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# The Use of Plant and Soil Analyses to Predict the Potassium Supplying Capacity of Soil

*A. E. Johnston and K. W. T. Goulding**

*Summary*

Rational K manuring policies are essential for farmers faced with ever increasing variable costs of food production in many parts of the world. Yet long-term soil fertility must not be jeopardised because of short term financial constraints. The need to apply K fertilizer is complicated because many soils can retain K and subsequently release it. Inputs and losses of K from soil are discussed in relation to its transfer between the various analytically defined categories of soil K. Policies for potassium manuring are outlined. For light textured soils with little buffer capacity annual K manuring is suggested to minimise possible leaching losses. For heavier textured soils rotational K manuring based on K balance and with periodic checks on changes in soil exchangeable K is likely to be adequate. The effectiveness of such manuring policies can now be checked by crop analysis.

Critical K concentrations in field grown crops can now be defined when K concentrations are expressed on a tissue water basis and this is discussed. Various methods for determining water soluble, exchangeable, fixed and matrix K are discussed in relation to either improving our understanding of potassium exchange processes in soil or to the more practical farming need of deciding whether supplementary K as fertilizers or manures should be applied to improve growth. For many soils, the determination of exchangeable K by extraction with ammonium salts is still the quickest and most reliable way to predict the need for supplementary K.

## 1. Introduction

The fertility of a soil can be defined as its capacity to produce the crops desired by the cultivator within the constraints of local climate. Such a definition encompasses various factors which control plant growth: i) soil structure which affects not only the workability of soil and its capacity to provide anchorage for roots but also suitable air/water relationships for active root growth and function; ii) the incidence of pests, diseases and weeds; iii) the availability of nutrients.

In well developed systems of food production many of the constraints to yield can be wholly or partly controlled. The fertilizer industry has developed to supply farmers with plant nutrients so that they can produce food to feed

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an ever increasing population. As yields per hectare of agricultural crops increase and more nitrogen (N) is used the need for potassium (K) increases and attention to the role of potassium in crop quality and in maintaining soil fertility becomes ever more important.

Whilst the application of potassium to agricultural soils rarely leads to environmental problems, improving the cost effectiveness of its use depends on our ability to correctly identify those situations where potassium is needed. This paper summarizes some current ideas about the usefulness of crop and soil analysis for estimating the potassium supplying power of soils, and seeks to develop rational K manuring policies to achieve optimum yield and the maintenance of soil fertility.

## 2. The potassium cycle in agricultural soils

Figure 1 shows a simplified potassium cycle for agricultural soils. Following the early work of *Hoagland and Martin [1933]* soil K is divided into four categories. Their precise definition is less important than the realisation that K can transfer in both directions from one category to another. The rate at which this transfer occurs and the direction of movement (i.e. the balance of the equilibrium) has important implications for the usefulness of soil analysis in predicting soil K status and crop requirement for potassium.

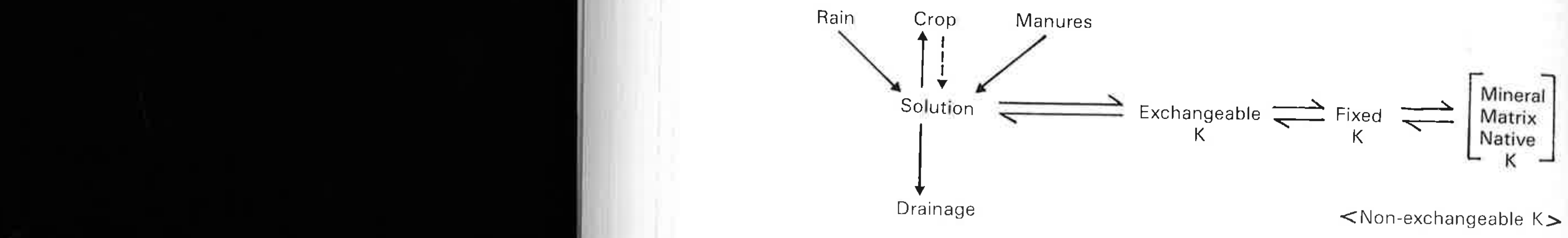

Figure 1. A diagramatic representation of the potassium cycle for agricultural soils.

### 2.1 Inputs

Inputs in rain are usually as soil dust. In Britain they are often less than 5 kg K/ha annually and have little effect on the total K balance.

Inorganic fertilizers and organic manures invariably supply K in water-soluble forms and are therefore interchangeable as sources of K when the farmer plans the manuring for each field.

### 2.2 Losses in drainage

A not insignificant proportion of the exchangeable K in soil is water soluble and at risk to loss by leaching. Losses are generally small and K poses no risk to health. Recent annual mean concentrations of K in water draining from a sandy loam soil were 3.4 mg/litre and from a sandy clay loam 1.3 mg/litre under arable and 0.5 mg/litre under herbage crops. Approximate annual leaching losses ranged from 0.2 to 5.0 kg K/ha from the clay loam and 3 to 20 kg K/ha from the sandy loam depending on cropping, rainfall and evapotranspiration.

The amount and type of clay in both the surface and subsoil affects the retention of K within the soil profile *(Johnston [1986])*. Potassium retained in the subsoil is available to deep rooted crops like sugar beet, winter wheat and lucerne. Benefits from subsoil enrichment with both K and P have been shown *(Johnston & McEwen [1984])*. *Kuhlman et al. [1985]* discussed methods for determining the amount of K taken up by crops from subsoils.

Rarely, however, is the readily extractable K content of subsoils determined. On many soils there is the difficulty of getting a representative sample and the additional cost of sampling and analysis to improve the fertilizer recommendation is probably not justified. However, poor correlations between crop response to K fertilizer and soil analysis values for surface soils could be explained in some cases by K uptake from the subsoil (see Section 6.1). Sugar beet, a deep rooted crop, invariably removes more K than other crops from soils which have been without K manuring for many years. In one experiment at Rothamsted on a silty clay loam with 80 mg/kg exchangeable K, cereals, potatoes and sugar beet contained 40, 30 and 120 kg K/ha in the harvested produce.

*Mengel [1989]* discussed the efficiency with which different crop species use potassium and this is a topic of considerable importance. When various crop species are compared in the field it will be necessary to distinguish between effects due to biochemical differences and those due to soil variation and crop rooting patterns in the soil profile.

### 2.3 Effect of K balance on exchangeable K in soil

The K balance can be defined as the difference between the amount of K applied to a crop and that removed from the field in the harvested produce. A positive balance enhances soil fertility, a negative balance depletes soil K reserves. *Johnston [1986]* showed how positive and negative K balances in long-term experiments related to increases and decreases in exchangeable K. Some examples are in Table 1. On soils which were cropped for many years without K manuring, large total negative K balances, 910 and 1350 kg/ha, caused little change in exchangeable K, only 8 and 6% of the K balance respectively. Much of the K had come from initially non-exchangeable reserves over the long period of cropping. Large positive K balances exceeding 3000 kg/ha increased exchangeable K by less than 45%; much of the excess K had become non-exchangeable. Such results might not be typical of the lightest textured sandy soils low in organic matter because they have little buffer capacity. However the results help explain why exchangeable K in many soils changes little over a number of years, a fact which often puzzles many farmers.

Table 1. Changes in exchangeable K related to positive and negative K balances when barley, clover and grass were grown continuously at Rothamsted

| Crop | Period | Treatment | K balance (kg/ha) | Change in exch. K (kg/ha) | Change in exch. K as a % of K balance |
|---|---|---|---|---|---|
| Barley | 1856–1903 | None | – 530 | + 10 | – |
| | | K | + 3760 | + 1100 | 29 |
| | 1903–1974 | None | – 910 | – 80 | 8 |
| | | (K)[1] | – 1840 | – 1040 | 56 |
| Clover | 1956–1966 | K | + 620 | + 260 | 42 |
| | 1968–1978 | K | + 1670 | + 690 | 41 |
| | 1979–1983 | K | – 1490 | – 560 | 38 |
| Grass | 1965–1976[2] | None | – 500 | – 80 | 16 |
| | | (K) | – 3460 | – 1470 | 42 |
| | 1970–1980[3] | None | – 1350 | – 80 | 6 |
| | | (K) | – 2110 | – 420 | 20 |

[1] K residues from applications between 1856 and 1903

[2] None: no K since 1856, (K): K residues from applications between 1856 – 1964

[3] None: no K since 1899, (K): K residues from applications between 1899 – 1969

A valuable laboratory screening technique for the assessment of the K fixing capacity of soil was discussed by *Johnston [1986]*. His results showed the importance of soil pH and past manuring on the amount of added K which remained exchangeable in soil after a cycle of wetting and drying episodes to simulate conditions in the field. (See also *York et al. [1953]; Karim & Malek [1957].)*

## 3. Potassium in plants

### 3.1 Amounts of potassium in crops

At harvest many crops contain similar amounts of potassium and nitrogen (Table 2). Although Table 2 shows that there is less K than N in grain plus straw of cereals at harvest, these crops often contain more K than N at anthesis. For example, between 1968 and 1978 winter wheat crops, given 144 kg N/ha and grown after a two-year break from cereals on Broadbalk at Rothamsted, yielded on average 5.84 t grain/ha each year. At anthesis the

above ground part of the crop contained 132 kg N and 203 kg K/ha whilst the grain plus straw at harvest contained 145 kg N and 135 kg K/ha. Table 2 also shows that if the straw of cereals or the tops of sugar beet are incorporated into soil then the amount of K removed from the field will be considerably less than that in the crop at harvest. Most of the K in plants and plant residues is water soluble and readily available to succeeding crops.

Table 2. Yields (t/ha), and nitrogen and potassium contents, N and K (kg/ha), of some important arable crops at harvest and for comparison grass/clover leys

| | Winter wheat | | | Winter barley | | | Spring barley | | |
|---|---|---|---|---|---|---|---|---|---|
| | grain | straw | total | grain | straw | total | grain | straw | total |
| Yield | 6.70 | 7.92 | | 8.48 | 6.85 | | 5.90 | 5.37 | |
| N | 114 | 47 | 161 | 170 | 33 | 203 | 81 | 25 | 106 |
| K | 29 | 89 | 118 | 39 | 135 | 174 | 24 | 54 | 78 |

| | Potatoes tubers | Kale | Grass clover ley (dry matter) |
|---|---|---|---|
| Yield | 48.0 | 75.0 | 11.7 |
| N | 161 | 211 | 231 |
| K | 252 | 246 | 290 |

| | Field beans | | | Oilseed rape | | |
|---|---|---|---|---|---|---|
| | grain | straw | total | seed | straw | total |
| Yield | 3.01 | 3.51 | | 2.80 | 6.67 | |
| N | 124 | 31 | 155 | 90 | 56 | 146 |
| K | 32 | 56 | 88 | 26 | 103 | 129 |

| | Sugar beet | | | Carrots | | |
|---|---|---|---|---|---|---|
| | tops | roots | total | tops | roots | total |
| Yield | 46.5 | 44.7 | | 27.1 | 64.5 | |
| N | 155 | 76 | 231 | 72 | 129 | 201 |
| K | 272 | 78 | 350 | 141 | 227 | 368 |

Thus it is important for farmers to ensure that in relation to other inputs, the maximum amount of K required by the crop will be readily available to it in the soil. The amount in fertilizers and manures should augment that which is supplied by the soil. In deciding on the amount of K to apply both the K status of the soil and the K balance must be considered. These concepts are discussed in Section 7 in relation to developing manuring policies.

### 3.2 Role of potassium in plants

Potassium has two main functions in plants: i) it has a vital and irreplaceable role in certain metabolic processes including protein synthesis and the translocation of the products of photosynthesis; ii) it appears to be the preferred cation for the generation of osmotic pressure to maintain cell turgor. Much larger quantities of K are needed for the second role than the first which explains why plants take up so much K.

A cellular explanation for critical K concentrations in plants was recently summarized by *Leigh [1989]* based on a more detailed discussion by *Leigh & Wyn Jones [1984 and the references therein]*.

### 3.3 Critical levels of K in plants

It has been accepted practice in agronomic studies to express the concentration of K in plants as a % in dry matter. This is analytically convenient and if dry matter yield is known K uptakes and balances can be calculated. However, attempting to relate % K in dry matter to crop response to either soil or fertilizer K invariably meets with little success for arable crops, because % K in dry matter declines appreciably during growth. For example, Figure 2a shows % K in dry matter of two crops of spring barley (*Hordeum vulgare* cv. Georgie) both grown on soil well supplied with K (330 mg/kg exchangeable K) but one given 96 kg N/ha, the other no N. Lack of nitrogen rather than K affected % K in spring barley early in the growing season and grain yield at harvest was 4.8 and 1.6 t/ha with and without N respectively.

Because most of the potassium in plants is used to generate osmotic pressure, which is a function related to the aqueous concentration of K within cells, *Leigh & Johnston [1983a & b]* examined whether expressing K concentrations on a tissue water basis had any benefits over % K in dry matter. Figure 2b shows the K concentrations for the crops in Figure 2a recalculated on the basis of tissue water. When expressed in this way both crops maintained the same concentration of K throughout the growing season until the onset of water loss as ripening commenced. The K concentrations were not affected by nitrogen manuring. Later studies *(Leigh & Johnston [1983b])* showed that neither drought nor phosphorus nutrition affected K concentrations in tissue water, but they did affect % K in dry matter.

Only when barley was grown on soils with different levels of exchangeable K (325 and 55 mg K/kg) were the levels of K in the tissue water different (Figure 2c), about 200 mM and 50 mM in crops grown on K sufficient and K deficient soils respectively. Both crops received 144 kg N/ha and yields on the low and high K soil were 2.6 and 4.8 t grain/ha respectively. There was no further increase in tissue K concentration in barley grown on soils containing even higher levels of exchangeable K (Table 3) *(Leigh [1989])*. On this very K deficient soil % K in dry matter was appreciably less than that in the crop grown on the K enriched soil, but for both crops the concentration declined throughout growth. Thus it would be difficult to use % K in dry matter to diagnose K deficiency unless the optimum concentration could be defined accurately for each growth stage for barley grown on a range of soils in different seasons.

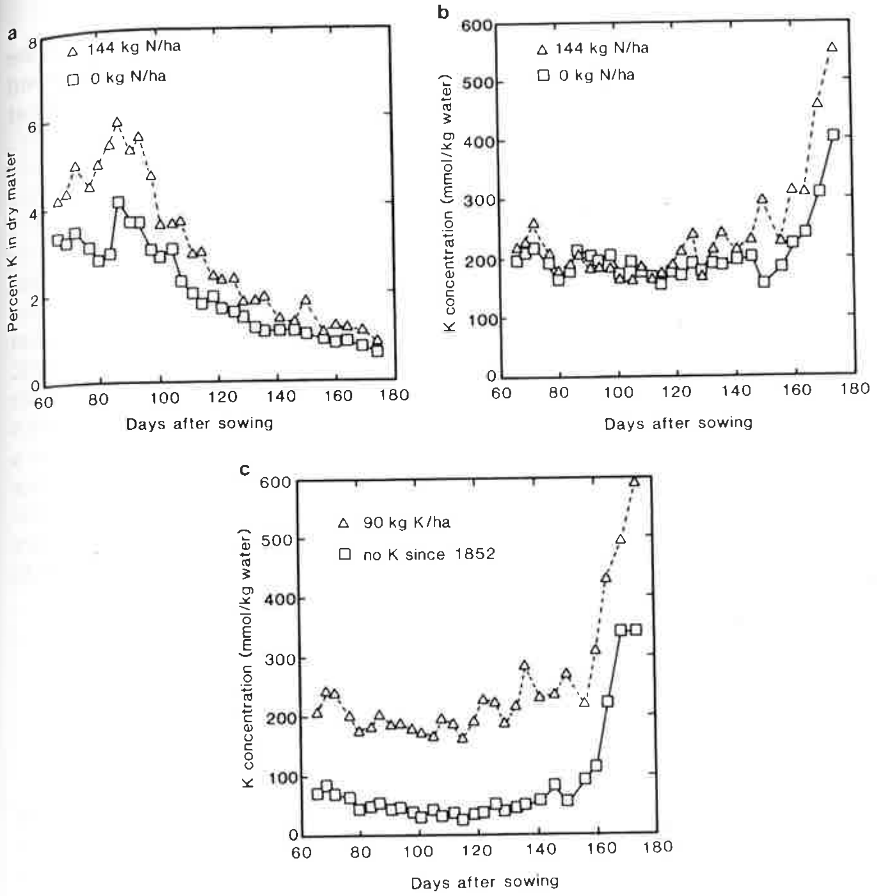

Figure 2. Concentration of K in field-grown spring barley (total above ground plant) from emergence to just prior to harvest.
a. percentage K in dry matter, crop given 0 or 144 kg N/ha
b. K in tissue water, crop given 0 or 144 kg N/ha
c. K in tissue water, crop given 144 kg N/ha and grown on soil given no K since 1852 or 90 kg K/ha each year.

Table 3. The effect of soil exchangeable K on the concentration of K in tissue water of spring barley grown on Hoosfield, Rothamsted in 1981

| Soil exchangeable K (mg/kg) | K in tissue water (mM/kg) |
|---|---|
| 55 | 57 ± 4* |
| 325 | 206 ± 7 |
| 827 | 219 ± 9 |

Mean ± s.e. over 75 days

Similar values for K in tissue water to those in barley, about 200 mM, have been found for well fertilized grass, but oilseed rape *(Brassica napus)* and field beans *(Vicia faba)* apparently maintain K concentrations only about 100 mM under conditions of ample K supply *(Leigh [1989])*.

### 3.4 Use of plant analysis in diagnosing K deficiency

The results above show clearly that barley, grass, oilseed rape and beans can be sampled at any time throughout growth during spring and summer and K deficiency can be readily diagnosed if the K concentration is expressed on a tissue water basis. Oilseed rape and beans apparently maintained lower K concentrations in tissue water than did cereals and grass when grown on soils on which there was no response to K fertilizer. Similar values for other crops must be determined experimentally under field conditions. We now have a method of expressing K concentrations in crops which allows us to tell whether the crop is K sufficient or K deficient. Although the method is excellent for diagnosing K deficiency which will allow corrective K applications for future crops, it is usually too late in the growing season to apply K to the crop in which deficiency is observed.

## 4. Soil analysis

### 4.1 Early work

In the early 1870s *von Liebig [1872]* used dilute acetic acid to determine both readily soluble K and P in the 0–23 cm depth of soil from five plots on the Broadbalk experiment at Rothamsted. He readily differentiated between soils which had or had not received K fertilizer for 20 years. During the next few years several workers used various dilute acids as extractants. *Dehérain [1891]* used dilute acetic acid to analyse the soils from the long-term plots at Grignon near Paris. *Dyer [1894, 1901, 1902]* used soils from both Broadbalk and Hoosfield at Rothamsted to check the usefulness of 1% citric acid as an extractant for K and P. 1% citric acid was chosen because the acidity of the solution approximated to that of plant sap, and it was widely held at that time that roots exuded solutions which dissolved soil constituents thus making plant nutrients available.

For potassium, *Dyer* compared 1% citric acid with constant boiling HCl for 48 hours and with dissolution in HF. He showed that it was only with citric acid that there was a sufficiently wide range of values, 8 or 10:1 between K manured and unmanured soils, to allow it to be used diagnostically. *Dyer* thus highlighted an important criterion for soil analytical reagents intended to estimate «plant available» nutrients: there must be a wide range of values between very responsive and non-responsive soils so that soils of intermediate response can be readily identified. A second criterion is that the reagent should not change its strength during the period of extraction. This invariably rules out the use of acid reagents on calcareous soils.

*Dyer* showed that the 48 hour boiling HCl extractant failed to distinguish between soils with and without K manuring for 50 years because it extracted too much K. For many clayey and loamy soils total K content rarely differentiates between soils with different K manuring even after this has continued for more than 100 years *(Johnston [1986])*. However, for sandy soils from the tropics total K is a good indicator of past K manuring *(Johnston, unpublished)*.

### 4.2 Exchangeable K

The idea that the exchangeable bases in soil are the source of cations for plants was put forward by *Knop [1871]*, who used a solution of ammonium chloride to extract them. *Prianishnikov [1913]* was probably the first to suggest the use of neutral ammonium acetate (2 M). An increasing awareness of the importance of base exchange reactions in chemical and physical properties of soil led to many investigations of analytical methods in the 1920s and 1930s.

The usefulness of any analytical method for assessing soil fertility must be tested in field experiments. *Schollenberger and Dreibelbis [1930a]* related K response by crops in the field to exchangeable K in soil estimated by extraction with ammonium acetate, as in the method outlined by *Schollenberger and Dreibelbis [1930b]*. Today the use of 1 M ammonium acetate or 1 M ammonium nitrate has been widely adopted; ammonium nitrate has analytical convenience where the acetate ion interferes with the determination of K in some analytical instruments. Both reagents are often used for exchangeable cations in those soils where the Olsen bicarbonate method *(Olsen et al. [1959])* is good for determining readily soluble P.

Many other reagents have been suggested and a number are widely used, e.g. ammonium acetate and acetic acid at pH 4.8 *(Morgan [1935])*, calcium lactate *(Egner and Riehm [1955])*, ammonium acetate-lactate (AL) *(Egner, Riehm and Domingo [1960])* and calcium acetate-lactate (CAL). A number of these reagents have the advantage that they extract both K and P in amounts which can be related to crop responses to these nutrients. In general the amounts of K extracted by such reagents are strongly correlated with those extracted by ammonium acetate.

### 4.3 Fixed K

Many research workers consider that the rate and amount of K transferring between exchangeable and fixed or non-exchangeable categories (Figure 1) appreciably affects the response of crops to K fertilizer. Much effort has been expended in attempting to find methods to determine the quantity of non-exchangeable K in soil. *Martin and Sparks [1985]* gave a comprehensive list and discussed sixteen of the methods. As yet there is no rapid, reliable method. However, it is necessary to clearly differentiate between their usefulness and applicability in predicting the availability of soil potassium to crops and their use in assisting our understanding, at a fundamental level, of K exchange processes in soil.

### 4.3.1 *Mineralogical analysis*

*Arnold [1962]* showed that the ability of many British soils to release K is correlated with the K content of the fine clay ($<0.1$ µm) and the percentage of fine clay in soil. Increasing amounts of fine clay could make up for decreasing K concentrations in the fine clay and vice versa. There was no similar correlation for the coarse clay (0.3–2.0 µm) fraction, and Arnold concluded that neither its amount nor % K were important in determining the K releasing power of the soils he studied. In these soils the clays were mainly micas and hydrous micas (illites) so in general the smaller an illite particle the faster it releases K. Unfortunately, estimates of the illite content of soil, based on the intensity of the 10 Å peak of the $<2$ µm clay cannot be used to predict K releasing capacity, because the micas and hydrous micas in the coarse clay dominate the spectrogram. Arnold also found that soils with a long history of K manuring gave anomalous results.

### 4.3.2 *Quantity/potential and quantity/intensity measurements*

The quantity/potential relationship *(Woodruff, 1955; Barrow et al. [1965])* relates change in the exchangeable K content of a soil to K potential defined as the free energy associated with replacing one equivalent of K by one equivalent of Ca *(Schofield [1947]; Woodruff [1955]; Arnold [1962])*.

K potential, $\Delta\bar{G} = RT \ln \mathrm{a_K}/\mathrm{a}^{1/2}_{\mathrm{Ca+Mg}}$

From the same measurements the relationship between change in exchangeable K and activity ratio $\mathrm{a_K}/\mathrm{a}^{1/2}_{\mathrm{Ca+Mg}}$ can also be drawn. This is usually called the quantity/intensity *(Q/I)* curve *(Schofield & Taylor [1955]; Beckett [1964])*.

The analytical procedures are time consuming but not difficult. For example, *Addiscott [1970a–c]* shook soils for 1 h with 0.01 M $\mathrm{CaCl_2}$ containing KCl from 0.00025 to 0.006 M (according to exchangeable K content) at a 1:10 soil to solution ratio. Usually six to eight K concentrations in solution were used for each soil. Soils were also shaken with 0.01 M $\mathrm{CaCl_2}$ only, at soil:solution ratios 1:10 to 1:250. The suspensions were centrifuged and the K, Ca and Mg determined in the supernatant liquid. Potassium potentials and activity ratios were calculated thus:

K potential, $\Delta\bar{G} = 2.303\ RT \log_{10} AR$

*where* $AR$ = activity ratio (intensity)

$$AR = \frac{\mathrm{a_K}}{\mathrm{a}^{1/2}_{\mathrm{Ca+Mg}}} = \frac{\mathrm{C_K}}{\mathrm{C}^{1/2}_{\mathrm{Ca+Mg}}}\ \frac{\mathrm{f}^{+}}{\mathrm{f}^{++1/2}}$$

where $\mathrm{f}^{+}$ and $\mathrm{f}^{++}$ are the activity coefficients of the monovalent and divalent ions. $\mathrm{f}^{+}/\mathrm{f}^{++1/2}$ was taken as 1.18 after *Beckett [1965]*, who found that the value varied little from this within the range of K and (Ca+Mg) concentrations in soil. The change in exchangeable K content of the soil ($\pm\Delta$K) was calculated from the gain or loss of K by the solution. Equilibrium K potentials ($\Delta\bar{G}o$) and equilibrium activity ratios ($ARo$) at which the soils neither gained nor lost K were interpolated from the quantity/potential and quantity/intensity relationships.

Both relationships are independent of the plant. The quantity/potential curve is often more useful in relating to measurements of K removed from the soil because the (logarithmic) potential scale is larger in the region of K removal. The quantity/potential relationship also gives a means of measuring K initially available to different plant species *(Arnold [1962]; Addiscott [1970b, c])*.

The *Q/I* relationship has been used more widely than the quantity/potential relationship (e.g. *Nair & Grimme [1979]; Sparks & Liebhardt [1981]; Evangelou et al. [1986]*). The curves have been used to estimate the extent to which available K is buffered by fixed K. Opinions are still divided about the usefulness of *Q/I* curves especially for practical advisory purposes (see e.g. *Sparks & Huang [1985] and Bertsch & Thomas [1985]*).

*Addiscott [1970c]* measured *Q/I* curves in soils with contrasted cropping and manuring over many years, taken from long-term experiments on different soil series at Rothamsted and Woburn. Within each experiment, *Q/I* curves for differently treated soils could be superimposed by appropriate horizontal and vertical shifts. The vertical shifts, on the *Q* axis, needed to bring the curves into coincidence were equal to the differences in exchangeable K. The *Q/I* curves from different experiments on the same phase of one soil series could also be superimposed but not those from experiments on different phases of the same soil series. There were marked differences in the shapes of the *Q/I* curves from different soil series.

Figure 3 (adapted from *Addiscott [1970c]*) shows the *Q/I* curves for soils from contrasted treatments on the Barnfield experiment at Rothamsted. Curves for treatments 5/0 and 7/0 are different, although neither has received K fertilizer since 1903. Before then treatment 5/0 had been without K manuring since 1843, whereas treatment 7/0 had K from 1843 to 1902, and this was replaced by Na and Mg from 1903. Although both soils had been without K manuring for some 60 years when sampled for these analyses the difference in K treatment in the previous sixty years, 1843–1902, was still detectable in the exchangeable K contents, 350 and 170 mg K/kg for 7/0 and 5/0 respectively, in the shape of the *Q/I* curves (Figure 3) and in the $ARo$ values $6.4\times10^{3}$ and $2.4\times10^{3}$ $(\mathrm{m/l})^{1/2}$ respectively. The persistent effects of K manuring between 1843 and 1902 were partly the result of not applying nitrogen to the crops grown between 1902 and 1967 so that the soil was not stressed to supply K.

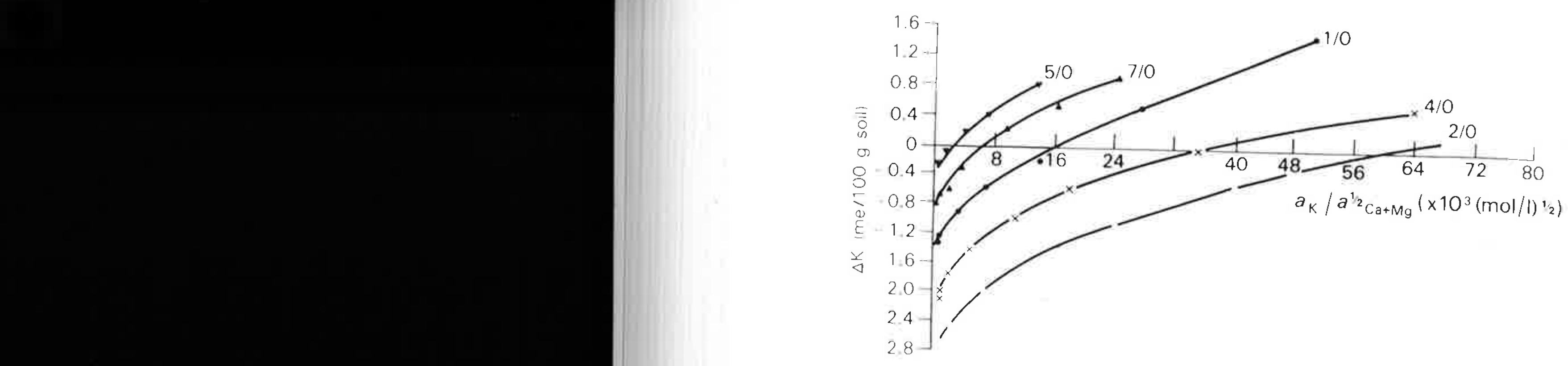

Figure 3. Effect of contrasted long-continued treatments with K on the *Q/I* curve for a silty clay loam soil from Barnfield, Rothamsted. No nitrogen was applied to fertilizer only plots. Key: 5/0 P only since 1843; 7/0 PK 1843–1902, P Na Mg since 1903; 1/0 P only 1845–1852, FYM since 1856; 4/0 PK Na Mg since 1843 (except 1861–70 no K); 2/0 P only 1845–1852, FYM plus P 1856–1902, FYM plus PK since 1903. Annual rates P 33 kg/ha, K 230 kg/ha, Na 88 kg/ha, Mg 22 kg/ha, FYM 35 t/ha containing on average 210 kg K/ha.

### *4.3.3 Buffer capacity*

The buffer capacity, *dQ/dI*, has been variously defined. *Beckett et al. [1966] and Beckett & Nafady [1967]* measured the potential buffering capacity of the linear section of the *Q/I* curve at large activity ratios. *Addiscott [1970c]* found that for many of the soils he analysed the *Q/I* curves were often not linear. Following *Talibudeen & Dey [1968]*, Addiscott took the buffering capacity as the slope of the tangent to the *Q/I* curve when $\Delta K=0$, i.e. $(dQ/dI)_{\Delta K=0}$. Buffer capacity, whichever way it is calculated, is a measure of the ability of a soil to maintain the concentration of K in solution. Some have found this a useful concept *(Beegle and Baker [1987])* but others have found it does not relate well to nutrient uptake *(Köchl [1987]; Novozamsky and Houba [1987])* nor is it suitable for routine analysis *(Villemin [1987])*.

This last point seems to be the chief reason for the very limited use of the *Q/I* concept in soil analysis. Although it gives more information than that given by simple extractants, the extra work required often outweighs the usefulness of the additional information. This is true in general of all methods involving ion exchange equations. Whilst they have increased our understanding of cation exchange processes they are unlikely to provide a rapid soil test for K availability.

### *4.3.4 Strong acids*

The extraction of fixed K from soil using boiling $HNO_3$ *(Haylock [1956]; MacLean [1961])* or HCl has been widely used. Attempts have been made to relate the results to categories of soil K called «available», «step» and «constant rate» K *(Jia Xian and Jackson [1985]; Sailakshmiswari et al. [1985])* but the amounts of K extracted often relate poorly to the response of annual field-grown crops to K fertilization. However, in exhaustion studies in pots in the glasshouse the amounts of K taken up in the latter stages of growth often relate quite well to K extracted by strong acids, presumably because initially non-exchangeable K is by then the main source of K supply to the crop. *Doll & Lucas [1973]* considered strong acids to be useful for research purposes but not for practical advisory work.

### *4.3.5 Electro-ultra filtration (EUF)*

The EUF methodology and its application have been described by *Németh [1982], [1985]*. Cumulative K in repeated water extracts is plotted against time and certain fractions correlated with K availability as measured in the field and laboratory. A number of research workers (e.g. *Sinclair [1982]*) found little advantage over other, less expensive procedures. Table 4 shows that for a number of soils with contrasted manuring history from long-term experiments at Rothamsted the total amount of K extracted by the EUF procedure was about the same as that extracted by ammonium acetate. Thus, the EUF procedure predicted K reserves in these soils no better than did exchangeable K. However, current EUF machines extract rather more K using higher temperatures and voltages and some organisations have adopted EUF multi-analysis techniques.

Table 4. Comparison of the EUF-K and exchangeable K (mg/kg) in soils from long-term experiments at Rothamsted

| | | EUF-K[1] | | | |
|---|---|---|---|---|---|
| Treatment | Experiment | I | II | I+II | Exchangeable K |
| None ................ | Barnfield | 78 | 28 | 106 | 144 |
| | Broadbalk | 62 | 21 | 83 | 100 |
| PK ................ | Barnfield | 475 | 134 | 609 | 680 |
| | Broadbalk | 246 | 76 | 322 | 356 |
| NPK ................ | Broadbalk | 170 | 74 | 244 | 260 |
| FYM[2] ................ | Barnfield | 471 | 210 | 681 | 802 |
| | Broadbalk | 559 | 160 | 719 | 686 |
| FYM+PK ........... | Barnfield | 661 | 157 | 818 | 1086 |

[1] EUF I 0–30 min, 200V, 20°C; II 30–35 min, 400V, 80°C

[2] FYM farmyard manure

### *4.3.6 Sodium tetraphenylboron (NaTPB)*

When the Na in NaTPB is exchanged by K the potassium salt precipitates out. NaTPB has been used in research especially on separated clays, less widely on total soils *(Quémener [1979], [1986])*. The salt itself is costly and though the analytical procedures are not difficult, the potassium salt must be dissolved from the soil residue before K can be determined. Both factors may explain why the method is not widely used in advisory work even though the amounts of K extracted often correlate well with K uptake by grass in pots. *Jackson [1985]* has recently proposed a scheme for use in the analysis of pasture soils in New Zealand: the current rapid advisory test, based on a short extraction with ammonium acetate, is used to screen out soils that are either unresponsive or very probably responsive to added K, and the NaTPB test is then used as a supplementary screen for those soils on which there was doubt about the need to apply K fertilizer immediately. The principle of this approach is similar to that of *Arnold [1962]*, who showed that K potential is a better predictor of K release to ryegrass from soils containing between 100 and 200 mg/kg exchangeable K than is exchangeable K itself.

### *4.3.7 Ion exchange resins*

Ion exchange resins have been used for many years to extract K and other ions from soil (see *Quémener [1979]*). Early workers used only single extractions and often the results were little better than those with salts such as ammonium acetate *(Arnold [1958]; Haagsma & Miller [1963])*. More recently multiple extractions of the same soil sample with Ca-resins, which act as an infinite sink for K diffusing into the solution, have allowed cumulative K release curves to be constructed *(Talibudeen et al. [1978]; Havlin & Westfall [1985])*. The curves, in the form ΣK: $t^{1/2}$, often have the same shape and magnitude as those obtained using cumulative K uptakes by ryegrass grown in pots in the glasshouse (c.f. Figure 4 and Figure 5). The curves invariably differentiate soils with different clay content, clay mineralogy, manuring and cropping history.

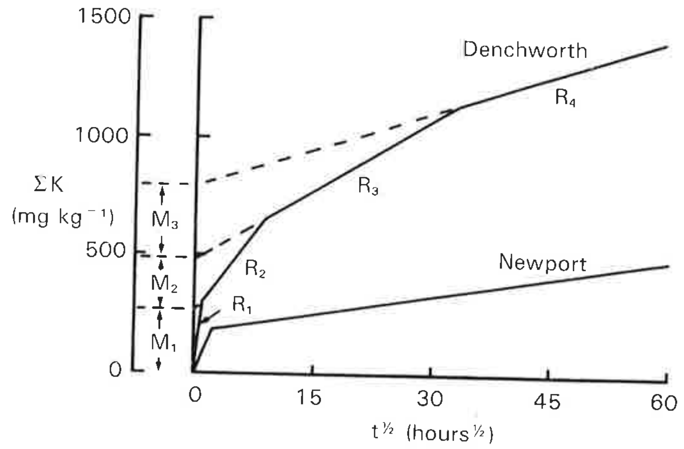

Figure 4. Relationship between the cumulative K release to Ca resin and time for two soils with differing clay content, Denchworth Series 49% clay, Newport Series 8% clay.

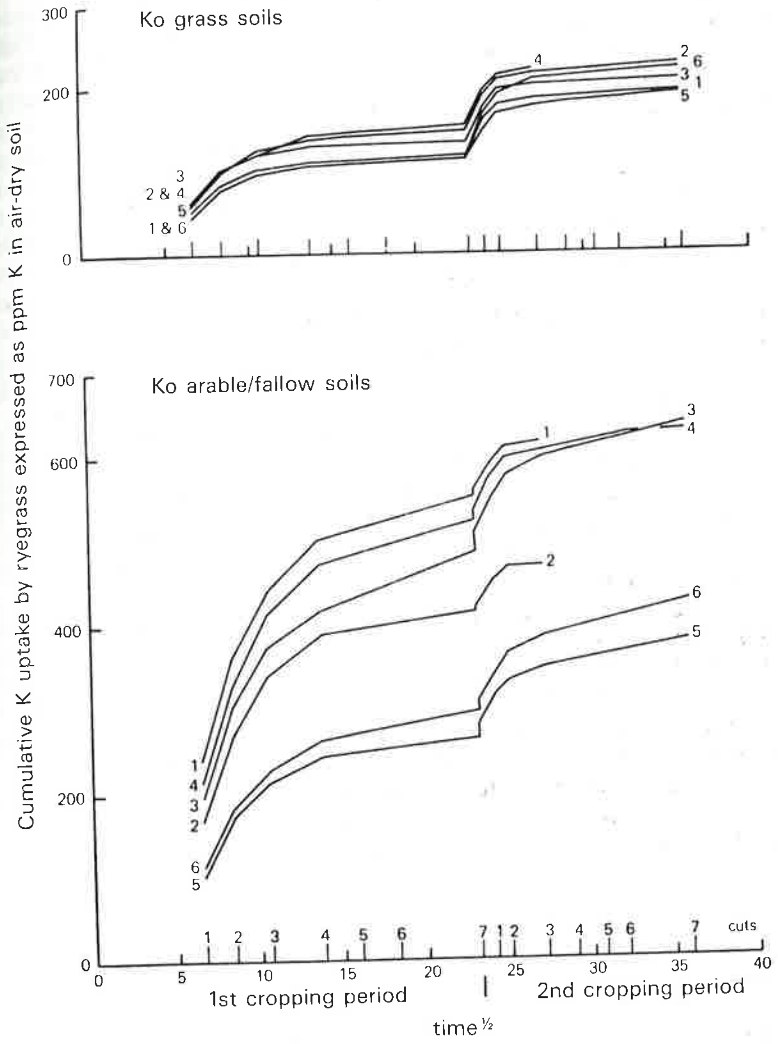

Figure 5. Relationship between cumulative K uptake by ryegrass in pots and $t^{1/2}$ for 12 soils of known cropping and manuring since 1848.
Manuring once every four years during 1848–1951: plots 5 and 6 unmanured, plots 3 and 4 PK Na Mg, plots 1 and 2 NPK Na Mg.
Cropping plots 2 4 6 turnips, barley, clover, wheat
plots 1 3 5 turnips, barley, fallow, wheat.
From 1958–67 no K was applied and half of each plot grew grass the other half arable crops or fallow. On the arable/fallow soils the greater uptake of K on plots 6 and 4 compared to 5 and 3 respectively is related to the larger clay content of these soils.

Like K uptake curves, resin curves have been interpreted as separating two, three or four main categories of soil K depending on clay content (e.g. Figure 4 and *Goulding [1984]*). This observation can be tested by fitting both a linear spline and the best smooth curve to each set of data using the Rothamsted Maximum Likelihood Program *(Ross [1980])*. The linear spline almost always has the least residual mean square. From the $\Sigma$K: $t^{1/2}$ curves amounts (M) and rates (R) of K release can be calculated. Amounts are obtained by extrapolating each linear segment back to $t^{1/2}=0$ and taking the difference between the intercepts, whilst rates of release are the slopes of each segment. Figure 4 shows that a sandy soil (8% clay, Newport Series) had a two-part curve, whereas a much heavier textured soil (49% clay, Denchworth Series) had a four-part curve. Unfortunately a full analysis of a soil can take 6 to 9 months and this and the complexity of the procedure makes it unsuitable for routine analysis. As a research tool the method has much to commend it; it is less expensive than pot experiments for determining the K releasing capacity of soil. *Goulding and Loveland [1986]* have suggested that the technique could be used to map K reserves in soils with different clay mineralogies and clay contents, especially soils without a history of long continued K manuring. The technique has been used by *Goulding & Stevens [1988]* to measure K reserves in a soil under forestry as affected by felling practice and the ability of the reserves to meet the nutrient requirement of the tree crop.

*Goulding & Johnston [unpublished]* have attempted to produce curves similar to Ca-resin curves but much more quickly by sequential extraction of soils with 0.5 M- or 1 M-HCl during a period of 10 hours. Unfortunately the total amount of K extracted was often little different from the exchangeable K, but sometimes linear splines fitted the data better than smooth curves, suggesting that the method separated different fractions within the total exchangeable K; it also proved to be a better predictor of K and Mg uptake and yield in pot and field experiments. Other acids and longer extraction periods may remove more fixed K and prove better predictors of nutrient availability.

## 4.4 Water soluble and matrix K

Potassium ions ($K^+$), present in the soil solution – or more accurately their activity – and potassium as a structural element in soil minerals – matrix or mineral K in Figure 1 – represent the extremes in plant availability and are rarely measured in soils.

### *4.4.1 Matrix K*

Both the rate and amount of matrix K released to plants depend on the quantity of clay, especially the smaller clay particles, and its mineralogy. For example, *Johnston [1986 and the references therein]* showed that only small amounts of K are now taken up each year by cereals grown on soils which have had no K additions for 80 or more years. On a sandy loam (10% clay) at Woburn, the amount is only 10 kg K/ha; on a silty clay loam (20% clay) at Rothamsted, 20-35 kg/ha; on a sandy clay loam (25% clay) at Saxmundham, 35 kg/ha. The clay fractions of all three soils are mainly interstratified expanding minerals with some mica and kaolin and the different amounts of K released relate principally to the amount of < 2 µm clay in each soil. For most cultivated soils the release of matrix K is of little practical consequence, because such soils have received applications of K in manures and fertilizers; reserves of exchangeable and fixed K rather than matrix K dominate the amount of soil K available to crops each year *(Goulding [1984]; Goulding & Loveland [1986])*.

### *4.4.2 Water soluble K*

*Mengel and Kirkby [1982]* pointed out that $K^+$ concentration in the soil solution largely controls the rate of K diffusion towards roots and therefore the uptake of K by plants. But amounts of K in solution are too small to supply crop needs. *Warren and Johnston [1962]* showed a strong relationship between water soluble and exchangeable K; about 15% of the exchangeable K above 170 mg K/kg was water soluble. *Johnston [1986]* suggested that it is worthwhile considering relating variation in the response of annual crops to K fertilizer on different soils to variation in the amounts of water soluble K. A simple measurement of water soluble K can, however, give no indication of the rate of replenishment.

## 4.5 Comparison of methods of soil analysis

Many comparisons have been made between different methods of soil analysis for K. *Johnston & Addiscott [1971]* used 52 soils varying in pH (water) from 5.4 to 8.0, with exchangeable K contents from 50 to 1100 mg/kg and with a range of organic matter contents, in an exhaustive cropping experiment with ryegrass in the glasshouse. Soil textures were silty clay loams and sandy loams. The soils were analysed for exchangeable K, $Ke$; equilibrium activity ratio, $ARo$; equilibrium K potential, $\Delta\bar{G}o$; K buffer capacity, $BCo$, (see Section 4.3.3) and the K removed from soil before the potential fell to -5600 cal/equivalent, the uptake potential of ryegrass, $K_{5600}$. Nine harvests of ryegrass were taken and the experiment lasted 608 days. Regressions on the quantity measurements, $Ke$ and $K_{5600}$, accounted for more variation in K uptakes in either the first three, or all nine cuts, than did regressions on the other K measurements. There was little to choose between $Ke$ and $K_{5600}$ because they were strongly correlated ($r=0.989$). The good relationship between K uptake and $Ke$ suggested that differences between soils in continuous grassland or arable cropping or ley/arable cropping, or with and without K fertilizers or farmyard manure, were attributable solely to differences in the quantity of exchangeable

K, not its rate of release. Currently it seems that the K status of soils can be classified as well by exchangeable K as by any other rapid analytical procedure.

## 5. Glasshouse experiments

Pot experiments have been widely used to measure the K releasing capacity of soils and to relate the data to laboratory soil tests. Pot experiments have also been used to help understand the processes governing the uptake of fixed K.

*Quémener [1979]* reviewed techniques for pot experiments. They are expensive and can last many months, possibly years, even when only small amounts (e.g. 400 g) of soil are used per pot. Often K taken up by the test crop during the first 8 to 10 months estimates that which is exchangeable and fixed (Figure 1); the period of cropping need only be extended if the release of matrix K is being studied.

### 5.1 Comparison of glasshouse and field experiments

Pot experiments are attractive because a direct simple relationship between K uptake by plants in pots and in the field might well be expected. This rarely happens for a number of reasons. Pot experiments are often conducted in the glasshouse with supplementary lighting and heating so that plants continue to grow throughout the year and there is a constant demand for K. Field-grown plants in temperate climates rarely grow continuously and when there is no plant demand for K non-exchangeable K can diffuse to exchange sites (see *Johnston [1986]*). The roots of plants grown in pots invariably exploit the soil more thoroughly whilst those of field-grown crops can explore deeper soil horizons than those usually sampled for pot experiments. When K uptake from the same soil was compared in the glasshouse and the field, ryegrass in pots took up as much K in 3.5 years as did the field-grown crop in 9 years *(Johnston & Mitchell [1974]). Moberg and Nelson [1983]* found that several years of exhaustive cropping in the glasshouse was the same as 60 years cropping in the field. Thus whilst pot experiments may appear to be a useful model for K release in the field, the relationship between K release data from pot and field experiments varies with many factors and the relationship is often poor (see *Ogunkunle and Beckett [1988]*).

### 5.2 Understanding the processes of K release

*Addiscott and Johnston [1974]* discussed reasons for examining the relationship between cumulative K uptake and $\sqrt{\text{time}}$, $t^{1/2}$, in glasshouse experiments. Figure 5 gives examples taken from *Johnston & Mitchell [1974]*. They grew ryegrass in pots in the glasshouse for two cropping periods, the first of 540 days, the second 734 days, and in each period seven harvests (cuts) of grass were taken. Between the first and second periods the soils were air dried before being resown with grass. They used 48 soils taken from a field experiment at Rothamsted where the cropping and manuring histories were known since 1848.

For soils which were in an arable/fallow rotation between 1958–1967, the amount of K taken up by the first cut of grass was larger than the decrease in exchangeable K during the first cropping period. This suggests that K taken up by the second to seventh cuts came from initially non-exchangeable sources. The $\Sigma K: t^{1/2}$ relationship for cuts 2 to 4 was almost linear and much steeper than the linear relationship for cuts 5 to 7. Such linear relationships suggest that a diffusion process most probably determined the rate of K uptake and that K diffused either from a larger «pool» or at a much faster rate for cuts 2 to 4 than for cuts 5 to 7.

The amount of K taken up during the first cropping period from the arable/fallow soils 1 to 4 (Figure 5) reflected the build-up of K residues during the period 1848–1958. The much smaller amounts of K taken up from «grass» soils 1 to 4 reflects the fact that during 1958–1966 those soils in the field grew grass which obviously removed much of the readily available K residues.

Air drying the soil between the first and second cropping periods hastened the release of some K, which was removed by the first and second cuts of grass in the second cropping period. For all soils the amounts of K taken up by cuts 3 to 7 were similar, suggesting release from the same source.

### 5.3 Cumulative K uptake related to initially exchangeable K

Using other data from the experiment described above, *Johnston & Mitchell [1974]* also showed that K uptake by ryegrass in the first cropping period and the exchangeable K in the soils at the start of the experiment were strongly correlated ($r = +0.94$) (Figure 6). The amount of non-exchangeable K released from each soil was about twice the decrease in exchangeable K during the first cropping period. Weaker correlations are often found when soils from a wide range of parent materials are included in the same experiment. This could be related to the size of the non-exchangeable K pool or to the rate of diffusion of K from the pool. However, results from Ca-resin extraction *(Goulding [1984])* show that including the rate of release of fixed K improves regressions of available K on plant yield and K offtake. This suggests that the rate of diffusion of non-exchangeable K is more important than its quantity.

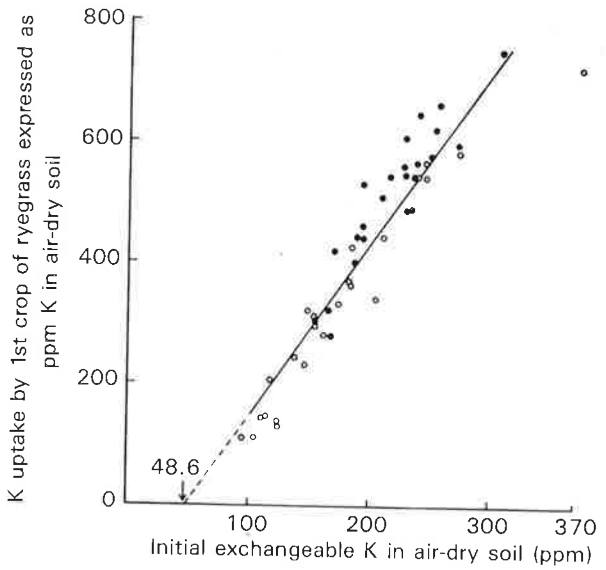

Figure 6. Relationship between K uptake during the first cropping period with ryegrass in the pot experiment and the initially exchangeable K in the soils from the Agdell experiment Rothamsted. Soils from grass ○ and arable/fallow ● plots in 1958–67 (slope y = 2.856x–13.88; r = +0.94).

## 6. Response of crops to soil and fertilizer K in the field

Many recent experiments have shown that on soils enriched with K residues (high K status) yields of arable crops often exceed those on impoverished soils (low K status) irrespective of how much K is applied in fertilizer or manures *(Johnston et al. [1970]; Johnston [1986])*. To offer farmers sound advice on K manuring requires a knowledge of two factors, the response of crops to soil K and the probable effect of K fertilizer at each level of soil K.

### 6.1 Crop response to exchangeable K

Figure 7 shows a linear relationship between the yield of potatoes and field beans *(Vicia faba)* and exchangeable K in an experiment at Rothamsted. The range of exchangeable K values was not wide enough to determine the level above which there would be no further increase in yield, but it was larger than 200 mg K/kg.

Figure 8 shows responses of barley grain and sugar from sugar beet, again in experiments at Rothamsted, but where there were more plots. Spring barley yielding about 6 t/ha grain did not need more than 80 kg/ha exchangeable K, but sugar yield was still increasing up to 200 mg/kg. For both crops the general relationship was clear but there was some scatter in the values, more for the sugar beet than the barley. Sugar beet roots explore subsoils more efficiently than do the roots of barley, and subsoil K could have supplied part of the K demand for the sugar beet, the amount varying from plot to plot with the amount of root in the subsoil (see also Section 2.2).

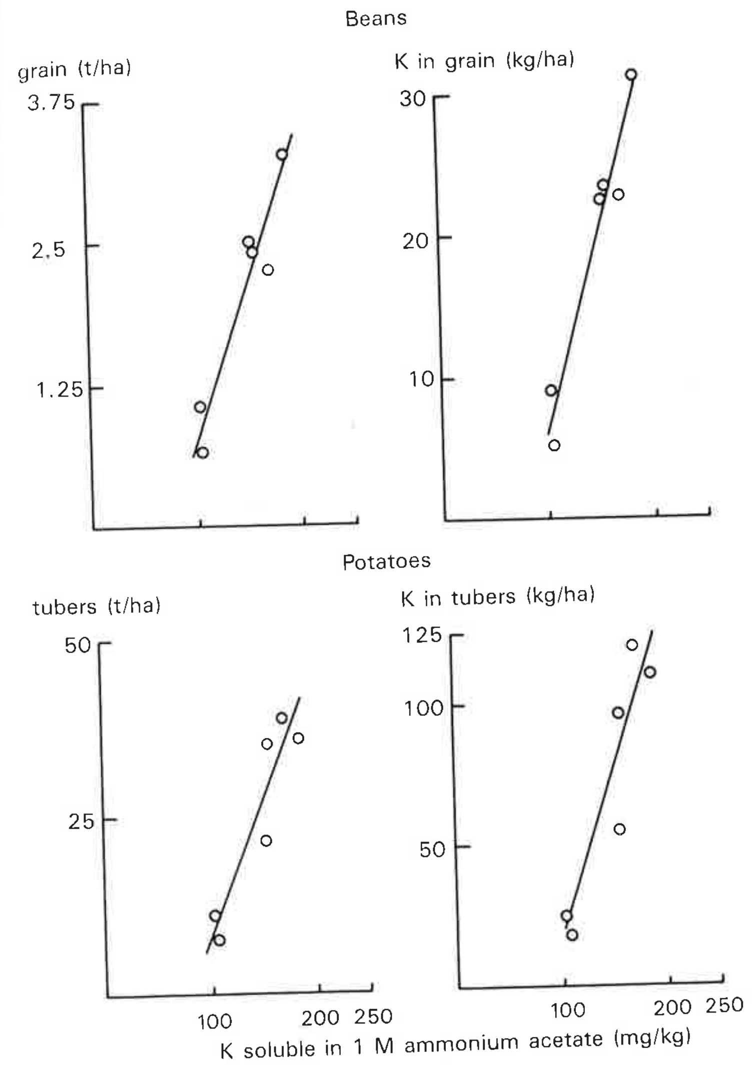

Figure 7. Relationship between yield of potatoes and field beans *(Vicia faba)* and exchangeable K in soil.

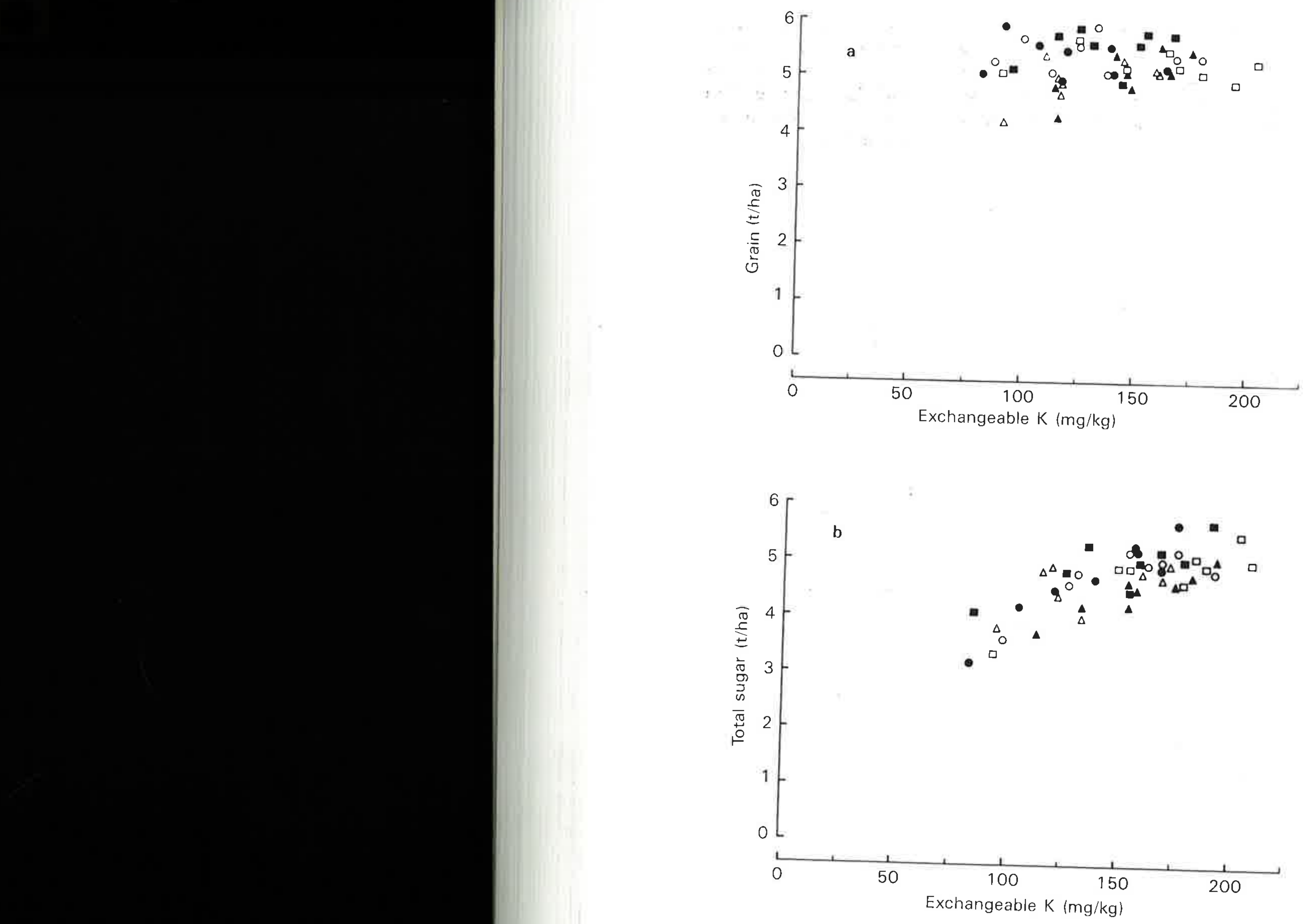

Figure 8. Relationship between yields of spring barley (a) and sugar from sugar beet (b) and exchangeable K in soil. Crops grown on soils with 1.5 and 2.4% organic matter (not shown) and manured from 1848–1951 with: NPK, circles; PK, squares; unmanured, triangles and when cropping was a 4-course rotation: turnips, barley, fallow, wheat, open symbols; turnips, barley, clover, wheat, closed symbols.

## 6.2 Crop response to fertilizer K

Crop response to freshly applied K fertilizer often depends not only on the exchangeable K content of the soil but also on soil type which affects the amount of K released during the growing season. Table 5 shows the response of four crops to freshly applied fertilizer on soils of different texture, each with two amounts of exchangeable K (poor and good). On the sandy loam and silty clay loam an application of potassium fertilizer increased the yield of spring barley on the low K soil to that on the high K soil. However, on the sandy clay loam so much K was released even on the low K soil that there was no response to potassium fertilizer. Also on this sandy clay loam winter wheat and winter barley yielded 8.5 and 7.9 t grain/ha respectively on both the low and high K soil, and applying K fertilizer gave no increase in yield. However, potassium fertilizer failed to increase the yields of potatoes, sugar (except on the sandy loam) and beans grown on all the low K soils to those on the high K soils. Yields of these three crops benefited from the presence of K residues in soil and fresh K fertilizer could not match these benefits. These results were all obtained on long-term field experiment sites where the various categories of soil K were in equilibrium. Such experimental sites are the only way of getting reliable information on crop response to both soil and fertilizer K.

Table 5. Effect of soil texture and potassium status on the yield (t/ha) of spring barley, potatoes, sugar, from sugar beet and field beans* and the response to fresh potassium fertilizer

| | | Soil texture | | | | | |
|---|---|---|---|---|---|---|---|
| | | Light | | Medium | | Heavy | |
| | | Soil potassium status | | | | | |
| Crop | K fertilizer applied | Poor | Good | Poor | Good | Poor | Good |
| Barley grain | No | 3.12 | 3.32 | 3.34 | 3.54 | 5.67 | 5.71 |
| | Yes | 3.38 | 3.31 | 3.56 | 3.56 | 5.67 | 5.86 |
| | Response | 0.26 | - 0.01 | 0.22 | 0.02 | 0 | 0.15 |
| Potatoes tubers | No | 32.9 | 41.2 | 17.1 | 27.6 | 28.8 | 43.1 |
| | Yes | 44.2 | 47.2 | 31.1 | 36.7 | 39.6 | 44.0 |
| | Response | 11.3 | 6.0 | 14.0 | 9.1 | 10.8 | 0.9 |
| Sugar | No | 3.59 | 4.60 | 3.76 | 4.94 | 6.76 | - |
| | Yes | 5.81 | 5.83 | 4.53 | 5.55 | - | 6.74 |
| | Response | 2.22 | 1.23 | 0.77 | 0.61 | - | - |
| Beans grain | No | | | 2.18 | 2.96 | 2.52 | 4.42 |
| | Yes | | | 2.67 | 2.97 | 3.60 | 4.38 |
| | Response | | | 0.49 | 0.01 | 1.08 | - 0.04 |

* Field beans: *Vicia faba*