The K-intensity of all soils, with or without manuring, decreased to nearly 10^{-3} $(\mathrm{M})^{\frac{1}{2}}$ in $(AR)_0$ units after 16 weeks cropping, although large differences in K-yield persisted until much later.

K-buffer capacity *per unit clay content* of the soil, measured by a laboratory method, was inversely related to the K-intensity of the uncropped soil. The K-buffer capacities of soils rich in potassium, measured in laboratory and glasshouse experiments, were significantly related, but were unrelated for 'poor' soils. The K-buffer capacity (laboratory method) of Rothamsted soils with different manurial treatments was only very approximately related to the cumulative K-yield.

Less K was taken up from all Rothamsted soils given nitrogen fertilizer in the field and their K intensities were also smaller than the corresponding soils without 'N'. Field liming of acid soils decreased their K-intensity and increased their K-buffer capacity, presumably because more potassium was removed by the field crop.

A rapid method is suggested for measuring potassium intensities of soils.

INTRODUCTION

Three soil properties have been suggested and used to determine the potassium status of soils: (1) the potassium intensity of the soil,

$$I_0 = \Delta G = RT \ln \frac{(\mathrm{K})}{(\mathrm{Ca})^{\frac{1}{2}}},$$

or more simply, the ratio, $(AR)_0 = (\mathrm{K})/(\mathrm{Ca})^{\frac{1}{2}}$, between the activities (K) and (Ca) of potassium and calcium ions in solution in equilibrium with the unextracted soil (Schofield, 1947; Woodruff, 1955*a*, *b*, *c*); (2) the potassium buffer capacity of the soil, i.e. the change in the amount of exchangeable potassium per unit change in the ion activity ratio of the equilibrium soil solution (Matthews & Beckett, 1962); (3) the total potassium released by the soil when exhaustively cropped in the glasshouse with ryegrass (Arnold & Close, 1961*a*, *b*).

Woodruff (1955*a*, *b*, *c*) correlated the potassium intensity of the soil with maize yields and Arnold (1962) obtained good correlations of intensity with the amount of K taken up by ryegrass grown for short periods in pots under glass. Taylor (1958) pointed out that rapid release of 'fixed potassium' in a potassium-fertilized soil or a naturally fertile soil would complicate a simple relation between the initial activity ratio $(AR)_0$ and potassium uptake. Matthews & Beckett (1962) suggested that 'fixation'

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and release of potassium is related to the amount of exchangeable potassium in the soil rather than its degree of potassium saturation. They also found that the equilibrium activity ratio $(AR)_0$ is regulated by the amounts or proportions of potassium in the 'fixed' state, which depends on manurial history and the minerals in the soil. Beckett (1964) concluded that the 'immediate' relationship between exchangeable potassium, Q, and $(AR)_0$ regulates potassium uptake over a single short period. However, crops exploit the same volume of soil over a long period during which the relationship between total K-uptake and the 'immediate' $Q:(AR)_0$ measurement may not be simple.

We planned to find: (1) whether the potassium intensity of the uncropped soil could define the K status of different soils when continuously cropped for long periods without K-fertilizer in the glasshouse; (2) whether the K intensity of the soil measured at any time *during* cropping could predict potassium uptake by the succeeding crop; (3) whether differences between the 'instantaneous' buffer capacities of soils were related to the cumulative release of soil potassium to the crop; (4) the effects of fertilizer residues on the potassium intensity and buffer capacity of the soil, crop uptake and the rate of release of potassium; (5) the effect of drying K-exhausted soils on subsequent K-uptake (Talibudeen & Dey, in preparation).

MATERIALS

Thirty-four soils from the Rothamsted Classical Experiments, taken in June 1963, were sampled 0–20 cm deep.

METHODS

1. *Exhaustive cropping in the glasshouse*

The soils were cropped and the treatments replicated in three randomized blocks. 200 g air-dry soil (< 2 mm) mixed with 50 g K-free quartz was put on top of 50 g quartz in brown glass pots standing in saucers. 0·100 g perennial ryegrass seed (S. 23), placed on the soil-quartz surface, was covered with 0·5 cm quartz. Repeated dressings of basal nutrients were given, the first to soils when setting up the pots, the second in the saucer when the seeds germinated and the third on the soil surface one week after germination. Thereafter the basal nutrients were given weekly, alternately on the surface and in the saucers, till the sixth cut of grass. To avoid salt toxicity, basal nutrients were given at half-rate weekly between the 6th and 7th cuts and at quarter-rate subsequently. The pots were watered alternately on the surface and in the saucer with demineralized water for the first 3 months and thereafter in the saucers. The grass was cut every 4 weeks, 1·25 cm above the soil surface, and the soil sampled to its full depth with four cores per pot, just before basal nutrients were given (see above). When yields became less than 50 mg dry matter/200 g soil, cropping was stopped.

Supplementary lighting to give a 18 h 'day' was from high-pressure mercury vapour lamps (500 W with internal reflectors) hung above the pots. The contents of the 'exhausted' pots were removed and air-dried, quartz particles and roots sieved out and soil stored air-dry to be cropped again later.

Soil temperatures were maintained at 27 ± 3 °C during cropping by enclosing the pots in warmed air, thermostatically controlled; the grass foliage was at glasshouse temperatures which ranged between 15–35 °C throughout the year. The soil temperature was above that for maximal growth of grass but was chosen to maintain rates of release of soil potassium reasonably independent of soil temperature over the year. That the experiment succeeded in this was proved by the smooth curves for the rate of 'yield of potassium' (Fig. 1) compared with those obtained in previous work (Arnold & Close, 1961*a*, *b*). About 2 g air-dry soil from three replicate pots were sampled after each cut of grass; potassium yields at each harvest were corrected accordingly; the sampled soil was kept damp until potassium intensity measurements had been made.

2. *Analytical methods*

(*a*) *Equilibrium activity ratio $(AR)_0$ of potassium*

(1) Uncropped soils—long method: the value of $(K)/(Ca)^{\frac{1}{2}}$ in the (K + Ca) chloride solution, which neither gave potassium to the soil nor removed any from it, was interpolated from the potassium buffer capacity curves (see later). (2) Uncropped soils—short method: 10 g air-dry soil, wetted with 2 ml water overnight, was shaken 15 min with 20 ml 0·01 M-$CaCl_2$ and centrifuged; the supernatant fluid was added to another 10 g prewetted soil and again shaken and centrifuged. This cycle was repeated once or twice, depending on soil pH, the K and Ca determined in the final supernatant fluid and the pH in the suspension. Several soils can be examined in a day by this method and $(AR)_0$ values of other ions could be measured in the same equilibrium solution. (3) Cropped soils: the fresh samples (about 3 g damp soil) were shaken each with 4 ml 0·005 M-$CaCl_2$ for an hour, centrifuged and the K and Ca determined in the supernatant solution. The pH of the remaining suspension was measured.

Replicate measurements of $(AR)_0$ values of the Hoosfield unmanured and K-fertilized plots before cropping gave values of 13 ± 5 and 149 ± 19 × 10^{-4} units respectively. Reproducibility with small concentrations of K seemed to be affected more by the manner and length of storing the solutions than by analytical procedures, but this was not investigated systematically.

(*b*) *Potassium 'buffer capacity' by instantaneous equilibration on uncropped soils* (*after Matthews & Beckett*, 1962)

Weighed samples of prewetted soils were shaken for an hour in solutions containing 0·01 M-$CaCl_2$ and from 0 to 10000 μM-KCl/l., centrifuged and K and Ca determined in the supernatant solution. BC values were calculated as the slope of the linear part of the curve relating the nett change in K content of the soil and the concentration ratio $K/\sqrt{Ca}$ in the equilibrium solution at the point where the K concentration of the added solution did not change in contact with soil. Replicate measurements of BC values of the Hoosfield unmanured and K-fertilized plots before cropping gave values of 105 ± 47 and 67 ± 20 respectively.

(*c*) *Yield of potassium or K-uptake by grass*

Harvested grass from replicate pots was dried, bulked and ground. Potassium from subsamples was extracted in cold 0·5 N-HCl and determined by flame photometry. The standard error for cumulative yields at 4 weeks was ± 10·7 %, at 16 weeks, ± 4·6 %, and at subsequent weeks ± 4·0 %. Exchangeable potassium in the soils was measured by M ammonium acetate extractions and cation exchange capacity by NH_3-distillation from the NH_4-saturated soils (Tables 2–5).

It was recognized that intensity values smaller than the correct values by the first two methods (used for measuring K-intensity of uncropped soils) might be obtained by the third method for cropped soils. Corrections based on the buffer capacity curve for each soil and the amount of K removed in solution were calculated but were insignificantly small, especially as the soil potassium became exhausted.

No corrections for the activity coefficients of K and Ca ions were made because we do not present potassium intensity as a 'free energy' term (Woodruff, 1955*a*, *b*, *c*; Arnold, 1962). The activity coefficient corrections remain sensibly constant for all values because of insignificant changes in the ionic strengths of the equilibrium solutions.

RESULTS

Tables 2–5 summarize the results of crop and soil analyses. Figs. 1–4 give more details of K-uptake and concentration in the crop and changes in soil K-intensity by cropping for Barnfield. The K-yields (ppm of soil) from the three Broadbalk plots used in this work are given below for comparison. K-intensities of the 'uncropped' soils from eight Broadbalk plots are given in the section on 'Park Grass'.

	'16 week' yield (ppm)	'60 week' yield (ppm)
No manures	165	230
PKNaMg	610	856
FYM	660	885

For convenience, the soils are classified as 'poor' or 'rich' if their initial K-intensities are below or equal to and above 50×10^{-4} units respectively. These two groups differ in the way soil K intensity changes with cropping, in the rate of uptake in the successive cuts (and, therefore, cumulative uptake) in the first 16 weeks, and in the K concentration of the crop in successive harvests.

The cumulative uptake: time relationship shows that there were two distinct mean rates of uptake during cropping up to and after 16 weeks, i.e. 10 ± 3 and 2·6 ± 0·6 ppm of soil per week for poor soils, and 35 ± 4 and 7 ± 2 ppm of soil per week for rich soils.

The increase in cumulative uptake with time from rich soils was almost linear up to 16 weeks, increasing thereafter more slowly to a maximum; this initial linear increase was not observed with poor soils as the following table shows:

Cropping period in weeks	Cumulative uptake in relative units	
	20 poor soils	13 rich soils
4	1·0	1·0
8	1·7	2·2
12	2·4	3·2
16	2·6	3·8

We regarded 25 mg dry matter, or 0·25 mg K per 100 g soil in one cut of grass the lower limit of exhaustive cropping. After 24 weeks, some Park Grass soils first showed signs of exhaustion (Table 5). Unlimed soils manured with K were exhausted earlier than limed soils, especially those given N in the field. After 36 weeks, yields dropped significantly and only a few soils rich in K residues from fertilizers and FYM released potassium much above the exhaustion limit. The unlimed Park Grass plot 11_1 soil (complete minerals with 129 lb N as ammonium sulphate/acre) had a pH of 3·06 in 0·01 M-$CaCl_2$ and did not grow any crop. For all soils except the poor soils from Park Grass (see section 'The Park Grass Experiment'), the NH_4-acetate exchangeable potassium was 70–99 % (mean 81 %) of the potassium released to the crop in the first 16 weeks. Potassium yields in 16 weeks and in the 16- to 60-week period (when mostly non-exchangeable K was released) followed the order of manuring

'K' or 'PK' ⩾ 'FYM' > 'None' 'N'.

The 'No manure' plots yielded more K in

Table 1. *Cropping and manuring*† *of the Rothamsted Classical plots from which samples were taken*

					Rate, nutrient lb per acre				
Field	Cropping	Manures applied	N as ammonium sulphate	N* as sodium nitrate	P as super-phosphate	K as potassium sulphate	Na as sodium sulphate	Mg as magnesium sulphate	FYM tons per acre
Barnfield	Roots since 1843	Annually	86	86	30	200	80	20	14
Broadbalk	Winter wheat since 1843	Annually	N_1 N_2 N_3 43 86 129	— N_2^* 86	30	80	—	10	14
Exhaustion Land	Winter wheat 1856–74	Annually	86	0	30	80	14	10	0
	Potatoes 1876–1901	Annually	86	86	30	120	14	10	14
	Cereals since 1902	Since 1940	56	0	0	0	0	0	0
Hoosfield	Spring barley since 1852	Annually	43	43	30	80	14	10	14
Park Grass‡	Permanent grassland since 1856	Annually	N_1 N_2 N_2 43 86 129	— N_2^* 86	30	200	14§	10	14

† For fuller details of the manuring history of these plots see: Details of the Classical and Long-Term Experiments up to 1962; Rothamsted Experimental Station (1966); Barnfield, Warren & Johnston, 1962; Exhaustion Land, Warren & Johnston, 1960; Park Grass, Warren & Johnston, 1964.

‡ Plots are halved and soils were taken from both the unlimed (*U*) and limed (*L*) halves. (*L*: ground chalk equivalent to 2000 lb CaO per acre applied every 4th year since 1920).

§ Plot 8: 1856–61, 28 lb Na; 1861–63, 70 lb; 1864–1904, 35 lb; 1905 to the present, 14 lb.

|| Plot 13: 1856–1904, N_2PKNaMg; since 1905, FYM and fish guano, 4 year cycle; FYM, year 1; fish guano, year 3, no manures in years 2 and 4.

Table 2. *Exhaustion Land, soil and crop results*

				Exchangeable K		$(AR)_0 \times 10^{-4}$				% K in crop			K yields (ppm of soil)		K buffer capacity ($\times 10^{-3}$)		
Plot no.	Manurial treatment from 1856 to 1901	pH in 0·01 M-$CaCl_2$	Organic carbon (%)	ppm in soil	in CEC	0	4 (weeks)	16 (weeks)	Final	4	16 (weeks)	Final	16 (weeks)	Final	Labora-tory	Glass-house	Cropping period weeks
1	None	7·3	0·97	90	2·7	8·0	2·0	9·0	4·4	1·9	0·72	0·70	87	160	161	167	44
5	N	7·3	0·89	98	2·5	11	1·5	8·0	2·9	2·1	0·84	0·82	103	194	142	65	44
6	N*	7·0	0·93	102	2·2	16	2·0	14	3·6	2·2	0·71	0·70	100	198	110	30	44
7	NPKNaMg	7·4	0·93	133	3·6	18	3·0	9·0	3·2	2·7	1·2	1·0	177	311	127	44	56
8	N*PKNaMg	7·0	0·97	133	2·9	14	1·1	10	3·6	2·7	1·2	1·0	183	321	142	71	56

N as ammonium – N; N* as nitrate – N.

Table 3. *Hoosfield—soil and crop results*

Plot no.	Manurial treatment from 1856 to 1901	pH in 0·01 M-CaCl$_2$	Organic carbon (%)	Exchangeable K		$(AR)_0 \times 10^{-4}$				% K in crop			K yields (ppm of soil)		K buffer capacity ($\times 10^{-3}$)		Cropping period weeks
				ppm in soil	% satn. in CEC	0	4 (weeks)	16	Final	4	16 (weeks)	Final	16 (weeks)	Final	Laboratory	Glasshouse	
1·0	None	7·4	0·89	109	3·0	13	1·0	15	2·8	2·49	0·81	0·74	131	189	105	45	32
1 A	N	7·4	0·93	94	2·5	12	1·0	17	3·0	1·08	0·65	0·70	109	160	133	43	40
1 AA	N*	7·4	0·93	102	2·9	10	1·1	14	3·5	1·76	0·75	0·73	120	191	137	61	44
3·0	KNaMg	7·3	0·97	530	12·3	149	70	11	9·2	5·10	2·67	1·40	530	809	67	30	56
7·2	FYM	6·9	3·2	760	11·7	349	96	20	9·6	5·21	2·53	1·20	725	1069	29	15	56

N as ammonium – N; N* as nitrate – N.

Table 4. *Barnfield, soil and crop results*

Plot no.	Manurial treatment from 1856 to 1901	pH in 0·01 M-CaCl$_2$	Organic carbon (%)	Exchangeable K		$(AR)_0 \times 10^{-4}$				% K in crop			K yields (ppm of soil)		K buffer capacity ($\times 10^{-3}$)		Cropping period weeks
				ppm in soil	% satn. in CEC	0	4 (weeks)	16	Final	4	16 (weeks)	Final	16 (weeks)	Final	Laboratory	Glasshouse	
8·0	None	7·5	0·77	180	3·6	17	2·5	8·4	3·2	3·3	1·2	0·5	270	369	324	59	52
8 A	N	7·4	0·73	129	2·8	11	1·2	8·2	3·0	2·4	0·7	0·7	150	209	182	69	40
8 N	N*	7·5	0·77	129	2·2	16	1·0	7·6	10·2	2·2	0·8	0·6	188	259	502	46	48
6·0	PK	7·5	0·58	547	10·1	69	24	10	8·9	5·4	3·8	1·8	730	1156	120	65	60
6 A	NPK	7·4	0·73	202	5·4	18	4·2	9·5	4·0	2·5	0·9	0·6	214	320	141	45	48
6 N	N*PK	7·5	0·62	160	2·7	24	3·7	9·5	3·7	3·5	1·5	0·6	420	577	149	75	52
1·0	FYM	7·2	2·6	625	8·1	254	23	9·5	8·8	5·3	2·7	1·8	750	1168	14	56	60
1 A	N + FYM	7·2	3·1	527	7·4	115	12	9·1	8·4	5·1	2·0	1·0	620	852	52	37	60
1 N	N* + FYM	7·2	2·7	410	6·2	109	25	7·0	8·5	5·2	2·4	0·8	668	980	76	66	60

N as ammonium – N; N* as nitrate – N.

Table 5. *Park grass, soil and crop results*

Plot no.	Manurial treatment from 1856 to 1901	pH in 0·01 M-CaCl$_2$	Organic carbon (%)	Exchangeable K		$(AR)_0 \times 10^{-4}$				% K in crop			K yields (ppm of soil)		K buffer capacity ($\times 10^{-3}$)		Cropping period weeks
				ppm in soil	% satn. in CEC	0	4 (weeks)	16	Final	4	16 (weeks)	Final	16 (weeks)	Final	Laboratory	Glasshouse	
3 U	None	4·70	3·0	74	1·3	14	2·8	8·0	5·0	0·84	0·35	0·27	51	57	738	21	24
3 L	None	6·70	3·2	55	0·82	10	1·0	9·0	7·0	0·84	0·40	0·27	40	45	374	27	24
8 U	PNaMg	4·66	2·6	67	1·2	11	2·5	26·0?	7·0	0·84	0·35	0·35	50	54	102	30	24
8 L	PNaMg	6·55	3·6	63	0·84	9	1·0	7·4	7·6	0·65	0·41	0·31	20	28	287	76	24
7 U	PKNaMg	4·20	2·2	680	13·3	615	66	8·6	8·0	5·94	1·80	1·70	680	854	13	25	40
7 L	PKNaMg	6·47	3·1	528	8·3	170	30	9·5	8·9	5·49	1·70	0·96	650	806	87	16	54
14 U	N$_2$*PKNaMg	5·48	2·5	493	9·1	213	25	9·7	4·7	5·03	1·80	0·90	585	763	42	20	48
14 L	N$_2$*PKNaMg	6·74	2·9	445	7·1	143	22	10	3·9	5·11	1·81	0·73	560	708	61	19	52
11/1 U	N$_3$PKNaMg	3·06	3·0	238	4·0	302	—	—	—	—	—	—	—	—	11	—	—
11/1 L	N$_3$PKNaMg	3·76	3·5	242	3·9	117	13·8	11	6·2	4·27	0·59	0·64	268	301	34	8	44
13 U	FYM	4·24	2·1	94	1·9	26	2·9	11	7·3	0·84	0·35	0·32	78	80	66	10	24
13 L	FYM	6·52	2·9	94	1·5	16	0·9	21	3·6	0·65	0·41	0·31	72	81	123	15	28

N as ammonium – N; N* as nitrate – N.

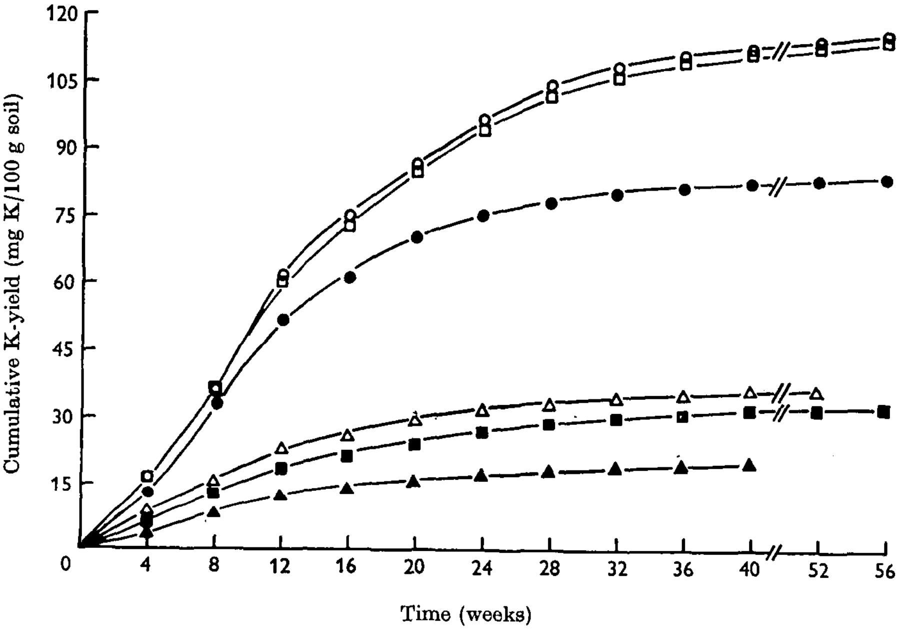

Fig. 1. Cumulative yield of potassium from the exhaustive cropping of Barnfield soils by ryegrass; ○ FYM, no N; ● FYM, $(NH_4)_2SO_4$; □ PK, no N; ■ PK, $(NH_4)_2SO_4$; △ O, no N; ▲ O, $(NH_4)_2SO_6$.

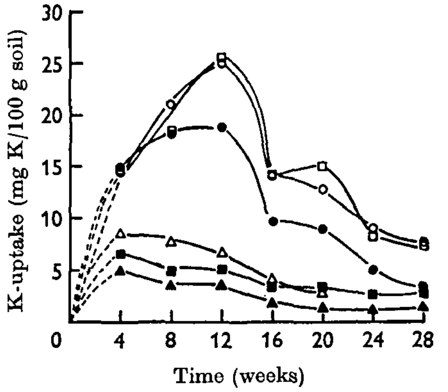

Fig. 2. Potassium yields in each cut from the exhaustive cropping by ryegrass of Barnfield soils (key as in Fig. 1).

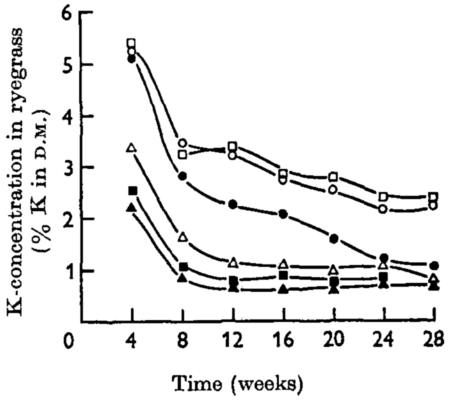

Fig. 3. Potassium concentration of ryegrass from the exhaustive cropping of Barnfield soils (key as in Fig. 1).

16 weeks (mostly exchangeable K) than the 'N' plots. Cumulative K-uptake by ryegrass from plots of similar manuring followed the order: (1) '*N*' *as nitrate or ammonium*: Barnfield > Hoosfield = Exhaustion Land. (2) *No manure*: Barnfield > Broadbalk = Hoosfield = Exhaustion Land. (3) *Complete minerals with* '*N*': Barnfield ($NaNO_3$) ⩾ Barnfield ($(NH_4)_2SO_4$) = Exhaustion Land. (4) '*K*' *with or without* '*P*': Barnfield > Broadbalk = Hoosfield; (5) 'FYM': Barnfield = Hoosfield > Barnfield ($NaNO_3$) > Barnfield ($(NH_4)_2SO_4$) = Broadbalk.

'*Intensity*' *of soil potassium*

All soils showed a sharp drop in intensity with cropping, corresponding with vigorous K-uptake initially (Fig. 4). The K-intensity of soils poor in potassium decreased to a minimum after 10 weeks cropping and then recovered almost to the original value after 18 weeks, falling gradually thereafter. The K-intensity of rich soils decreased continuously with cropping, except between 10 and 18 weeks when the rate of decrease was slow. At 28 weeks, the $(AR)_0$ values of *all* cropped soils were between 3 and 7×10^{-4} $(\text{M})^{\frac{1}{2}}$ regardless of previous manuring. Thereafter, K intensity values decreased little.

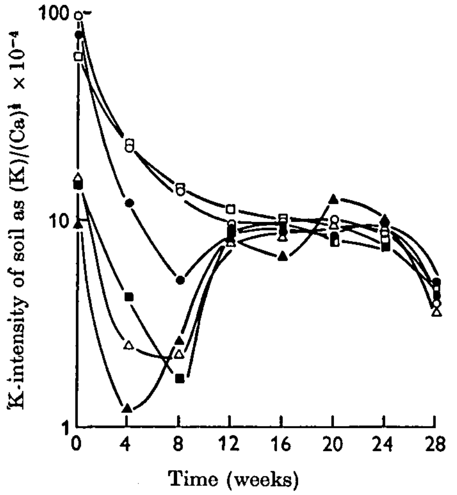

Fig. 4. Potassium intensity of Barnfield soils on exhaustive cropping with ryegrass (key as in Fig. 1).

The manuring regime in the Rothamsted Experiments affected the potassium intensity of the plots in the following order:

Uncropped soil.

'K' or 'PK' > FYM > NPK > 'None' > N = PNaMg:

(1) In the 'No manure' plots, the order was Broadbalk > Barnfield > Hoosfield > Exhaustion Land; (2) intensity values in 'N' plots did not differ significantly between the sites, but the NO_3-N plots averaged slightly larger values; (3) intensity values of 'full minerals with N' plots were only about twice those on 'No manure' or 'N' plots, compared with much larger differences between the latter and 'full minerals only'.

After 28 weeks exhaustive cropping. Unmanured and fertilized soils from all the experiments, irrespective of soil pH or organic matter content, gave $(AR)_0$ values between 3·5 and $7 \cdot 0 \times 10^{-4}$ $(\text{M})^{\frac{1}{2}}$; the cumulative yield at this stage was about 0·5 m-equiv/100 g for unmanured plots and 2·0 m-equiv/100 g for 'K' or 'FYM' plots respectively.

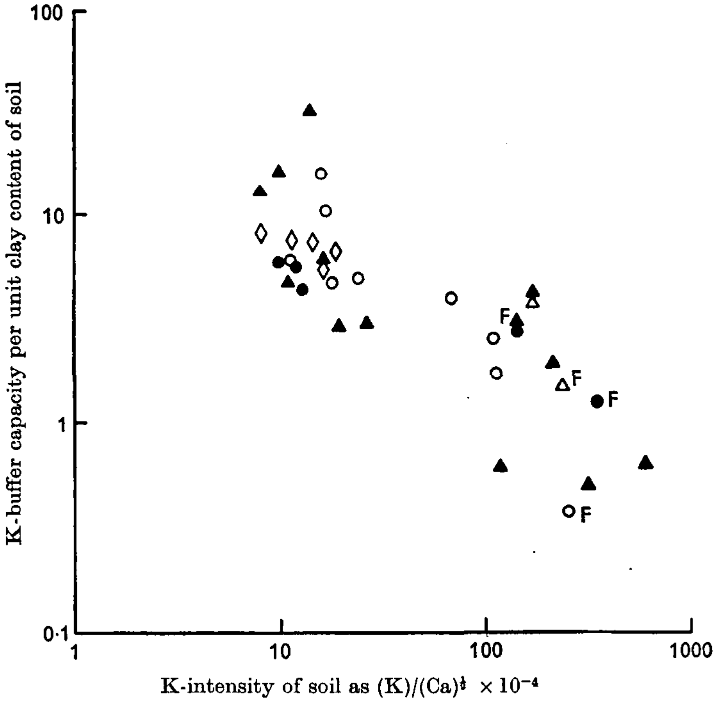

Fig. 5. The relation between potassium buffer capacity per unit clay content and potassium intensity of uncropped soils from the Rothamsted Experiments: ○ Barnfield; ● Hoosfield; △ Broadbalk; ▲ Park Grass; ◇ Exhaustion Land; '*F*' FYM plots (excluding Exhaustion Land). (r^2 = 0·670***).

Potassium buffer capacity by instantaneous equilibration

The buffer capacity of uncropped soils from the *arable Rothamsted Experiments* followed the order 'No manure' > N > K with or without N > FYM; i.e. intensity and buffer capacity of the soil are, qualitatively, inversely related.

Potassium buffer capacity by glasshouse cropping

The buffer capacity by glasshouse cropping was the cumulative K-uptake from 100 g soil per unit change in $(AR)_0$ during any cropping period. The entire cropping period was divided into sections during which buffer capacity did not vary rapidly. The weighted mean capacity 'C_m' was calculated from the potassium uptake in each period expressed as a fraction of the total K-uptake and the buffer capacity in each period. Tables 2–5 compare the weighted mean capacity (C_m) from glasshouse cropping and buffer capacity by instantaneous equilibration. Changes in K-uptake (Figs. 1 and 2) and soil K-intensity (Fig. 4) during cropping show that: (1) rich soils with large K-saturation of exchange sites (i.e. high K-intensity) had a small buffer capacity up to 16 weeks (mean value 11) and a larger buffer capacity for K-release (97) thereafter; (2) poor soils (small K-saturation and K-intensity) had a small buffer capacity (10) over the maximum K-uptake period during the first 4 weeks, a 'negative' buffer capacity (-36) between 4 and 12 weeks and a large buffer capacity (43) thereafter.

C_m for rich soils correlated closely with the BC value although the latter was usually much larger (correlation: $r^2 = 0{\cdot}70^{**}$; regression of BC on C_m: $y = 17{\cdot}8+(1{\cdot}25 \pm 0{\cdot}37)\,x$). The change during cropping from smaller buffer capacity values initially to larger values in later cropping was more pronounced for rich soils. Cumulative potassium residues from past manuring decreased BC and C_m of 22 arable Rothamsted soils in the same direction; this decrease was most in the Barnfield PK plot, the correlation between BC and C_m excluding this Barnfield soil was fair ($r^2 = 0{\cdot}339^*$).

DISCUSSION

Potassium uptake by ryegrass

The difference between the rates of K-uptake and soil intensity change in the 16–28 week period and those in earlier and later periods can be attributed to the slower release of initially non-exchangeable potassium from the soil, because despite the smaller dry-matter yield, the K-concentration in the grass changed little after 8 weeks. The slower release of potassium from the soil after 16 weeks must therefore govern dry-matter yield. However, Arnold & Close (1961*b*) concluded that the rate K released from soil was independent of the change in dry-matter yield in 600 days cropping.

The $(AR)_0$ values after each harvest were not related directly with subsequent K-uptake and could not be used to predict succeeding yields.

Potassium intensity and buffer capacity by instantaneous equilibration and by glasshouse cropping

If the clay fraction of British soils governs their cation exchange properties, K-buffer capacity *per unit of soil clay* should be more quantitatively related to the fractional coverage of exchange sites by potassium (and, therefore, to soil K-intensity) than the K-buffer capacity of the soil. K-intensity and K-buffer capacity/unit clay content for soils from the *Rothamsted Experiments* ($r^2 = 0{\cdot}670^{***}$; Fig. 5) is more precise than for soils from 'other centres' (Talibudeen & Dey, in preparation). The limiting K-intensity value (expressed in $(AR)_0$ units) for vanishingly small surface coverages of potassium for soils from *all* the Rothamsted Experiments is about 10^{-3}, equivalent to a potassium concentration of 10^{-4}M in $0{\cdot}01$M-$CaCl_2$. Although the results are not accurate or numerous enough to distinguish *between* the Rothamsted Experiments, they do suggest that the asymptotic value of K-intensity at surface coverages tending to 0% K saturation is half as much greater for 'Barnfield' soil than for soils from the other fields, i.e. the soil matrix in Barnfield differs somewhat from that in the other fields. That plots given FYM (and Park Grass soils) differ little from the remaining soils is unexpected because they contain much more organic carbon, suggesting that organic carbon has little effect on the K-intensity and K-buffering of soils.

There was no simple relationship between the total potassium released by a soil and its 'instantaneous' Q/I relationship. That most laboratory K-buffer capacity values were substantially greater than the glasshouse C_m values probably means that $(AR)_0$ values do not measure soil K-intensity satisfactorily to predict changes in K-intensity during cropping. The buffer capacity of soils during the initial cropping period was quite different from that later, which implies that the soil K-intensity recovered sufficiently later because of potassium diffusing out of soil particles and the peripheral weathering of soil minerals. Vaidyanathan & Talibudeen (1965) observed a similar 'recovery' of phosphate intensity and quantity in an Indian soil, using ion exchange resins to exhaust the soil. The largest variation in the K-buffer capacity values was with poor soils, emphasizing that buffer capacity depends on the nature of the potassium adsorption isotherm (Deist & Talibudeen, 1967), and that, for the same small K-intensity, soils may differ a great

Table 6. *Statistical relations between potassium yields, Y, in ryegrass and log (potassium intensity), X_1, soil pH in* 0·01 M-$CaCl_2$, X_2, *and organic carbon content,* X_3

Experiment	Cropping period in weeks	Variance accounted for by regression (%)	Regression coefficients X_1	X_2	X_3
Broadbalk, Barnfield,	16	X_1: 90·2	36·1*** ± 2·59	—	—
Hoosfield, Exhaustion Land	60	X_1: 85·8	63·4*** ± 5·61	—	—
Park Grass	16	X_1: 90·4	35·4*** ± 3·61	—	—
		X_1X_2: 96·0	37·5*** ± 2·42	5·0** ± 1·36	—
		$X_1X_2X_3$: 95·8	37·0*** ± 2·58	5·4** ± 1·51	−2·8 n.s. ± 3·7
	60	X_1: 87·2	51·4*** ± 6·00	—	—
		X_1X_2: 95·0	54·9*** ± 3·98	8·3** ± 2·24	—
		$X_1X_2X_3$: 95·1	53·7*** ± 4·06	9·3** ± 2·38	−6·6 n.s. ± 5·89

deal in their ability to maintain the K-intensity of the labile pool against K-exhaustion and therefore to release potassium during exhaustive cropping.

Quantitative relationships between various measurements

The relationships between K-uptakes after 16 and '60' weeks exhaustive cropping and K-buffer capacity by instantaneous equilibration were just significant (both $r^2 = 0·25^*$) for Rothamsted soils.

Statistical relationships between the K-intensity of the uncropped soil and cumulative K-uptakes after 16 and 60 weeks cropping show that, for Rothamsted soils, rapidly released potassium taken up by ryegrass in 16 weeks is slightly better related to K-intensity than K-uptake in 60 weeks (Table 6). Allowing for variance from soil pH improved both relationships most in Park Grass soils. Allowing for variance from pH *and* organic carbon content did not significantly affect either relationship for Park Grass soils.

The Park Grass experiment

Park Grass soils not given K-fertilizer and those given 'organic manures' were among the first to show signs of K-exhaustion during cropping (Table 5). Cropping for 16 weeks and for the total period could only remove 70 and 77 % of the exchangeable potassium respectively from these soils (see earlier in 'Results'). For most manurial treatments, the K-intensity of the uncropped soil was similar to that in the arable Experiments, except the 'complete minerals with N' plots especially where NO_3–N had been given; these had much larger intensities in the Park Grass Experiment compared with the Barnfield plots. The K-intensities of the corresponding Broadbalk plots were only slightly less, as shown below:

			NH_4–N		NO_3–N
Manuring	No N	N_1	N_2	N_3	N_2
None	19	—	5	—	—
PKNaMg	170	149	134	105	123
FYM	231	—	—	—	—

However, the soil pH of these Park Grass plots is from 0·9 to 4·1 units less than of the Broadbalk plots, therefore K would be leached much more strongly from the former. This suggests that under comparable rates of loss by leaching, K-residues would accumulate more in the 'permanent grass' plots than in the 'arable crop' plots.

The smaller K-intensities of the limed soils, and K-uptakes from them, are mostly caused by permanent grass in the field removing more potassium from them. Differences in K-intensity between limed and unlimed plots were *much* larger than in K-uptake because the aluminium activity in the soil solution was not taken into account.

The effect of increasing N × K interactions on the potassium removed by 'permanent grass' during a hundred years is shown by the decreasing intensity of plots given more 'N' with 'complete minerals', limed or unlimed (cf. the Broadbalk Experiment above, and the PK and FYM plots in the Barnfield Experiment, Table 4), although the extreme acidity of Plot 11/1 does not permit a full comparison in the unlimed plot. The 'organics' plot cannot be compared with those of the arable Experiments because its manuring is so different (Table 1).

Liming increases the numerical value of the K-buffer capacity in 'instantaneous equilibration' measurements in five of the six pairs of Park Grass soils because the effective calcium saturation of the soil increases on liming, and also because limed soils are poorer in K from additional K removed by the field crop. The only exception to this is the pair of unmanured plots, for which no explanation can be given.

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