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# **Measurement and Assessment of Soil Potassium**

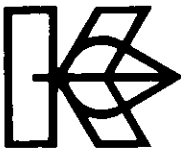
**H. Mutscher**

**International Potash Institute Basel / Switzerland**  
**1995**

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# Measurement and Assessment of Soil Potassium

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## Symbols and abbreviations used

K	Potassium in general as element or nutrient regardless of status or form.
K <sup>+</sup>	Potassium in the ion form in crystal lattices or adsorbed or in solution.
K <sub>t</sub>	Total K content of rocks, minerals, soils or plant material.
K <sub>str</sub>	Structural K in the framework of silicate minerals.
K <sub>sol</sub>	Potassium ions in the external soil solution (not affected in their mobility by the electrical surface charges of soil solids).
K <sub>ads</sub>	Potassium ions bound to negatively charged external surfaces of inorganic and organic, mostly fine-grained solid soil constituents.
K <sub>ex</sub>	"Exchangeable K", a fraction of K <sub>ads</sub> defined by the extraction technique applied.
K <sub>lab</sub>	Labile potassium, the sum of K <sub>sol</sub> and K <sub>ads</sub> .
K <sub>i</sub>	Interlayer potassium, potassium ions in the interlayer space of primary or secondary layer silicates ( native or fixed).
K <sub>ier</sub>	Easily releasable K <sub>i</sub> , a fraction of the interlayer K only conventionally delimitable.
K <sub>fix</sub>	Fixed potassium, K ions entrapped in the interlayer and not placed there during mineral formation; they can not be extracted under conditions stipulated for the determination of K <sub>ex</sub> , but they may be included in K <sub>ier</sub> .
K <sub>nonex</sub>	Potassium in the structures of tectosilicates like feldspars and feldspathoids.
K <sub>org</sub>	K organically bound, i.e. K in organic compounds released by mineralization.
V <sub>K</sub> %	Degree of saturation of the exchange complex with potassium ions; derived parameter.
CEC	Cation exchange capacity of soils in general.
CEC <sub>min</sub>	CEC of inorganic soil constituents.
CEC <sub>org</sub>	CEC of organic soil constituents.
CEC <sub>eff</sub>	Effective CEC, CEC of soils with variable charge measured at natural pH level.
DLW	Degree of leaching and weathering of inorganic soil constituents.
AR	Activity ratio (some authors also "adsorption ratio") $AR = (K^+)/\sqrt{(Ca^{2+}) + (Mg^{2+})}$ for ions in the equilibrium solution.
EUf	Electro-ultrafiltration.
BC	Buffer capacity ( immediate buffering).

- LBC** Linear buffer capacity; buffer capacity in the range of linearity of the Q/I isotherm according to Beckett.
- AR<sub>0</sub>** AR corresponding to the point of intersection with the abscissa of the Q/I isotherm according to Beckett.



## 1. Introduction

"The measurement of Soil Potassium" written by J. Quemener was published by IPI in 1978 as No. 4 in the series IPI-Research Topics. This text matched well the interest of researchers and practitioners concerned and became a frequently quoted reference. The new title "Measurement and Assessment of Soil Potassium" expresses the wish of the publisher to devote more attention to problems of data evaluation. In full agreement with the publisher's intention, the author has tried to outline the problems of measurement of soil K with a view to parameter evaluation and interpretation and finally to the efficiency of K assessment for agronomic purposes.

Studies of soil potassium pursue two distinct targets:

1. Investigation of soil K in order to improve our understanding of states and transformation processes of this element in soils.
2. Measurement of soil K in order to assess the K supply to a growing crop and to plan corrective measures for optimizing the nutrient supply to crops according to the yield level to be attained.

The two aims are interdependent and support each other though their methodological approaches and their techniques differ considerably. We take the view that agronomic aspects are of primary concern and therefore, treat the problems of measurement and assessment of soil potassium with full regard to the second of the above targets. Essentially, two levels of K assessment are considered: the study of K supply of benchmark soils and the field-related routine testing for advisory work and monitoring of the K status.

Most techniques of measurement of soil K are empirical. They provide numeric data mirroring various aspects of the K status of soil. For agronomists, such data attain their full significance only if we can relate them to the K uptake of crops or to their K demand, and that quantitatively and with a high degree of reliability. Virtually, the problem is to answer the following questions:

1. Which characteristics of the K system of soil are measurable?
2. What is the inherent meaning of a measured parameter as concerns the K system of soil on one side and the K supplying capacity to crop on the other?
3. What kind of algorithm is disposable or realizable to evaluate measured numeric data and to relate them to crop growth in order to adopt measures for optimizing K supply?
4. What kind of measurement is appropriate to support the decisions to be made by agronomists?
5. How can a reliable K assessment be realized at lowest cost?

We attempt to answer these questions on the basis of our present-day knowledge about soil K.

Our actual understanding of soil K is the result of many years of research and practical experience in fertilizer use. This text relates to both, but space limitations do not allow us to go into detail and the possibility to quote sources is also restricted. Selected references are given in the case of fundamental facts or statements and for techniques of measurement or evaluation. To compensate for this shortcoming, a list of important sources is added at the end of the text, study of which may be useful for anybody who wishes to deepen his knowledge beyond the information given here. The limited volume of the text renders it impossible to give detailed descriptions of techniques for measurement. The reader is directed to the numerous handbooks available. The author thinks it much more important and urgently necessary to discuss aspects of the efficiency of the assessment of soil nutrients rather than to describe the procedures of measurement.

Reviewing the voluminous literature concerning soil K assessment soon makes it evident that in the past, much work and money have been expended on measurements applying new techniques or testing new soils, but without raising the question of assessment. Measurements have been made which could not be decoded as concerns their inherent information in terms of the K transfer in the soil/plant system, and which therefore, were never used for decision-making. Sometimes, one has the impression that the principle was: "the more parameters we measure, the better we are informed". This is quite erroneous. The aim should rather be to minimize measurements and to qualify the interpretation of parameters measured.

The design of a rational strategy of soil testing for K should be based on a clear delimitation of information required for a well defined decision to be made. It is nonsense to make measurements which cannot be translated into decision-supporting terms. The target-oriented concept of soil testing should take into account:

1. the mode of soil sampling and sample treatment,
2. the selection of appropriate parameters and testing techniques for measurement,
3. the quality of disposable algorithms for parameter evaluation and status assessment,
4. the interpretation of parameters and the assessment of the K supplying capacity in terms of the dynamic soil/plant system.

None of the tasks in assessing the K supplying capacity of soils can be resolved without a comprehensive idea about the state and behaviour of K in soils. This is why the K system of soil is outlined in the second chapter as a basis for all other considerations.

The author was for long engaged in studying the nutrient systems of tropical soils and in agriculture of the tropics in general. For this reason, he felt the necessity to direct the attention of the reader to the specific problems of highly weathered tropical soils and to the gaps in our knowledge with regard to the assessment of their K status. Moreover, we should avoid the trend to see soil K assessment mainly as a problem of intensive cropping on less weathered soils. We need to pay more attention to K turnover in cropping systems with no or low external inputs in order to contribute to the development of site-specific sustainable systems in the tropics.

Last not least, the reader may be surprised by the K-related terms used in this text, differing to some extent from what is common. But any insider knows to what extent there is confusion concerning terms applied and their meaning. The terms used here are necessary for a clear separation of what exists or happens in soil and what we measure and evaluate. Targeted measurements and decision-related assessments may profit from well-defined terms.

The author hopes that the facts outlined and the concepts developed in the following chapters may help to improve the assessment of soil K and of the nutrient status of soils in general.

## **2. Potassium in the soil**

### **2.1. K system and K status: definition of terms**

The nutrient status of a given soil is not simply a question of nutrient content. Any nutrient exists in soil in various states or forms and the incessant transformation of the nutrient from one form into another as well as the gains and losses of the nutrient generate a dynamic nutrient system. This is as true for K as it is for other nutrients.

The **K system** of soil represents the entirety of K forms and their interactions expressed in distinct transformation processes and controlled by a complex of internal and external factors.

The term "K status" of soil is used in this text in a specific sense differing from that of the term "K system".

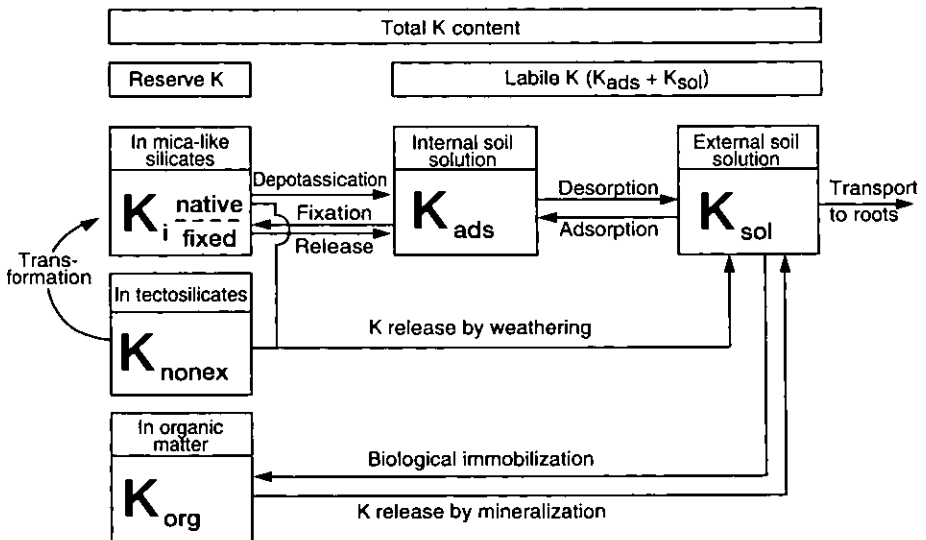
The **K status** of soil is the actual state of the K system represented by the types and respective amounts of K forms in a given soil and by the potential rates of possible transformation processes.

## 2.2. The K system of soil

Without knowledge about the K system, components of the system can be measured, but the significance of measured data in terms of the system must remain obscure and, consequently, their interpretation more or less uncertain and imprecise. Therefore, an understanding of the K system is indispensable for any meaningful interpretation of measured data of the K status.

The K system differs from N or P systems by its stronger and more exclusive dependence on the mineralogical composition of parent material and on modification of mineralogical constituents produced by weathering and leaching. Consequently, the K system and its function in potassium supply to crops or in transformation of fertilizer K depend on both inorganic parent material and degree of leaching and weathering of the soil constituents.

Figure 1 gives a schematic representation of the K system. Forms and transformations of K need brief comments.



**Fig. 1.** The K system of soil - schematic representation of K forms and their transformation.

### 2.2.1. K content and K forms

The total K content of soils varies between less than 0.1 and more than 4% with a clear maximum of frequency between 0.3 and 2%. This K occurs in soil in three main forms:

- structural K in minerals, mostly silicates,
- K adsorbed on negatively charged particle surfaces,
- solution K in the soil water beyond the influence of electrical fields of charged surfaces.

#### 2.2.1.1. Structural K ( $K_{str}$ )

$K_{str}$  comprises all  $K^+$  which is a constitutional part of the framework of crystals of minerals. In practice, a large number of minerals, mostly silicates, may be involved. In relation to the K system of soil, three main groups are important:

- feldspars and feldspathoids,
- micas,
- micaceous clay silicates.

These groups are founded structurally and functionally, the latter with regard to conditions and rates of K release from this source:

1. The  $K_{str}$  of feldspars and feldspathoids is liberated by destruction of the silicate framework by weathering. This is valid for all members of this group, though the weatherability and the rate of K release vary over a wide range.
2. The  $K_i$  of micas may be liberated by chemical decomposition as K of the feldspar group, but additionally it can, at least partly, be released by diffusion out of the interlayer space and this, without destruction of the crystal structure.
3. Mica-like clay silicates behave like micas with the distinction that the diffusive release of  $K_i$  proceeds more rapidly due to weaker bonds and shorter diffusion paths.

#### 2.2.1.2. Adsorbed K and solution K ( $K_{ads}$ and $K_{sol}$ )

K ions in soil water belong either to the adsorbed form or to the solution K.  $K_{ads}$  is bound to the negatively charged surfaces of solids. Clay silicates and organic matter can adsorb  $K^+$ , under certain circumstances also free oxides. At least in mineral soils with loamy or heavier textures, most of the  $K_{ads}$  is attached to clay silicate surfaces. All  $K^+$  beyond the effects of electrical fields of solids moves freely in soil water and diffuses along concentration gradients or may be transported by massflow of soil water.

No sharp boundary exists between  $K_i$  of micaceous minerals and K adsorbed on their surfaces. The gradual "opening" of the interlayer space towards the edge (formation of wedge-shaped openings of interlayer margins, see Fig. 2) is the reason for this.

### 2.2.1.3. K organically bound ( $K_{org}$ )

K in soils does not occur to any appreciable extent in complex organic compounds and differs in that from other nutrients like N or P.  $K_{org}$  can be neglected.

### 2.2.2. K transformations

The forms of K in soil are not independent. K can pass from one state to another, a phenomenon which is called "transformation". The various transformations of K differ:

- in their dynamics and kinetics,
- in their specific significance from soil to soil,
- in their role for K supply to plants and for the transformation of fertilizer K.

#### 2.2.2.1. Equilibrium between adsorbed K and solution K

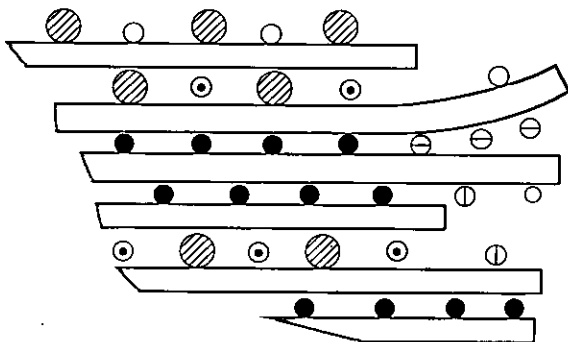
There is a dynamic equilibrium between  $K_{ads}$  and  $K_{sol}$ . The dynamic character of this equilibrium is due to the incessant transfer of ions between the two forms through diffusion, which enables rapid establishment of the equilibrium. The latter is affected by K uptake of organisms, decomposition of organic matter, leaching losses, application of fertilizer, liming and other factors. The highly dynamic equilibrium  $K_{ads} \longleftrightarrow K_{sol}$  is of outstanding importance for K supply to roots and the fate of fertilizer K.

The equilibrium  $K_{ads} \longleftrightarrow K_{sol}$  is a part of the overall equilibrium of all ion species in the soil water and their counterparts adsorbed by the exchange complex of the soil. Consequently, this equilibrium is affected by all factors controlling the whole system:

- charge and diameter of competing ions,
- concentration of the electrolytes in soil water,
- density and location of the charges on the exchanger,
- steric selectivity of the exchangers.

For the distribution of  $K^+$  between  $K_{ads}$  and  $K_{sol}$  the rule holds: the higher the relative binding force of the exchanger sites for K, the more the equilibrium shifts to the left and the lower is the concentration of  $K^+$  in the external soil solution.

The exchange complex is not materially homogeneous and the exchange sites are not qualitatively equal. This is true not only for the exchange sites of materially distinct constituents of the exchange complex, but also for those of an individual particle. For instance, the exchange sites of an illite particle have different binding strength and selectivity properties. For this reason, several proposals for a classification of the exchange sites have been made. One is presented in Figure 2.



- K<sup>+</sup> on external planar binding sites (p-position type A)
- ⊙ K<sup>+</sup> in totally expanded interlayer spaces (p-position type B)
- K<sup>+</sup> in non-expanded illitic interlayer spaces (i-position)
- ⊖ K<sup>+</sup> in laterally expanded wedge shaped openings of interlayers (e-position type A)
- ⊕ K<sup>+</sup> on lateral positions with increased binding strength due to overlapping of electrical fields (e-position type B)
- ⊗ Complementary cations

Fig. 2. Schematic representation of binding sites with distinct binding strength and selectivity for K ions.

An important rule follows from the occurrence of exchange sites with different binding strength: with increasing saturation of the exchange complex with K<sup>+</sup> the binding forces for K<sup>+</sup> decrease and the corresponding equilibrium concentration of  $K_{s0l}$  increases. This is explained by the fact that the exchange sites are consecutively occupied by K<sup>+</sup> according to the binding strength exerted. Sites with the highest binding force and the lowest equilibrium concentration are saturated first and then, step by step, sites with weaker binding are involved.

Generally, the relationship between  $V_K$  and concentration of  $K_{s0l}$  is not linear (Figure 3). The shape of the graph may vary considerably according to the composition of the exchange complex.

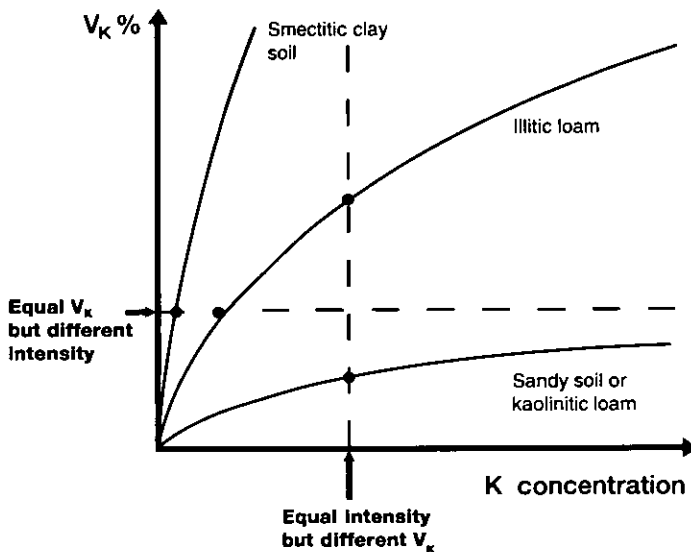


Fig. 3. Relationship between K saturation of the exchange complex ( $V_K \%$ ) and K concentration in the external soil solution.

Factors affecting the relationship are:

- kind and proportion of the constituents of the exchange complex,
- charge density of negatively charged particle surfaces,
- origin of charge (e.g. tetrahedral or octohedral isomorphic substitution),
- occurrence of positively charged sites,
- concentration of electrolytes in soil water,
- valency and diameter of ions competing with K,
- pH and anions in soils with variable charges.

#### 2.2.2.2. Potassium replenishment

There is not only a coupling between the two forms of  $K_{lab}$  realized by the adsorption/desorption equilibrium with its specific dynamism, but there is also a link between  $K_{lab}$  and  $K_{str}$ . Chemical weathering liberates  $K^+$  from the structural reserve, the ions passing into the soil solution. It produces a permanent transfer of  $K^+$  from  $K_{str}$  to  $K_{lab}$ . This process is called "K replenishment". The reverse transfer is also possible and known as "K fixation" (see section 2.2.2.3.).



### *Driving forces of K replenishment: weathering and plant growth*

The liberation of  $K^+$  by weathering of rocks and minerals is a precondition for the build-up of a pool of labile K in soils. The appearance of  $K_{sol}$  generates the possibility of leaching losses. At the same time, the establishment of a plant cover interferes by withdrawal of  $K^+$  from soil solution. Both processes open the K system of soil. The K replenishment counteracts the decrease of the pool of  $K_{lab}$  due to leaching and K uptake of plants.

In K replenishment, two distinct transformation processes are operating:

- decomposition of silicates by chemical weathering and,
- release of  $K_i$  of micaceous minerals by diffusion of  $K^+$  out of the interlayer space.

Chemical weathering destroys the structures of silicates thus liberating silicic acid, hydroxides of metals and soluble salts as weathering products. Other cations than  $K^+$  are also liberated. Destruction of silicate constitutes the precondition of this way of transformation of  $K_{str}$  to  $K_{lab}$ . Even under favourable circumstances, rates of release remain low and do not satisfy the demands of a developed plant cover. This is true for both natural vegetation and agricultural crops. Although the dry matter production of plants in an ecosystem influences the biological activity and hence, weathering intensity in soil, the rates of K-release from silicates by decomposition can, in practice, be considered independent of the intensity of plant growth.

In this respect, the second process of release of  $K_{str}$  - the slow migration of  $K^+$  in the interlayer space of layer silicates towards the edges and their final release into soil solution - differs from the foregoing. Numerous experimental studies in the sixties and seventies have shown that this kind of K transformation reposes on a slow interdiffusion of  $K_i$  with cations of the soil solution, namely  $Na^+$  and  $H^+$ . It was proven that the release of  $K_i$  depends on the concentration of  $K^+$  in soil water in such a way that lowering of the concentration of  $K_{sol}$  or  $K_{ads}$  intensifies the release of  $K_i$ . This signifies that a second equilibrium process operates besides the equilibrium  $K_{ads} \longleftrightarrow K_{sol}$ ; this is the equilibrium  $K_i \longleftrightarrow K_{lab}$ . The decisive difference between the two is that the second equilibrium needs more time to be established. The main reason is the hindering of diffusion of  $K^+$  in the interlayer space by friction or mechanical obstacles.

The release of  $K_i$  is triggered not only by low concentrations of  $K_{sol}$ , but also by high concentrations of cations able to enter into the interlayer space, like  $Na^+$  and  $H^+$ . Practically, the release of  $K_i$  is, at least partly, a slow exchange process. Hence, the term "non-exchangeable K" often used is misleading. It should be applied exclusively for the  $K_{str}$  of tectosilicates.

A fact of overriding importance is the active role of plants in this process. Plants absorbing K lower the concentration of  $K_{\text{sol}}$  and in the second step of  $K_{\text{ads}}$ , thus propelling the release of  $K_{\text{i}}$ . In experimental studies, mostly executed in the seventies, it could be shown that agricultural crops are able to lower the concentration of  $K_{\text{sol}}$  in the immediate vicinity of active roots to such an extent ( $< 3 \mu\text{g l}^{-1}$ ), that noticeable  $K_{\text{i}}$  release is induced. Of course, these short-term dynamics of  $K_{\text{i}}$  release do not concern the whole pool of  $K_{\text{i}}$  in soil. Only the marginal spaces of interlayers with short diffusion paths to soil solution are involved. Nevertheless, research showed that in certain soils, rates of  $K_{\text{i}}$  release as high as  $50 \text{ kg ha}^{-1} \text{ d}^{-1}$  are possible and this, over several weeks (Mutscher, 1980). But such rates are confined to soils with high contents of illites in the clay fraction or micas in the silt.

### *Replenishment capacity*

Considering the mechanisms of the release of  $K_{\text{str}}$  is a precondition for understanding K replenishment. However, more is needed to achieve correct estimates of the replenishment capacity and several factors and their interrelationships should be taken into account.

Chemical weathering of noticeable intensity requires an aqueous environment. Water enables the hydrolytic/protolytic destruction of silicates and under humid climatic conditions, the disturbance of reaction equilibria by leaching of soluble weathering products. Consequently, the longer the wet season and the more humid the climate, the higher is the site-specific weathering potential. This potential is reinforced by acidification of the soil. Acidification is a function of acid inputs from the atmosphere, intensity of acid formation in soil, biological activity on and in the soil, buffering of the soil and intensity of leaching of basic compounds.

On a given site, the actual  $K_{\text{str}}$  release due to chemical weathering is not only a function of the climatic weathering potential, but also of the amount and kind of K bearing minerals contained in the soil. With a given weathering potential, the rates of K replenishment increase with the content of K bearing minerals and with their weatherability. The two mechanisms of K release from silicates render important the proportion between tectosilicates and layer silicates. With equal total content of K, the rates of replenishment may vary over a wide range according to the proportion of the two groups. However, both groups include a large number of mineral species of different weatherability. For this reason, with a given weathering potential, the real flux of K depends not only on the proportion of tecto- and layer silicates, but also on the composition of either group.

Among the feldspars, Ca/Na feldspars are more weatherable than K feldspars. Biotite has a higher weatherability than muscovite. Also illites, the most important highly dispersed K bearing clay minerals, vary in their ability to release K. These differences are not only caused by structural features like grain size, degree of depotassication, kind and extent of isomorphic substitution, but also by secondary modifications generated by soil formation. In this sense, the most important impact comes from weathering crusts covering grain surfaces and from precipitates of hydroxides in the interlayer space hindering K diffusion and changes of sheet spacing.

From all this, we have to conclude that K release from the pool of  $K_{str}$  is a phenomenon controlled by numerous static and dynamic factors. The replenishment capacity is defined by the releasable pool of K, by the actual rate of K release under the given site conditions, and by the decline of the rate of release with diminishing releasable pool.

#### 2.2.2.3. K fixation

K fixation is the installation of  $K^+$  in the interlayer spaces of clay minerals in a manner that does not allow easy exchange with cations of salt solutions as defined for  $K_{ex}$ . Consequently, fixation occurs mainly in soils with an appreciable content of three layer silicates in the clay fraction. The most important fixers of K among layer silicates are vermiculites and partly expanded illites. The ability of oxides in the clay fraction of some soils to fix small amounts of K is still under discussion and further investigation (Poss *et al.*, 1992).

This type of transformation of K can take place by two distinct mechanisms:

- Contraction of layer silicates with entrapping of  $K^+$  in interlayers or wedge-shaped marginal openings of interlayers;
- Slow diffusive intrusion of  $K^+$  into the interlayer space.

Both mechanisms require, at least locally, high concentrations of  $K_{sol}$  brought about for example, by application of fertilizer. The phenomenon of fixation became apparent when it was observed that applying K fertilizer did not produce the expected increase in crop yield. Fixation is most relevant in the practical field when large amounts of fertilizer are used, but it should not be overlooked that it may also occur in natural ecosystems.

High concentrations of  $K_{sol}$  are not only created by application of fertilizers. In soils rich in  $K_{ads}$ , more or less severe drying of the soil may also produce high concentrations of  $K^+$ . The most severe fixation is to be expected when soils with a high fixation capacity are submitted to drying after application of large amounts of fertilizer and/or when K fertilizer is badly distributed and incorporated in the field.

#### 2.2.2.4. Use of fertilizers and K transformation

Whenever fertilizer is applied, the  $K^+$  ions of the fertilizer are submitted to transformations typical for the given soil. The transformation processes after application continue until the soil-specific equilibrium between the K forms is reached. The applied K salt dissolves and supplies  $K^+$  to the soil solution. The concentration of  $K_{sol}$  increases. Immediately, exchange reactions start and a part of the added K is adsorbed. A second reaction besides adsorption of K may be its fixation.

It was long thought that fixation was inevitably disadvantageous. However, research in the seventies brought about a change in this view. Investigation of K uptake by plants showed that fixed K can easily be released from interlayers as soon as the concentration of K in solution falls to sufficiently low levels. This is especially the case in the rhizosphere of crops with intensive K uptake. High yielding K demanding crops induce the release of fixed K and involve it in the short-term K transformation triggered by K uptake. Generally, fixed K is more easily released than native  $K_f$ . Thus, K fixation improves the short-term buffering of labile K by K release. Fixed K is by no means "lost" and can contribute to yield formation, even in intensive cropping.

### 3. The soil/plant system

#### 3.1. The new entirety

The growth of a plant forces the soil to react on life processes and their impacts. The link between soil and growing plant is not confined to water, nutrient and heat supply to roots, it is much more complex and implicates factors like dry matter input and its influence on biological activity in soil, nutrient recycling, impacts of root activity, etc. Plant growth generates a new dynamic entirety: the soil/plant system. We are not concerned here with internal plant processes or with problems of dry matter production which are not related to soil. The question to be addressed is: "How does the nutrient system of the soil react when plants take up nutrients and what factors control this reaction?"

Figure 4 depicts the elements of the soil/plant system relevant to K supply. The following points must be emphasized:

1. K demand is a function of the crop grown and of the site-specific and management-supported yield potential of the chosen variety. Consequently, the reaction of the K system and the capacity of the soil to cover K demand are necessarily related to the level of K requirement or cropping intensity.

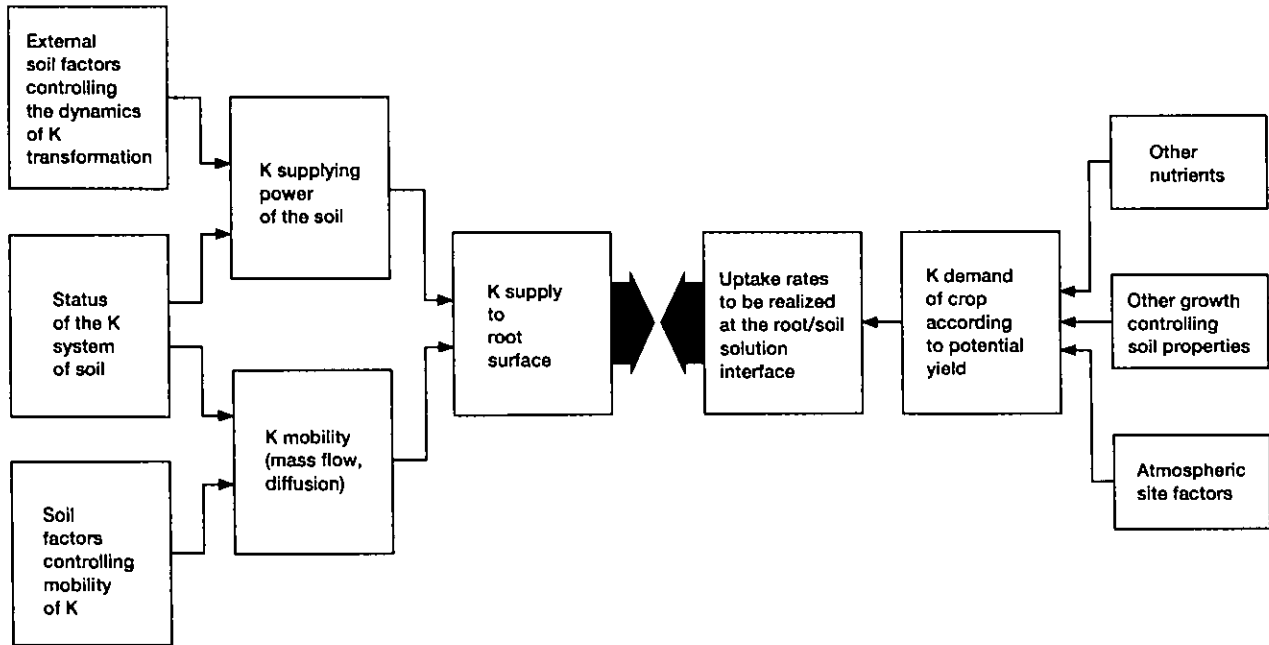


Fig. 4. The dynamic system of K demand of crop and K supply to root surface by the soil.

2. The nutrient demand of a crop is a dynamic feature. At different growth stages, the soil has to cover variable uptake rates and the capacity of a soil to satisfy the dynamic K demand is an important soil quality we have to assess.
3. K supply to the root is the result of two distinct soil-related processes:
  - the transfer of  $K^+$  from other forms to  $K_{sol}$  by various transformation processes,
  - the transport of  $K^+$  by diffusion or massflow to the root surface.
 The transport of  $K^+$  is very often the limiting factor for better K supply to roots and may mask a high release potential of the K system. In practice, this distinction between performance of the K system and K transmission to roots is often neglected in interpretation of soil test values and K assessment.
4. Growing plants play an active part in transformations of K: the K uptake lowering the concentration of  $K_{sol}$  induces equilibrium reactions and operates as a driving force triggering dynamic processes in the K system.

### 3.2. K system and K supply

It is useful to analyze in more detail how the K system works when plants absorb  $K^+$ . Only on this basis does it become possible to conclude what kind of procedure can help us to make appropriate measurements and reliable assessments of the K supplying capacity of soil. Figure 5 shows the principal facts and connections.

Assuming the K system of the soil to be in equilibrium, whenever plants start to take up  $K^+$  from soil solution, three steps or levels of reaction of the soil are possible:

1. The absorption of K lowers locally the concentration of  $K_{sol}$  below the equilibrium concentration. The generation of concentration gradients induces diffusion of  $K^+$  towards root surfaces.
2. The lowering of the concentration of  $K_{sol}$  disturbs the equilibrium  $K_{ads} \longleftrightarrow K_{sol}$ . The soil counteracts by desorption of  $K_{ads}$ . This desorption tends to increase the concentration of  $K_{sol}$  and to compensate the effects of K withdrawal by roots. Because the exchange reactions are rapid, this process realizes an "immediate buffering" of  $K_{sol}$ .
3. K uptake causes a particularly strong decrease of the concentration of  $K_{lab}$  in the immediate vicinity of roots. If soil contains mica-like layer silicates, the lowering of the concentration of  $K_{lab}$  induces a release of  $K_i$ . This process is slower than the desorption of  $K_{ads}$ , nevertheless, it represents a factor of buffering, because it tends to offset the loss of  $K_{lab}$ .  $K_i$  release operates as a plant induced short- to medium-term buffering.

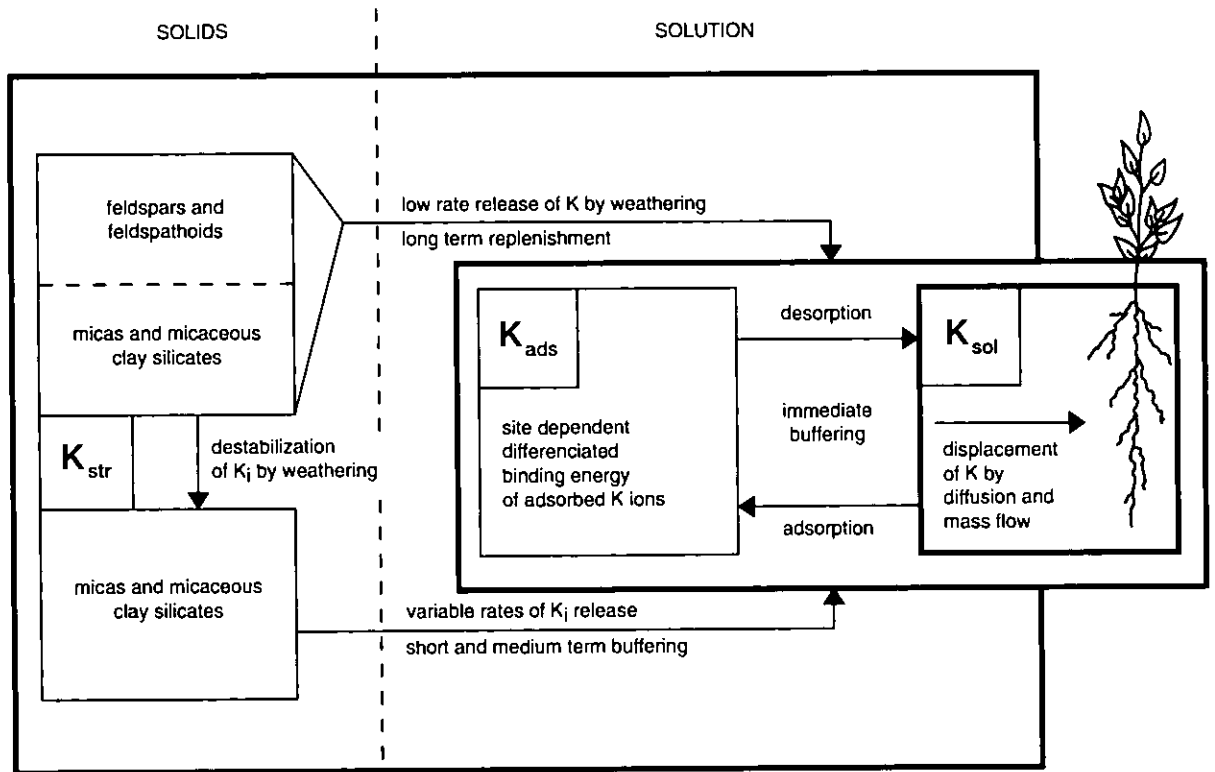


Fig. 5. The potassium supply to crop: levels of operation.

The three foregoing reactions are triggered by plants and follow the dynamics of K uptake within the limits set by the soil-specific K system. In the background, release of  $K_{str}$  through chemical weathering provides long-term buffering. This process is mainly controlled by factors other than plant growth or K uptake and does not play an important part in intensive agriculture. It is obvious that in the soil as a whole, these processes go on simultaneously.

### 3.3. Bioavailability of soil K

Considering the existing confusion as concerns the use of terms like "available K" or "absorbable K", it is necessary to interpret bioavailability of K in the light of the explanations given above.

Strictly speaking, the only fraction of soil potassium which is immediately available to plants and which can be absorbed by roots without involving any transformation in the K system is  $K_{sol}$ . But  $K_{sol}$  in the whole rooted soil volume amounts to only 0.5-15 kg ha<sup>-1</sup> K quite inadequate to supply the needs of even a low yielding crop and, therefore, other forms of K have to contribute to the K uptake of the crop. But, this participation of other K forms in the K supply inevitably implicates transformation processes, hence these fractions are physically not directly "absorbable" or "available". In practice, the term "available" as normally used includes  $K_{sol}$  plus all potassium in the soil which is transferred to the soil solution by short-term transformations.

### 3.4. The role of K mobility

Plants absorb  $K^+$  from the external soil solution. Most of the  $K_{sol}$  is located more or less distant from the root/solution interface and must be transported in order to be absorbed. All aspects of K translocation in solution are summarized by the term "mobility". The transport of  $K^+$  is realized either by diffusion or by mass flow. Since the work of Barber (1962, 1963, 1965, 1966), it has been repeatedly shown that diffusion is the kind of movement for quite more than 75% of the K transport to roots.

Diffusion and mass flow of  $K^+$  are partly dependent on characteristics of the K system. The most important factors are the concentration of  $K_{sol}$  and its buffering. The higher this concentration the better the conditions for formation of steep gradients. Buffering weakens the build-up of gradients and, for this reason, diffusive transport is inversely related to buffer power. Clearly, mass transport of  $K^+$  with water flux is the higher, the higher the concentration of  $K_{sol}$ .

Besides factors of the K system, other soil characteristics strongly influence K mobility. The most important characteristics are:



- parameters of the soil-specific pore system (pore size distribution, continuity and tortuosity of pore channels),
- parameters of the water regime, particularly the dynamics of moisture content.

These factors modify the relationship between K mobility and K system to such an extent that only a general rule holds: the higher the equilibrium concentration of  $K_{sol}$ , the higher is the potential K transportation. But the high concentration alone does not guarantee intensive K translocation. For this reason, K mobility assessment should be separated from the assessment of K supply by the K system. K mobility is not normally determined in soil testing for K and is not considered in the following.

## 4. Characteristics of the K system

### 4.1. Generalities

K supplying capacity is a soil quality in the sense of the FAO land evaluation system (FAO, 1976). This soil quality may be assessed using estimated or measured data. Only the latter are considered here.

"Characteristics" of the K system comprise all kinds of quantifiable information about forms of K or K transformation allowing an assessment of the K supplying capacity of the soil in terms of the K system. The term characteristic stresses the kind of information about the K system obtained by measurement. It is a tool to improve the understanding of K supply to crop and the concepts for assessment of the K status.

The term "**K parameter**" is used in the following text in the sense of a measured value, as a rule obtained by standardized techniques of measurement. K parameters are related to the K status and are used for K assessment of individual soils.

We shall not concern ourselves here with methods for investigating the functioning of the K system; our interest is rather in standardized or standardizable techniques for assessments of K status for agronomic purposes.

As discussed in Chapters 2 and 3, a knowledge of different types of soil characteristics is needed for assessment of the K supplying capacity. Such characteristics are descriptive of K quantity, of K intensity (= K concentration in soil solution) and rates of K transformation\*. Characteristics of buffering combine the foregoing characteristics. Characteristics reflect distinct elements of the K system and only their combination provides the

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\* Note that the terms nutrient quantity, intensity, rate and capacity have, since their introduction, not always been given the same meanings. The meanings used here are detailed in the text.

possibility to assess the K supplying capacity as a dynamic soil quality (see section 6.2.). The soil K characteristics and their measurability are discussed under the headings: quantity, intensity and rate.

## 4.2. Quantity characteristics

As a first approximation, the K supplying capacity is a function of the quantity of K contained in a soil. Quantity information is the basis of any assessment irrespective of its significance in terms of K forms. Scientifically, quantity characteristics related to defined K forms are more meaningful and easier to interpret, but for practical agronomic purposes, quantity information derived from empirical extraction methods, while not necessarily interpretable in terms of K forms, has proved to be useful.

### 4.2.1. Total K content ( $K_t$ )

The amount of  $K_t$  is a basic information about the stock of K contained in a soil but, nevertheless, this parameter does not represent a reliable indicator of the K supplying capacity. Relating statistically the data of  $K_t$  and K uptake by crops for a group of soils of different geological origin and of various DLW yields generally a highly significant correlation with a relatively low degree of determination. This indicates that  $K_t$  possesses a significance for K supply to plants, but other factors modify its role strongly. The main reason for the low degree of determination is the low share of  $K_t$  supplyable to plant. No useful conclusion can be drawn about actual K supply from soils differing little in  $K_t$ .

$K_t$  is of little use in monitoring K status for agronomic purposes, furthermore, its determination is costly.  $K_t$  measurement is worthwhile on benchmark soils in a regional or countrywide reference network or in soil investigations connected with field trials on nutritional problems. Benchmark soils are usually sufficiently differentiated to render  $K_t$  an useful information.

### 4.2.2. Quantity characteristics related to defined K forms

Since all of the forms of K have specific roles, it would be useful to measure the amount of K in each form. However, there are difficulties in realizing this objective because:

- the boundaries between K forms (e.g.  $K_{ads}/K_i$ ) are blurred,
- K transformation ( $K_{ads} \leftrightarrow K_{sol}$ ) is rapid,
- measurements are sensitive to changes in the chemical environment during extraction.

There are no techniques for selective extraction of some of the K forms (e.g. forms of  $K_{str}$ ). Nevertheless, some of the K forms are measurable or can be estimated from measurements which can be made.

#### 4.2.2.1. K in the external soil solution ( $K_{sol}$ )

$K_{sol}$  is the immediate source of K for plants. Regardless this fact, the measurement of the quantity of  $K_{sol}$  has little practical value. Owing to the rapid ion exchange and establishment of the equilibrium  $K_{ads} \longleftrightarrow K_{sol}$ , the quantity of  $K_{sol}$  is subject to quick fluctuation. Any change in moisture content and in concentration or composition of solutes in soil water (e.g. caused by fertilizer application, liming, changing biological activity in soil, leaching or other impacts) causes variation in the quantity of  $K_{sol}$ . For this reason, the quantity of  $K_{sol}$  is not measured except in special cases.

#### 4.2.2.2. Adsorbed K ( $K_{ads}$ )

The stock of  $K_{ads}$  is by far the most important quantity characteristic for the short- and medium-term K supply to crops. It represents the pivotal point of information about the K supplying capacity and its measurement is therefore indispensable. For many soils, the relative time-related variability of  $K_{ads}$  is much less than for  $K_{sol}$  because the seasonal K uptake of plants, as well as fluctuations of  $K_{ads}$  coupled with K exchange, are relatively low in comparison to the stock of  $K_{ads}$ . However, in sandy soils and soils with a predominantly variable charge (high DLW), this quantity of  $K_{ads}$  is also subject to strong fluctuation depending on the dynamics of other soil processes and of management impacts.

The use of the content of  $K_{ads}$  as basic quantity information needs appropriate techniques of measurement for this pool of K. Since  $K_{ads}$  is involved in the double equilibrium  $K_i \longleftrightarrow K_{ads} \longleftrightarrow K_{sol}$ , its measurement presents practical problems, as discussed in section 5.1.1. In any case, the quantity of  $K_{ads}$  measured is inevitably affected by the technique used for ion exchange and leaching of replaced K and this must be taken into account with regard to the evaluation of measured parameters (see Section 6.3.1.1.).

#### 4.2.2.3. Forms of structural K ( $K_{str}$ )

It follows from the functional differences between the K of tectosilicates (feldspars and feldspathoids) and layer silicates (micas and micaceous clays) that it would be useful to make separate measurements of the K contained in each group of minerals. Numerous experimental findings have demonstrated K uptake by crops to be more closely correlated with  $K_i$  than with  $K_t$  or acid extractable K from soils with large amounts of K in weatherable feldspars.

In the past, techniques for separating the two forms of  $K_{str}$  have been proposed (e.g. Kiely and Jackson, 1965) but, these are not very reliable or may be very expensive. They have been used in research but are not important for agronomic purposes, even for reference soils. No routine technique is available and such a technique is no longer sought; methods available for measurement of releasable fractions of  $K_i$  supply all the information needed for practical tasks (see Section 5.2.).

#### 4.2.2.4. Easily releasable interlayer K ( $K_{ier}$ )

The  $K_i$  of layer silicates may be released by a slow diffusion-controlled exchange process. For agronomists, the total content of  $K_i$  is not as important as the fraction of  $K_i$  which can be released in the short (days, weeks) or medium (a few years) run. Only this fraction affects K uptake by plants. On the other hand, the internal exchange sites involved may also be important for transformation of fertilizer K (fixation and buffering).

Several techniques have been tested and proposed to quantify this fraction of  $K_i$ . It is evident that the technique of extraction strongly influences the share and origin of  $K_i$  extracted. Thus, the quantities of  $K_i$  measured are conventional. Nonetheless, the techniques are  $K_i$  specific, i.e. specific to a defined K form.

From the techniques reposing on the equilibrium character of  $K_i$  release, the term "difficultly exchangeable K" was proposed in order to make a distinction between  $K_i$  release and desorption of  $K_{ads}$ . This term may be misleading, because the remaining  $K_i$  is also exchangeable in the long run. It seems better to speak about a conventional fraction as "easily releasable  $K_i$ " which takes into account the agronomic importance of this quantity characteristic. At least in soils with noticeable contents of layer silicates, the amount of this  $K_{ier}$  is significant for reliable K assessment.

#### 4.2.3. Conventional quantity characteristics, unrelated to K forms

Countless attempts have been made to improve K assessment using routine soil test techniques and many ostensibly reliable methods for extracting the so-called "available K" have been proposed (Table 1; Section 5.1.4.). The priority in testing these empirical procedures was to relate the amount of K extracted to K uptake by plants, paying little attention to the soil-related interpretation of the parameter. Investigations involved pot and field trials with graduated amounts of fertilizer applied. However, no perfect technique for the determination of the quantity of K available to plants was ever found and, as we know today, cannot be found: the processes of K supply to roots in a soil are too complex and too dynamic to be mirrored

perfectly by a single quantity value. Nevertheless, the search for better empirical extraction techniques continues despite the fact that significant improvement is no longer likely or even possible.

A quantity characteristic obtained by an empirical extraction technique may be regarded as satisfying if the quantity data measured are reliably and closely enough related to K uptake and fertilizer efficiency. For many empirical extraction techniques, highly significant correlation coefficients were found, regardless of the kind of extractant used. But it was also observed that the correlation depends on factors like type of soil, diversity of soils tested, level of K demand of the test crop, etc. The explanation is easy to find if the extraction techniques are interpreted in terms of the K system of soil and of its functioning in K supply according to K demand.

Various extractants are used to determine the quantity of "available" K: water, unbuffered or buffered salt solutions, dilute acids. All these seize a bigger or smaller part of the  $K_{ads}$  in the soil which is the main source for short-term K supply, hence the correlation between soil test value and K uptake. However, the correlation differs not only between extraction techniques, but also according to the conditions of determination of the soil test/crop response relationship. In detail, the following factors have been found to affect this correlation:

- kind of extractant,
- proportion of  $K_{ads}$  extracted by the technique,
- amount and form of  $K_{str}$  involved,
- K status of soils,
- mineralogical and textural diversity of soils,
- intensity of K uptake by the test crop.

Distilled water is the "softest" extractant possible. At a given soil:water ratio, water extracts only that part of  $K_{ads}$  with the lowest binding strength. This fraction of  $K_{ads}$  is closely correlated with the concentration of  $K_{sol}$ , hence the good soil test/crop response correlation for water extracts in high K demanding intensive cropping, where intensity has a large influence on K supply. In terms of the soil/plant system K extractable with water at constant soil:water ratio is a combined quantity/intensity characteristic. To monitor K using water extracts in intensive cropping requires frequent testing. With lower K demand and less influence of intensity on K supply, stronger extractants are preferable because they measure  $K_{ads}$  as a pool more completely.

The extractive power of empirical extractants can be reinforced by adding salts in order to intensify cation exchange and to increase the fraction of  $K_{ads}$  extracted. The larger the share of  $K_{ads}$  in the total quantity of K extracted, the looser is the relationship to K intensity. Therefore, the soil

test/crop response relationship is now preferably indicated by the quantity aspect of the test value. The relationship is affected by the differential binding strength of  $K_{\text{ads}}$  according to the state of the exchange complex.

The extractive action of salt solutions varies. It depends on the relative binding strength of the cation used in comparison to K, the bulk concentration, buffering and pH. In many extractants,  $\text{Ca}^{2+}$  is used for exchange of  $K_{\text{ads}}$ .  $\text{Ca}^{2+}$  replaces preferentially  $\text{K}^+$  adsorbed on external surfaces of clays. The more e-positions the clay has, the less is the share of  $K_{\text{ads}}$  extracted by  $\text{Ca}^{2+}$  solutions.  $\text{NH}_4^+$  is more efficient because it is able to exchange  $\text{K}^+$  in e- and even i-position.  $\text{NH}_4^+$  solutions are the most efficient extractants for  $K_{\text{ads}}$ , especially if the solution is buffered. The more completely  $K_{\text{ads}}$  is extracted, the stronger becomes the influence of the binding strength of K on the soil test/crop response relationship for soils in which three layer silicates are the dominant clay minerals. In other soils, this factor is less important.

Lowering the pH of the extractant (acidified salt solutions) increases the impact of  $\text{H}^+$  on the extraction.  $\text{H}^+$  is a powerful counterion for the exchange of K. However, more significant for the extracted quantity of K is the fact that with acid salt solutions, protolysis becomes possible and  $K_{\text{str}}$  is involved in extraction. This is still more important if dilute acid is used as extractant. In all these cases, according to the CEC of soil, its saturation with K and the mineralogical composition of soil, the amount of K extracted is composed of variable shares of  $K_{\text{lab}}$  and  $K_{\text{str}}$ . The question emerges as to how the involvement of  $K_{\text{str}}$  in the extraction affects the soil test/crop response correlation. This differs between forms of  $K_{\text{str}}$ .

The dissolution of tectosilicates by the extractant and hence the liberation of K from a form which does not really contribute to short-term K supply, must affect the soil test/crop response adversely. If different amounts of feldspar K are extracted from the soils tested, the relationship cannot be close. But if the soils tested do not vary greatly in mineralogy and content of K bearing tectosilicates, the relationship is less affected and high correlation coefficients may be observed. Consequently, soil test/crop response correlation depends on the mineralogy of soils.

The situation is different for the  $K_i$  of layer silicates. If the acid extractant used dissolves or replaces a certain amount of  $K_{\text{ier}}$ , which actually takes part in K supply to crops, the soil test value yields more valuable information. On the contrary, the data obtained are no longer pure quantity characteristics, because the amount of  $K_{\text{ier}}$  is closely related to the short- and medium-term buffering of  $K_{\text{lab}}$ . According to the cropping system and crop K demand, this involvement of short- and medium-term buffering may even improve the value of empirical soil test data and the correlation soil test/crop

response (see Section 6.3.2.1.).

Numerous conflicting observations have been reported in the literature concerning soil test/crop response correlation. In the light of the foregoing explanations, this is understandable; from soils differing in their mineralogy, variable amounts of  $K_{str}$  are extracted and measured with equally varying proportions between  $K_i$  and  $K_{nonex}$ . The distinct functions of the latter in short- and medium-term K supply make the interpretation of test values fallible. The higher the share of  $K_{str}$  in the total quantity of K extracted and the higher the variability of the proportion of  $K_i:K_{nonex}$  in this quantity, the lower will be the correlation soil test value/crop response.

To sum up, test values obtained by empirical extractants for routine testing have different meanings with regard to quantity, intensity and buffering. Their significance depends much on soil mineralogy and the K status of soils. Their interpretation has to be referred to the level of K demand (see Section 6.3.1.3.).

#### 4.2.4. K fixation capacity

In certain cases, the quantity of K which can be fixed by a given soil assumes importance. The fixation capacity may be regarded as a quantity characteristic of soil, because it is essentially the amount of K fixed which is of interest. The fixation capacity is limited by a theoretical fixation potential according to the mineralogical composition and content of clay. Under natural conditions, the amount of K actually fixed depends on a set of internal soil conditions. It increases with:

- increasing concentration of  $K_{sol}$ ,
- strong drying or frequent wetting/drying cycles,
- duration of high concentration levels of  $K_{sol}$ , and

it decreases with a high concentration of competing  $NH_4^+$ .

It follows that the measurable fixation capacity is a conventional quantity value depending upon how it is measured.

#### 4.3. Intensity characteristics

Chapter 3 showed that the K uptake of plants is not solely a function of disposable K quantities. The concentration of  $K_{sol}$  exerts an important influence in two senses:

1. Over a wide range of concentration, the intensity of K uptake is proportional to the K concentration at the solution/root interface.
2. The concentration of  $K_{sol}$  controls K mobility and therefore, translocation of K to roots.

Both effects render the concentration of  $K_{sol}$  an important characteristic of the soil/plant system.

The intensity of K flux into the root is the amount of  $K^+$  taken up per unit of root surface (approximately per unit length of root) and per unit of time. Because it is proportional to the concentration of  $K^+$  in the soil solution at the soil solution/root interface, the term "intensity" has been applied to the concentration of solution K.

K uptake by roots generates concentration gradients in the external soil solution and changes the bulk concentration. A soil characteristic must be reproducibly measurable and qualify the state of the system. Therefore, The K intensity in a given soil is the concentration of  $K_{sol}$  in state of equilibrium with  $K_{ads}$  (and possibly  $K_i$ ) at a defined water content. This intensity is a function of the least tightly bound adsorbed K.

The term intensity was introduced by Beckett (1964) with a different background and meaning. On the basis of Schofield's so-called Ratio Law, he used the term intensity for the activity ratio:

$$AR = (K^+) : \sqrt{(Ca^{2+}) + (Mg^{2+})}$$

In this concept, the K intensity is a ratio which reflects the K concentration only if Ca+Mg is kept constant. This is far from the case in soils. In the seventies, the AR as an intensity characteristic, attracted widespread interest. It corresponds to the K/Ca potential proposed by Ulrich (1961) as a characteristic of the K supplying capacity of soils. But, with the exception of extreme proportions between K and Ca or Mg in solution, the K uptake of plants from soil is practically independent of the concentration of Ca or Mg. Pot and field trials, mostly executed in the seventies, have shown the AR value less meaningful as concerns K supply to roots than the K concentration. Thus, the concentration of  $K_{sol}$  can be taken as an intensity characteristic in most cases. The significance of AR and of the Ratio Law came about through the attempts to introduce thermodynamic considerations in the chemistry of soils with permanent charges.

In a certain sense,  $V_K$  may be considered an intensity characteristic, because with increasing K saturation, the concentration of  $K_{sol}$  also increases, signifying that  $V_K$  indirectly reflects intensity. However, considering different soils, it must be taken into account that the relationship  $V_K$ /concentration of  $K_{sol}$  depends on clay content and clay composition. Consequently, soils with equal values of  $V_K$  may have different intensity values. The higher the content of three layer silicates and the higher the proportion of illites with pronounced K selectivity, the lower is the corresponding intensity at equal  $V_K$ . This restricts the utility of  $V_K$  as an intensity characteristic.



#### 4.4. Rate characteristics

A complete description of the K supplying behaviour of a soil needs, besides quantity and intensity information, also rates of K transformation. The rapidity of exchange reactions  $K_{ads} \longleftrightarrow K_{sol}$  makes the measurement of rates of transformation for this equilibrium superfluous. For practical purposes, the reactions may be considered instantaneous.

This does not apply to the release of  $K_{str}$  and the equilibrium  $K_i \longleftrightarrow K_{lab}$ . These reactions proceed much more slowly. However, the rates of release of  $K_{str}$  vary greatly. They depend upon mineral structures, grain sizes, coatings of weathering products enveloping the grains, degree of depotassication of interlayers and chemical environment. From the agronomist's point of view, the most important rate information is that of  $K_i$  release by layer silicates. These rates vary extremely and decrease with progressive removal of K from interlayer margins. Technically, it is possible to measure time functions of the  $K_i$  release of the bulk soil, but the data obtainable are related to the conditions set by the extraction technique and differ to a certain extent from the real rates of transformation in the field soil. Nevertheless, they allow comparisons between soils and even absolute estimates of release rates.

Agronomically, the rates of K release due to chemical weathering of K bearing minerals are of less interest, at least in intensive agriculture. They are relevant in natural ecosystems and low-input agricultural systems. They can be derived from long-term balances or experiments under laboratory conditions. The latter may concern individual minerals or bulk soil.

In any case, all rate data obtained under experimental conditions must be interpreted with care. The possibility of extrapolating them to field conditions is restricted, because it is very difficult to simulate in the laboratory the environment controlling the transformation of  $K_{str}$  in field soils.

Fixation is to some extent time-dependent. In the agronomical context, fixation mostly means the entrapping of  $K^+$  by contraction of the layers of silicates. This type of fixation proceeds very quickly as soon as the K saturation of exchange sites surpasses a threshold value or range. Rate determination is of no concern and practically all techniques for routine determination of K fixation refer to the quantity of K fixed by collapsing clays. Rates are only of interest for the K fixation by slow intrusion of  $K^+$  into interlayer space of silicates or the pore system of amorphous free oxides or allophanes. There are few reports of experiments with time functions of K fixation in the literature.

#### 4.5. Combined characteristics

Besides single quantity, intensity, and rate characteristics of the K system, more complex characteristics are possible combining quantity and intensity or quantity and time to obtain buffering or rate dynamics, respectively. The quantity/intensity curve became by far the most important combined characteristic of the equilibrium  $K_{ads} \longleftrightarrow K_{sol}$ . It depicts the relationship between the concentration of  $K_{sol}$  (intensity) and quantity of  $K_{ads}$ . Owing to the variation in binding strength of fractions of  $K_{ads}$ , the graph is not linear but more or less curved. The shape of the graph is soil-specific and depends basically on the types and amounts of exchange sites present, according to the mineralogical composition of clay and organic matter content. This is demonstrated by the graphs shown in Figure 6.

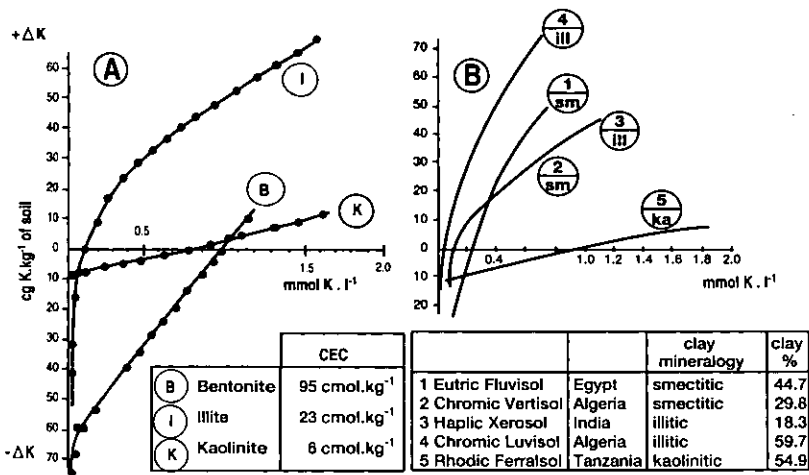


Fig. 6. Q/I graphs of clays (A) and soils (B) all saturated with K at 3% and with the K concentration as intensity characteristic, showing the effects of clay quality on the equilibrium between  $K_{ads}$  and  $K_{sol}$ .

The Q/I graphs supply the following information about the equilibrium  $K_{ads} \longleftrightarrow K_{sol}$  (see also Fig. 9):

- the equilibrium concentration corresponding to the actual  $V_K$  or content of  $K_{ads}$ ;
- the immediate buffering for any range of interest (of course, within the limits of measurements made);

- an amount of  $K_{ads}$  desorbable against an equilibrium solution free of K for a selected soil:solution ratio;
- a maximum amount of K adsorbed under the conditions of measurement chosen.

Originally, the concept Q/I isotherms was proposed by Beckett (1964) with the AR as intensity value. Depiction of the equilibrium system referring to the competition  $K^+ \leftrightarrow (Ca^{2+} + Mg^{2+})$  is thermodynamically founded and well suited to characterize the adsorption/desorption behaviour of soil. But, for reasons discussed in Section 4.3., the graph using the concentration of  $K_{sol}$  as intensity term is more meaningful and covers practical needs sufficiently. Additionally, fewer measurements are needed and it is less costly.

The Q/I graphs do not represent the only combined characteristic of the K system. Others are all time functions of K release by minerals or of K fixation. They have been discussed in Section 4.4. and are of less practical interest.

## 5. The measurement of K parameters

The following discussion deals only with the principles and advantages or disadvantages of selected methods used for measuring soil K parameters. It is not concerned with the measurement of K in the extracts obtained by these methods which are not relevant to the assessment of K status.

### 5.1. Parameters of labile K ( $K_{lab}$ )

#### 5.1.1. Adsorbed and exchangeable K ( $K_{ads}$ and $K_{ex}$ )

Any technique of extraction of  $K_{ads}$  reposes on the laws of ion exchange.  $K_{ads}$  is replaced by another cation added in excess and is subsequently leached in solution. Results depend on the conditions of extraction, particularly on the cation used for the substitution of  $K^+$ , how much of the  $K_{ads}$  contained in the soil is desorbed, leached and finally measured. Most techniques use  $NH_4^+$  as replacing cation, because it is the most efficient ion able to replace  $K^+$  even on sites with steric selectivity for  $K^+$ . Having exchange properties similar to those of  $K^+$ , the  $NH_4^+$  gives a clearer endpoint for short-term exchange than ions like  $Na^+$  or  $Ca^{2+}$ . This improves the reproducibility of measurement. But this is valid only for soils with three layer silicates. In soils in which kaolinite and sesquioxides are the dominant clay minerals, there are no such differences in exchange behaviour because of the absence of e- and i- positions (Horner, 1986).

Taking 1M  $\text{NH}_4^+$  acetate as standard extractant, the soil:solution ratio influences the completeness of the desorption of  $K_{\text{ads}}$ . With regard to the shaking technique, an extreme widening of the ratio for a more complete extraction of  $K_{\text{ads}}$  decreases accuracy in measurement (weighting the sample, measuring low concentrations) or increasing consumption of chemicals. If a more complete extraction is required, application of leaching techniques is recommended. However, leaching techniques need more time and also cause more consumption of chemicals with the corresponding output of waste water.

It has already been indicated (Section 4.2.2.2.) that the measurement of the pool of  $K_{\text{ads}}$  raises several technical problems resulting from the equilibrium  $K_i \longleftrightarrow K_{\text{ads}} \longleftrightarrow K_{\text{sol}}$ .

Firstly,  $K_{\text{sol}}$  is leached from the sample together with the  $K_{\text{ads}}$  desorbed. Hence the quantity of K extracted is always the amount of  $K_{\text{ads}}$  extracted plus  $K_{\text{sol}}$ . In principle, it is possible to determine the amount of  $K_{\text{sol}}$  for a conventional water content and to subtract it from the measured value  $K_{\text{ads}+\text{sol}}$ . But for the reason discussed in Section 4.2.2.1., this operation makes little sense. Moreover, under field conditions,  $K_{\text{sol}}$  is only a relative small fraction of the sum (<10%, frequently ~1%). Therefore, the measured sum is often taken for  $K_{\text{ads}}$  or  $K_{\text{ex}}$ . Although in most cases, it is not explicitly indicated that  $K_{\text{sol}}$  is included in the parameter, it should strictly be so.

Secondly, the gradual transition between  $K_{\text{ads}}$  and  $K_i$  makes it necessary to fix a conventional boundary between the two forms which is achieved by standardizing the measurement of  $K_{\text{ads}}$ . In most countries, the amount of  $K_{\text{ads}}$  extractable with 1 M  $\text{NH}_4$  acetate, pH 7, soil:solution = 1:20, 1 h shaking, is taken as  $K_{\text{ads}}$  and called "exchangeable K" ( $K_{\text{ex}}$ ). In the text, the term "exchangeable K" is exclusively used for the fraction of  $K_{\text{ads}}$  extracted by this technique.

However, this convention does not obviate all the problems. If the extraction of  $K_{\text{ads}}$  is realized by permanent or stepwise percolation of soil with the extractant, more  $K_{\text{ads}}$  is extracted. This is to be explained by the equilibrium character of the exchange process. Particularly in soils with high contents of partly opened illites (high capacity of e-positions) in the clay fraction, a considerable fraction of  $K_{\text{ads}}$  may be neglected using  $K_{\text{ex}}$  as reference parameter for  $K_{\text{ads}}$ .

It must always be kept in mind that any modification of the extraction regime applied for  $K_{\text{ads}}$  (pH of solution, kind and concentration of replacing cation, soil:solution ratio and others) changes the measured value.

### 5.1.2. EUF extractable labile K

Electro-ultrafiltration (EUF) uses the displacement of  $K^+$  in solution in an electric field for K extraction (electrodialysis). The soil sample in a permanently stirred aqueous suspension is put in an electric field between two electrodes. The cations accumulated near the cathode are separated from the suspended soil by a slow waterflow passing a filter. The migration of  $K^+$  to the cathode and its subsequent elimination from the system causes a lowering of the concentration of  $K_{sol}$  and a step-by-step desorption of  $K_{ads}$ . The intensity of ion migration to the electrodes increases with increasing field strength. The lowering of the extractive power with extraction time (decreasing K concentration) can be compensated by increasing the voltage. With temperatures in the range 18... 25°C and tensions up to 400 V, this technique extracts mainly the loosely bound part of  $K_{ads}$ , essentially adsorbed on planar sites of silicate clays (see Fig. 2).

This technique, known and occasionally used since the twenties, was sophisticated and intensively propagated in the seventies (Nemeth, 1979). Its application is supported by manufactured standardized equipment, though some laboratories use their own equipment. Nemeth (1970) proposed a standardized 35 min. duration procedure at 20°C with measurements of the extracted K in 5 min. intervals. During the extraction time, the voltage is systematically raised: 5 min. at 50 V, then 25 min. at 200 V and finally, the last 5 min. at 400 V. In this manner, 7 consecutive fractions of loosely bound  $K_{ads}$  are obtained. In a simplified version, only two fractions are measured after 10 and 35 minutes. Figure 7 shows a schematic drawing of the apparatus and an example of the extraction dynamics.

EUF is suitable for routine use and is used in several countries. High cost of the manufactured equipment and of filters needed is its main disadvantage. Advantages are low consumption of chemicals, fewer problems with waste water and the possibility for carrying out simultaneous measurements of other nutrients.

### 5.1.3. Isotopic exchange for measuring $K_{lab}$

When a solution of a K isotope ( $^{42}K$ ) is added to a soil suspension, an interdiffusion with native soil K takes place. Soil K is a mixture of the isotopes  $^{39}K$ ,  $^{40}K$  and  $^{41}K$  (8250:1:79). In short-term reactions, an equilibrium with  $K_{lab}$  of the soil is established. With longer reaction times  $K_{ier}$  is involved. The use of longer reaction times in experimental investigation is restricted by the short half-life periods of K isotopes ( $^{42}K = 12.3$  hours). The change of concentration of the added isotope and of proportions between the isotopes in the liquid phase of a soil suspension

allow estimation of the amount of soil K comprised in the equilibrium reactions. Primarily,  $K_{ads}$  is concerned,  $K_i$  takes a secondary place.

The estimation of  $K_{lab}$  by isotopic exchange has the advantage that no chemical compounds are added which modify the K status by shifts in the relationship between K forms and changes in their reactivity. But the technique requires sophisticated equipment and highly skilled laboratory staff; it is expensive and consequently, not suitable for routine testing.

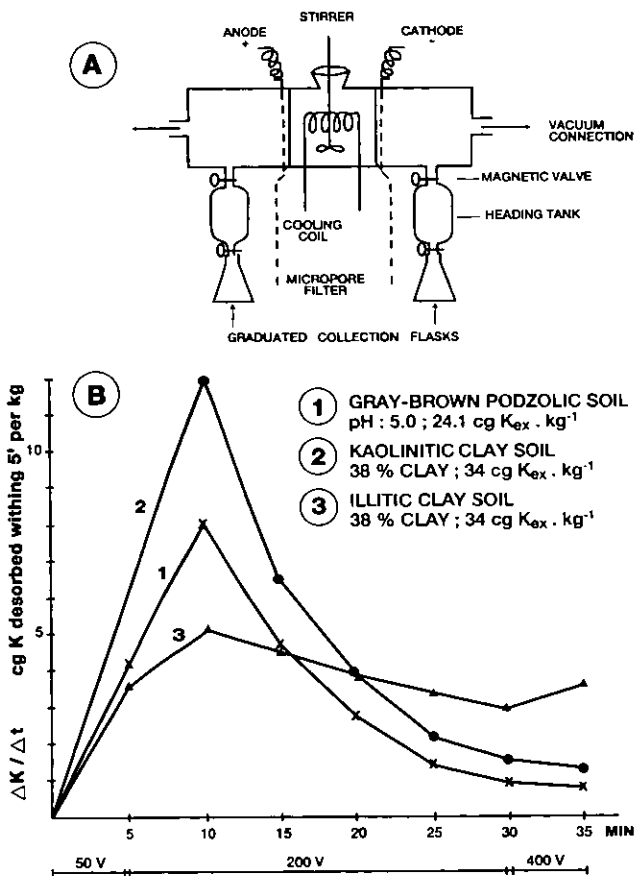


Fig. 7. The EUF technique:

- A) Schematic representation of the EUF apparatus,  
 B) Graph of K extraction dynamics of three soil samples,  
 obtained by Nemeth (according to Grimme and Nemeth, 1979).

#### 5.1.4. Empirical chemical extractions for "plant available" K

Numerous empirical techniques for the extraction and estimation of "available" K or simply K-related fertility have been proposed and used to some extent in routine soil testing. Haby *et al.* (1990) alone listed 14 tests used in the USA and Canada. Table 1 gives information concerning selected extraction techniques.

The various extractants differ in their extractive power according to the conditions of extraction chosen. In detail pH, concentration, kind of replacing cations, soil:solution ratio and reaction time are varied. The consequences as concerns the amount of K extracted, the K forms involved and the resulting informative value of data obtained have been discussed in Section 4.2.3. Virtually,  $K_{ads}$  is extracted, but to a variable extent and always together with  $K_{sol}$ . Some techniques extract variable amounts of  $K_{str}$ . Consequently, each of the extraction techniques requires its own evaluation algorithm for the parameters measured and a precise delimitation of the kind of soils for which the algorithm is valid.

#### 5.1.5. Degree of K saturation of the exchange complex ( $V_K\%$ )

The degree of K saturation is a derived parameter. It is calculated from the measured values of CEC and  $K_{ads}$  according to the formula

$$V_K \% = \frac{K_{ads} (\text{cmol} \cdot \text{kg}^{-1}) \cdot 100}{\text{CEC} (\text{cmol} \cdot \text{kg}^{-1})}$$

In soils with dominantly permanent charges, the measurements offer no difficulty. But the amounts of  $K_{ads}$  should be determined by the same technique (shaking or leaching;  $\text{NH}_4$  as replacing ion) as used for CEC in order to avoid over- or underestimation of  $V_K$ . In soils with variable charge, the  $\text{CEC}_{eff}$  should be used for the calculation of  $V_K$  in order to avoid misleading results. The  $\text{NH}_4$  acetate pH 7 technique applied to permanently charged soils is not suited to measure  $\text{CEC}_{eff}$  owing to its buffered pH level. For  $\text{CEC}_{eff}$ , the sum of cations extracted with unbuffered salt solutions is preferred.

#### 5.1.6. K concentration in the soil solution

The concentration of K in solution varies with changes in water content or of soil:water ratio respectively, the more so the lower the immediate and short-term buffering of  $K_{sol}$ . Any data of K concentration in soil solution needs complementary information about the water content to which it refers. The equilibrium concentration of K derived from Q/I graphs (see Section 5.1.7.) is an exception from this rule because the technique used for its indirect determination eliminates the influence of soil:water ratio on its value.

**Table 1.** Selected empirical techniques for the extraction of "plant available" ("labile" in the terminology of some authors) soil potassium.

	Extractant	Conditions set	Proposed or recommended by
1.	Water, dist.	pH 6...7	Van der Pauw, 1973
2.	0.05 M Ca lactate + 0.05 M Ca acetate + 0.03 M acetic acid	pH 4.1; 1:20; 2 hours	Schüller, 1969
3.	0.0125 M CaCl <sub>2</sub>	1:10; 1 hour	Schachtschabel and Heineman, 1974
4.	1 M NH <sub>4</sub> HCO <sub>3</sub> + 0.005 M DTPA	pH 7.6; 1:2; 15'	Soltanpour and Schwab, 1977
5.	0.02 M Ca lactate + 0.02 M HCl	pH 3.7; 1:50; 2 hours	Egner, 1932 and Riehm, 1943
6.	0.1 M NH <sub>4</sub> lactate + 0.4 M acetic acid	pH 3.0; 1:20; 2 hours	Egner, Riehm and Domingo, 1960
7.	0.025 dodecyclamine chlorinehydrate	24°C	Zabavskaya, 1977
8.	0.2 M NH <sub>4</sub> acetate + 0.015 M NH <sub>4</sub> F + 0.02 M NH <sub>4</sub> Cl + 0.012 M HCl	pH 2.90; 1:10; 5'	Mehlich (II), 1978
9.	0.013 M HNO <sub>3</sub> + 0.015 M NH <sub>4</sub> F + 0.2 M acetic acid + 0.25 M NH <sub>4</sub> NO <sub>3</sub> + 0.001 N EDTA	pH 2.0; 1:10 vol. basis; 5'	Mehlich (III), 1984
10.	2% NaHCO <sub>3</sub> + 0.7% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>		Neikova-Boceva, 1977
11.	0.05 M NaHCO <sub>3</sub>	pH 8.5; 1:20; 30'	Olsen <i>et al.</i> , 1954
12.	0.1 M HCl + 0.2 oxalic acid	1:20; 1 hour	Standard in The Netherlands



There are three main ranges of soil:water ratios to be distinguished with regard to concentration measurements:

- water content below field capacity,
- soil is saturated with water,
- soil:water ratio wider than in saturated soil.

The most convenient and most frequently used technique is the determination of the concentration of  $K_{sol}$  in the so-called saturation extract according to Richards (1954). This technique does not use a strictly constant soil:water ratio. Water is added to the soil sample under stirring until a soft paste is formed and a thin layer of free water appears on its surface. The water content of the paste is higher than that of the undisturbed soil at full saturation. After equilibration, the solution is separated and K measured. A disadvantage is that large samples (about 100 g or more) are needed. Nevertheless, it gives an acceptable basis for comparisons.

Soil:water ratios wider than that of the saturation extract are not suited to measurement. Considerable deviations from the real range of K concentration must be assumed and the increasing effects of buffering eliminate the possibility to compare concentration data obtained under such conditions.

The isolation of soil solution from soils with water contents at or below field capacity requires more equipment and/or labour than the saturation extract. However, the concentration values measured in this range of moisture content are generally more realistic for any consideration of K intensity. This is an important advantage. There are various techniques for getting soil solution (displacement, suction at low pressure, pushing out with high pressure, etc.), which cannot be described here. They allow isolation of solution from undisturbed or disturbed soil and each of them has its own advantages and disadvantages.

In the case of water draining from lysimeters, its K concentration does not give any information about the K system of soil, because the water flow through the soil does not allow equilibration and does not involve the whole soil mass (so-called "by-pass-flow"). It is impossible to estimate the difference between the equilibrium concentration in the soil solution and K concentration in the lysimeter water. Lysimeter data are only of interest in investigating leaching of K and calculation of balances.

#### 5.1.7. Q/I graphs and immediate buffering

For drawing a Q/I graph of labile K, several pairs of corresponding quantity and intensity values, measured in the equilibrium state, are required. Different procedures are available for obtaining these data pairs.

In principle, it is possible to construct Q/I graphs by adding different amounts of K to aliquots of a soil sample and measuring the concentration of K in the saturation extract and  $\text{NH}_4$  acetate extractable K after equilibration. This is how the graphs in Figure 8 were obtained. However, the K concentration in the saturation extract is only an approximate value and the Q/I relationship is difficult to measure in the range of low contents of  $K_{\text{ads}}$ .

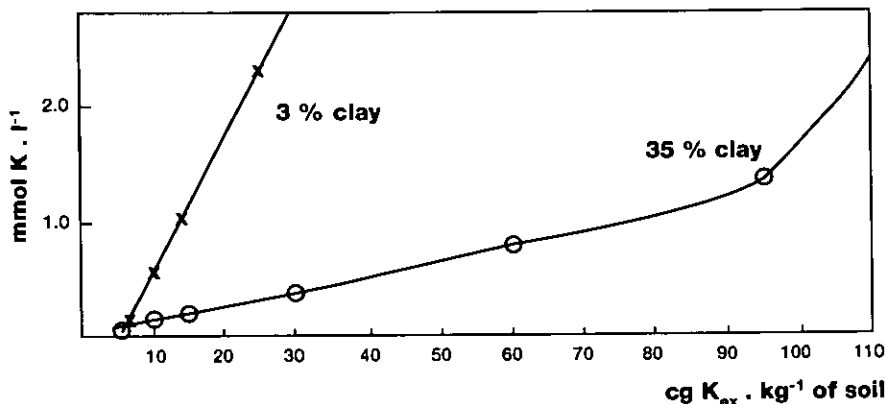


Fig. 8. Q/I graphs based on measurement of  $K_{\text{ex}}$  and K concentration in the saturation extract, here used to demonstrate the influence of clay content on the Q/I relationship (adapted from Grimme *et al.*, 1971).

For this reason, a procedure based on the following principles is preferred:

Aliquots of a soil sample are equilibrated with equal volumes of solutions with different K concentration (KCl dissolved). The range of K concentrations of the solutions used should be chosen in a manner that some of the final concentrations after equilibration are above, and some below the equilibrium concentration of  $K_{\text{sol}}$  for the given soil in the natural state. Equilibration of soil aliquot and added solution produces adsorption or desorption of  $\text{K}^+$  according to the relationship between K concentration of the added solution and equilibrium concentration of the soil tested. The final concentrations of K in the solution after equilibration are measured. The initial concentration is known. Both values are used to calculate the difference, that is the amount of K adsorbed or desorbed respectively. Each of the quantities calculated and referred to the weight of the soil aliquot together with their corresponding equilibrium concentrations constitutes a data pair of one point on the graph as presented in Figure 9.

Some problems of detail and the technical conventions resulting therefrom are inherent in the procedure:

1. Different soil:water ratios may be used; 50 ml solution for 5 g soil (sieved, 2 mm) have proved appropriate.
2. The soil solution contains various cations. In order to make the exchange conditions for equilibration more realistic, the K solutions are prepared with a matrix concentration of 0.02 M CaCl<sub>2</sub>.

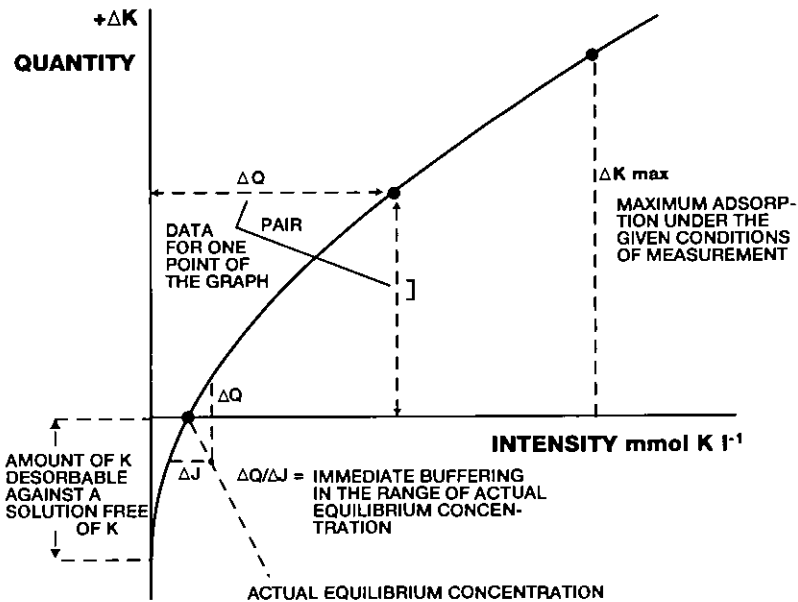


Fig. 9. Schematic representation of a Q/I graph with the K concentration as intensity and of the parameters which can be derived.

3. The range of K concentrations for equilibration and the number of solutions (= number of points of the graph) may be varied according to the K status of soils to be investigated and to the aim of the work. Considering the non-linear shape of the graph, at least 5 points should be measured. K concentrations in the range 0... 2 mmol l<sup>-1</sup> are used frequently.
4. The equilibration reactions proceed quickly. This is why Beckett (1964) spoke about the "immediate Q/I relation" of labile K. Generally, 1 hour is sufficient, some authors prefer less. The longer the equilibration time, the higher the probability for impacts of K<sub>i</sub> release or K fixation on the measured data.
5. The equilibration depends on temperature. For this reason, the samples should be equilibrated under constant temperature ("Q/I

isotherms"). Most workers use temperatures in the range 20 to 24°C with a maximum fluctuation of  $\pm 1^\circ\text{C}$ .

6. Frequently, the desorption range of the Q/I graph is of particular interest. Then additional points of this part of the graph can be obtained lowering the soil:solution ratio for solutions without K down to 1:50. Desorption of  $K_{\text{ads}}$  is reinforced in this way.
7. The shape of the graph is not affected by the point on the quantity scale taken as zero. For several reasons, it is preferred to refer to the actual content of  $K_{\text{ads}}$  as zero point:
  - a measurable zero point of  $K_{\text{ads}}$  content does not exist,
  - this type of the graph refers to the actual K status of the soil tested and is easier to read; it furnishes at the first glance the actual equilibrium concentration as important information,
  - this type of graph corresponds to the technique of determination.

Note that the technique outlined is not applicable to soils with a high fixation capacity and that the shape of the graph depends on the scales chosen for the coordinates. Often, a relation  $5 \text{ cg kg}^{-1}$  to  $0.1 \text{ mmol l}^{-1}$  is used.

If Q/I graphs according to Beckett, i.e. with AR as intensity parameter, are desired, additional measurements of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the equilibrated solution are necessary. The ion activities required for the calculation of AR are then calculated according to the equation of Debye and Hückel or taken from published nomograms (Pagel *et al.*, 1982).

The immediate buffering of  $K_{\text{lab}}$  is given by the slope of the Q/I graph. It is calculated as  $\Delta Q:\Delta I$  for a fixed range of the graph. Because the buffering is a function of  $K_{\text{ads}}$  content, it has to be decided for which range the immediate buffering capacity should be calculated. In most cases, the buffering in the range of the actual equilibrium concentration of the soil tested is of primary interest.

Due to the numerous measurements required, Q/I graphs are costly and the determination time consuming. However, the graph once obtained can be used for many years as a reference characteristic for the given soil. The determination of Q/I relationships is not a technique for routine purposes, but very useful for benchmark and other selected soils.

## 5.2. $K_i$ specific extractions of structural K

Besides parameters of  $K_{\text{lab}}$ , the measurement of parameters of  $K_{\text{ier}}$  are useful. There are several techniques which can be used to quantify this  $K_{\text{ier}}$ . With quantity data of this pool, estimates of the short- and medium-term buffering of  $K_{\text{lab}}$  by  $K_{\text{ier}}$  are possible. However, it should be taken into account that the quantity of  $K_{\text{ier}}$  is only one element of the short- and medium-

term buffering. The second is the reaction time, i.e. the rate of release, which can be neglected for the immediate buffering. In any case, regardless the technique of determination used,  $K_{lab}$  must be subtracted from the quantity of K extracted whenever a quantity parameter of  $K_{ier}$  is required.

### 5.2.1. Extractions with water or diluted salt solutions

The equilibrium  $K_i \longleftrightarrow K_{ads} \longleftrightarrow K_{sol}$  makes it possible to extract  $K_i$  with water or salt solutions. The only condition is lowering the concentration of  $K_{sol}$ . There are several techniques to extract  $K_i$  by these means:

- widening of soil:solution ratio in a static system,
- repeated extraction of the same sample,
- continuous percolation with solution.

Solutions of Na salts have been found efficient to replace  $K_i$ . Such techniques were used frequently in the past. But they take time and consume considerable quantities of chemicals. Thus, they are less suited to routine testing. However, they not only give a quantity parameter, but also the possibility to estimate rates of release and their dynamics, if K is measured in fractions of the solution passing through the sample or at intervals in the solution of static systems.

### 5.2.2. Extractions with sodium tetraphenylboron (NaTPB)

Since the extensive investigation of the release of  $K_i$  from minerals and soils in the sixties (e.g. Scott *et al.*, 1960; Reed and Scott, 1966), NaTPB has been used as extractant for easily releasable  $K_i$  by several authors. NaTPB precipitates  $K^+$  in aqueous solution as KTPB. After adding NaTPB to a soil suspension,  $K^+$  in solution is precipitated immediately. The concentration of  $K_{sol}$  is lowered and kept at levels below  $1 \mu\text{mol l}^{-1}$  (Mutscher and Tran Vu Tu, 1988). This extreme perturbation of the equilibrium  $K_i \longleftrightarrow K_{ads} \longleftrightarrow K_{sol}$  triggers desorption of  $K_{ads}$  and then release of  $K_i$ . The release of  $K_i$  is intensified if Na salts are added. The process of combined action of exchange and precipitation has been investigated by several scientists (e.g. Smith and Scott, 1966; Duthion and Grosman, 1971). The extractive power can also be reinforced by higher concentration of NaTPB (Mutscher and Tran Vu Tu, 1987).

The technique of extraction of  $K_i$  with NaTPB has been used for agronomic purposes (Duthion and Grosman, 1971; Cabibel, 1972; Quemener, 1974; Mutscher, 1980; Mutscher and Shaanyenenge, 1990). The advantage of this technique is that it causes reactions similar to those induced by K uptake of plants without significant changes in the pH of the system. Thus, it

can be assumed the  $K_i$  extracted by soil testing corresponds to the fraction which may be involved in K supply to crops. The quantity and the high price of the chemicals needed as well as the time consuming operations in the laboratory render the technique questionable for routine testing. It is hardly suitable to automatization. But all investigators who have compared soil test with crop response have also stressed the high informative value of data obtained by this technique. In comparison with biotests (see Section 5.5.), the NaTPB extraction is cheaper and quicker to realize whenever estimates of the K replenishment by  $K_i$  release are needed.

In most published studies, a 0.02 M NaTPB solution was used for extraction, sometimes without adding Na salt, sometimes with 1M NaCl (Quemener *et al.*, 1974; Mutscher, 1980). Prolonged extraction times increase the amount of  $K_i$  extracted, but 1 hour is enough for the purpose of a routine test. Information about the dynamics of the release rates is obtainable by extracting several aliquots of a soil sample under identical conditions varying only the extraction time. With progressing extraction and lengthening of the diffusion path for  $K_i$ , the rates of release decrease. Table 2 demonstrates the dynamics of rates measured with 0.05 N NaTPB + 1 N NaCl extraction and compares them with the uptake rates obtained in a pot experiment with ryegrass.

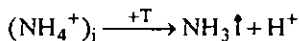
**Table 2.** Dynamics of rates of  $K_i$  release of an illitic dystric Cambisol measured with the 0.05 N NaTPB + 1 N NaCl extractant as compared with rates calculated from a pot experiment with ryegrass (according to Mutscher and Tran Vu Tu, 1988).

	Duration (days)	Mean rates (cg kg <sup>-1</sup> d <sup>-1</sup> )
Extraction with NaTPB/NaCl		
1st hour	0.04	922.00
1st to 10th hour	0.36	120.00
10th to 100th hour	3.75	14.64
100th to 630th hour	22.08	3.12
630th to 1000th hour	15.42	1.44
1000th to 6300th hour	222.83	0.22
Depletion experiment in pots with ryegrass		
Up to the 2nd cut	54	0.20
between 2nd and 4th cut	67	0.08
between 4th and 7th cut	122	0.03

For the dissolution of the KTPB precipitate and the subsequent measurement of K, several techniques have been proposed (e.g. Reed and Scott, 1961; Schulte and Corey, 1963). The technique with acetone proposed by Schulte and Corey is complicated and time consuming. It is easier to dissolve the KTPB by boiling after addition of HgCl<sub>2</sub>. Dry digestion by heating is also possible. Jackson (1985) proposed measuring the K of KTPB in an acetone medium directly by atomic absorption spectro-photometry.

### 5.2.3. Thermic treatment for K<sub>i</sub> extraction

Kolterman and Truog (1953) proposed a thermic treatment for the extraction of K<sub>i</sub>. The principle of the technique is the partial destruction of layer silicates by a thermic dissociation of interlayer NH<sub>4</sub><sup>+</sup>. Pre-treatment of the soil sample with 1 M NH<sub>4</sub> acetate solution causes the penetration of NH<sub>4</sub><sup>+</sup> into the marginal interlayer space by the same equilibrium reaction as described for K. The sample is then exposed to temperatures of 550°C in order to decompose the NH<sub>4</sub><sup>+</sup> according to:



The gas produced widens the interlayer and may even dislodge neighboured elementary sheets of the layer silicate. Subsequent leaching of the sample extracts the K<sub>i</sub> liberated by the foregoing step. A single thermic treatment extracts principally K<sub>ier</sub> from clay and silt sized layer silicates. Several consecutive treatments of the same sample extract more K<sub>i</sub>, but with decreasing amounts per treatment (see Fig. 10). The authors of the technique believed that it should be possible to calculate the total K<sub>i</sub> content of a soil by extrapolation the data of a tenfold extraction. Results obtained by this means have been very uncertain and the method could not be established in soil testing. A single thermic extraction was proposed as complementary to routine soil testing by Richter (1976).

### 5.2.4. Extraction of K<sub>i</sub> with exchange resins

Exchange resins have been repeatedly used for K extraction (Talibudeen *et al.*, 1978; Singh *et al.*, 1983; Van Raij *et al.*, 1986). But in the last years, resin tests were mostly studied or applied for multiple nutrient testing (Van Raij *et al.*, 1986; Yang *et al.*, 1991) with mixed resins. Usually, the resin is added to the soil in its H<sup>+</sup> form. Here it acts as a sink for K, first lowering the concentration of K<sub>sol</sub> and then, inducing the desorption or the release of K<sub>ads</sub> and K<sub>i</sub> respectively in a second step. A precondition for a high extractive power is that the capacity of the sink is high in comparison to the CEC of the soil. The capacity of the resin must not become a limiting factor

for trapping  $K^+$  and lowering K concentration. There is a problem in using the resin technique for calcareous or saline soils with their high contents of cations competing with  $K^+$  for the resin sites.

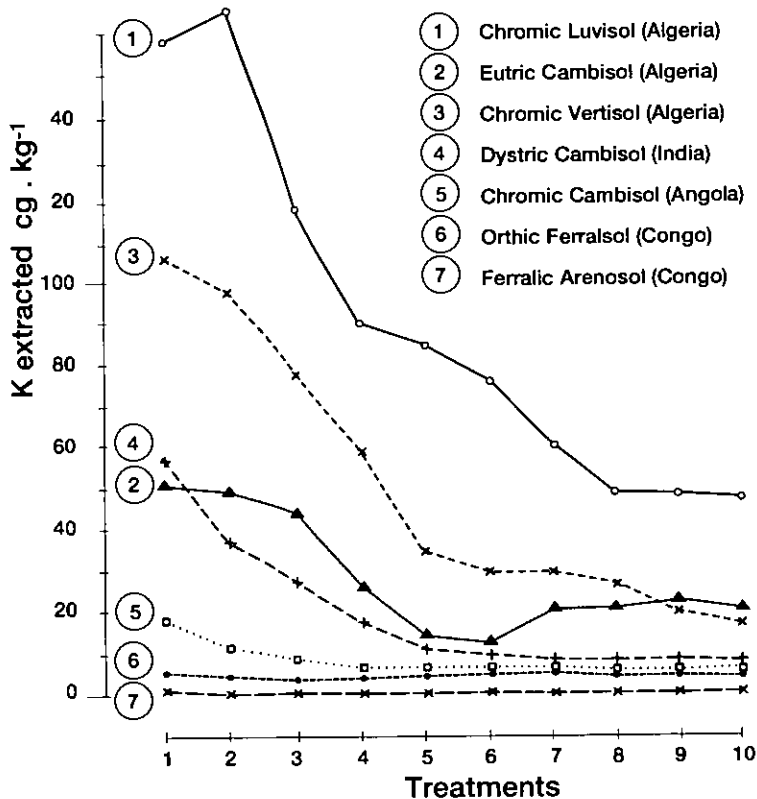


Fig. 10.  $K_i$  extracted by ten consecutive thermic treatments according to the technique proposed by Kolterman and Truog from different soils.

The effect of a  $H^+$  saturated resin is, in principal, similar to that of an active root. The addition of large quantities of  $H^+$  resin causes acidification and, on top of the sink effect, exchange reactions and hydrolic destruction of silicate structures increase the quantity of K extracted. This explains observations that  $H^+$  resin sometimes extracts similar amounts of K as  $HNO_3$ . This silicate destruction eliminates the selectivity of the technique for  $K_i$ .

Before the K extracted can be measured, the resin sink with the  $K^+$  stored must be separated from the soil; the  $K^+$  is then replaced, leached and measured. The separation of the resin from soil by sieving is somewhat difficult, especially if - as does happen - during shaking the resin surfaces



are eroded by friction with soil particles. Any incomplete separation falsifies the data obtained. This is why addition of the resin in bags may be preferred (Yang *et al.*, 1991). Recently, Thien and Myers (1991) proposed a flotation technique to overcome these problems. As with NaTPB also with resin, the determination of time functions of K release is possible (Singh *et al.*, 1983). Parallel samples of one soil are left to react with the resin over different periods.

### 5.3. Non-specific extractions of structural K

Some techniques of K extraction allow the measurement of  $K_t$  or of fractions of it without any possibility to relate the amount extracted to defined K forms, especially those of  $K_{str}$ . A stock of  $K_{str}$  can be calculated, which allows at least the comparison of different soils. The significance of the K reserve for the actual K supply to crops remains obscure however. The only statistically founded general rule which applies is: the higher the amount of reserve K the higher the K supplying power of soil. In detail, the K supplying capacity of single soils may deviate considerably from regression equations.

#### 5.3.1. Total K content ( $K_t$ )

The determination of  $K_t$  requires the total destruction of K bearing silicates. Several techniques are used to bring this about:

- decomposition in an alkali melt,
- dissolution in HF with or without increased atmospheric pressure,
- tri-acid digestion ( $HNO_3 + H_2SO_4 + HCl$ ).

The last does not always guarantee complete decomposition, but it has the advantage that it can be carried out with normal laboratory equipment. The first and the second techniques need special material. In any case, the measurement of  $K_t$  is expensive and not suited to routine testing. However,  $K_t$  is an objective soil feature with no boundary problem and for this reason, a reliable basis for the analysis of the K status of soil.

#### 5.3.2. Extractions with strong acids

Much easier than the measurement of  $K_t$  is the measurement of K extractable with strong acids. Table 3 lists a selection of proposed methods. As it shows, various acids have been used and conditions like concentration, soil:acid ratio, reaction temperature, etc., have been widely varied. Single extractions were used as well as multiple treatments. Various strong acid extracts were compared. Regardless of differing extractive power correlations between different methods for extracting K have been close

Table 3. Some techniques proposed for the extraction of labile and reserve K with strong acids.

Acid used	Concentration	Conditions	Proposed or recommended by
1. HCl	0.1 M	cold	Brupbacher <i>et al.</i> , 1965
2. HCl	1.0 M	50°C	Schachtschabel, 1961
3. HCl	2.0 M	cold	Neikova-Bočeva, 1977
4. HCl	0.01 M		Garman, 1957
5. H <sub>2</sub> SO <sub>4</sub>	1.38 M		Hunter and Pratt, 1957
6. H <sub>2</sub> SO <sub>4</sub>	6.0 N		Hunter and Pratt
7. H <sub>2</sub> SO <sub>4</sub>	10.28 N		Hunter and Pratt, 1957
8. HNO <sub>3</sub>	1.0 M		Wood and De Turk, 1941 Reitemeier, 1951
9. HNO <sub>3</sub>	1.0 M	boiling; 1:10; 25'	Pratt and Morse, 1954
10. HNO <sub>3</sub>	1.0 M	boiling; 1:100; 15'; repeated extractions	Haylock, 1956
11. HNO <sub>3</sub>	0.5 M		Tamhane and Subbia, 1960
12. HCl + H <sub>2</sub> SO <sub>4</sub>	0.05 M + 0.025 M	1:5; 5'	Mehlich (I), 1953
13. HF + H <sub>2</sub> SO <sub>4</sub>			Scheffer and Schachtschabel, 1970
14. HCl + HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>			Harrison (Bonfils, 1967)

(Mutscher, 1980; Yadev and Swami, 1984), signifying that acids differentiate between soils in an essentially similar manner.

Strong acids dissolve K bearing silicates to variable degrees according to their structure, development of weathering coatings impeding acid attack and conditions set by the technique of extraction. The extraction residue contains K silicates highly resistant to chemical weathering, which also under natural conditions are decomposed only after a long time ( $10^2 \dots >10^4$  years). This fraction is agronomically of no practical interest.

The most widely used technique is extraction of K with boiling nitric acid. But, as with all other strong acid techniques, measured data give only a general indication of the stock of K in soil. It is impossible to allocate the K extracted to feldspar or mica or to grain size fractions, hence to make reliable estimates of K replenishment. To overcome this disadvantage, Haylock (1956) and Haylock and Metson (1956) proposed a method to distinguish two categories of reserve potassium using consecutive 15 min extractions with boiling 1 M  $\text{HNO}_3$  after removal of  $\text{K}_{\text{ex}}$ : "constant rate K" which corresponds to the quantity of K extracted when the figures become constant and "step K" which is beyond the constant rate K in the first extractions (see Figure 11).

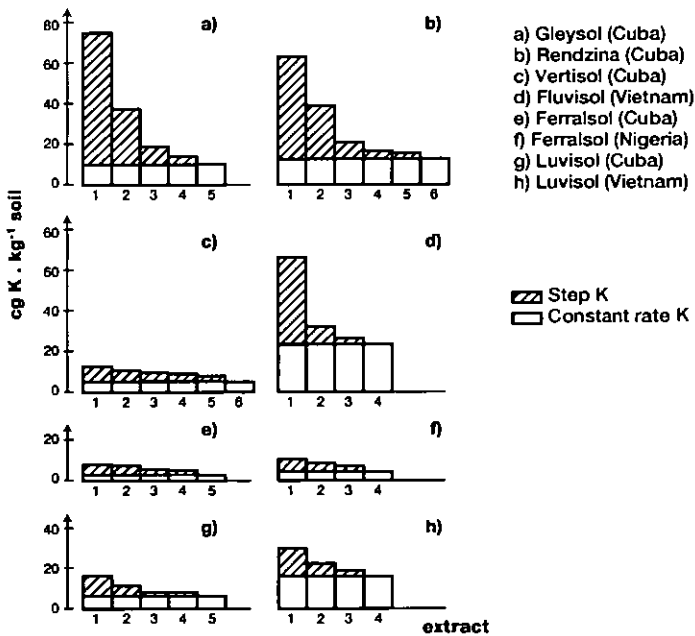


Fig. 11. Step and constant rate K extracted by consecutive treatments with boiling  $\text{HNO}_3$  according to Haylock (1956) from various soils.

The authors tried to interpret the two fractions mineralogically and to relate them to K supply to crop. However, this procedure does not eliminate the principal weak points of acid extractions. Single acid extractions are widely used and are popular for their ease of execution and sometimes applied as routine tests.

### 5.3.3. Electro-ultrafiltration (EUF)

The EUF technique (Section 5.1.2.) to extract  $K_{lab}$  can also be used for the extraction of  $K_{str}$  if the temperature is increased. It was proposed after the procedure at 20°C to continue the process for a further 10 or 15 minutes at 80°C and with 400 V tension (Nemeth, 1979). Several workers by so doing obtained large amounts of K of the same order as quantities extracted with boiling  $HNO_3$  (Buondonno and Fellaca, 1988). Such results indicate that, not only the diffusive release of  $K_i$  is involved, but that the treatment also liberates  $K_{str}$  by breakdown of silicate structures. The implication of  $K_{str}$  of tectosilicates has not yet proven experimentally; in any case, such EUF fractions of K do not participate in short- or medium-term buffering of  $K_{lab}$ .

## 5.4. K fixation capacity

In order to estimate the K fixation capacity of soil, the K fixation must be produced under laboratory conditions. This is done by adding to the soil sample K salts in amounts high enough to induce fixation. The addition of K in the form of an aqueous solution is to be preferred to solid salt because in this way, the reaction conditions are easier to standardize. The amount of K fixed depends much on the conditions set: changing K concentration of the salt solution added, soil:solution ratio, reaction time or other factors results in different measured values. Consequently, only parameters obtained by the same technique are comparable. Unfortunately, there is no generally accepted and applied technique to determine the fixation capacity. Most frequently, the techniques proposed by Van Der Marel (1954) and Schlichting and Blume (1966) were used. A convenient K load to test fixation is the application of 1 g K per kilogram of soil added as 0.005 M KCl solution.

The fixation capacity measured after fixation of K in a moist soil or in an aqueous suspension of the sample has been designated "wet fixation". Under these conditions, layer silicates remain in the swollen state and ions fully hydrated. Measurement of so-called "dry fixation" involves severe drying of the sample. This causes a shrinking of clay and dehydration of ions and favours the contraction of clay sheets. As a result, the measured fixation capacity is higher for dry than for wet fixation if other conditions are

identical. The drying of the sample for measurement of dry fixation is best carried out at 105°C, because this temperature guarantees a good comparability. Sometimes, samples are dried at a lower temperature.

Adding salts to a soil causes fixation only at a given potential. According to the equilibrium  $K_i \longleftrightarrow K_{\text{ads}} \longleftrightarrow K_{\text{sol}}$ , the addition of  $K^+$  produces shifts in the quantity of  $K_{\text{ads}}$  and  $K_{\text{sol}}$  which must be taken into account when the amount of K fixed is calculated. For this reason, the method used to measure fixation capacity should use two parallel samples of the same soil:

Samples A and B are treated in the same manner except that sample A receives the same volume of water as that of the KCl solution added to B. Following shaking, the same volumes of the exchange solution are added to the suspensions to replace and measure  $K_{\text{ads}}$ . Fixation capacity is then given by:

$$\text{Fixation capacity (cg kg}^{-1}\text{)} = (K \text{ added} + K_{\text{lab A}}) - K_{\text{lab B}}$$

For the exchange and determination of the  $K_{\text{lab}}$  after fixation mostly a  $M$   $\text{NH}_4$  acetate solution is used. However, it is to be noted that  $\text{NH}_4^+$  can be fixed in the same way as  $K^+$  owing to its similar properties relevant to fixation. Due to the equilibrium character of the system,  $\text{NH}_4^+$  can, during the reaction time, replace a part of the K fixed before and gives misleading values for the fixation capacity. To avoid this, Van der Marel (1954) proposed substituting Mg acetate for  $\text{NH}_4$  acetate. The techniques described measure the short-term fixation caused by contracting silicate layers. Special arrangements are required for determination of long-term fixation.

## 5.5. Biotests for soil K measurement

Any of the soil tests described in Sections 5.1. to 5.4. affects the K system to a certain extent by changing the environment, some tests strongly, others to a lesser degree. This is obvious for all techniques using salt solutions or diluted acids, where mainly the concentration of solutes, the conditions for ion competition and pH are modified. But this is also true for water extracts, because the soil:water ratios used do not mimic field soil conditions. As a result, the measured data reflect a modified state of the K system.

Biotests avoid this disadvantage with regard to the assessment of the K status and measure the K supply to crops under more realistic conditions, relating the measurements to the soil/plant system. However, there are also disadvantages:

1. Biotests with living plants require more time and labour than pure laboratory soil tests using chemical reactions and physico-chemical behaviour for measurements. Results from biotests are disposable later as those from soil tests. Pot experiments need much larger samples.

2. Biotests using living plants for K extraction are linked with manifold standardization problems different from those with soil testing. This is due to the variability of test plants and the influence of atmospheric growth conditions. The role of the geometry and physiology of the root system is important. The choice of the test plant and physical properties of soil affecting root growth and K mobility exert an influence on K extraction by the plant. The variability in crop response caused by factors other than nutrient supply means that tests have to be replicated thus increasing the volume of trial, the time spent and costs.
3. Biotests work at natural water contents of soil. This is an advantage. But K transfer to roots depends also on rooting characteristics. Thus, the K extraction in biotests is affected by factors which do not play any important role in chemical or physico-chemical soil testing.
4. Biotests cannot, in practice, be used for large numbers of different soils. They must be restricted to important reference soils and research purposes.

Biotests with living plants are made with various plants and using different quantities of soil. In fact, field trials are also biotests, but biotests, as considered here, include all experimental arrangements with living plants, allowing a higher degree of standardization and a stronger control of growth conditions than possible under field conditions and using less than about 10 kg of soil per pot. Two kinds of such tests may be distinguished:

- pot experiments with several kilograms of soil per pot and,
- microtests with 50... 500 g soil per test.

Biotests extract K by uptake of K by plant roots and the plant operates as a sink for K. To get meaningful results with regard to the K supplying capacity, the supply of nutrients other than K must be optimized. One essential advantage of biotests is that the K demand can be varied by modifying factors of the test conditions like:

- duration of the test,
- shape and volume of the pots,
- number of plants per pot,
- kind of the test plant,
- fertilizer dressings and water supply,
- dilution of soil with purified quartz sand or other inert materials.

The information obtainable from biotests largely depends on the measurements made, the latter with regard to both components of the soil/plant system. The determination of the amount of K extracted by plants requires the measurement of dry matter produced and of the K content in dry matter. The quantity of K extracted allows the comparison of soils tested

with regard to their K supplying capacity. Whether the K supply was a growth limiting factor can only be decided when data from a treatment with optimum K supply are available. Some indication can be derived from the visual evaluation of the appearance of above-soil plant parts during growth.

Measured plant data permit only general estimates of the K supplying capacity of soils. Any more detailed assessment needs additional measurements of soil parameters. It is useful to measure K characteristics of the soil before and after the biotest. The changes in soil parameters can serve to make calculations and conclusions as concerns:

- tightly bound residual adsorbed K,
- involvement of  $K_{\text{ier}}$  in K supply,
- buffering behaviour and buffering capacity of soil.

The most commonly used test plants are corn, barley and various grasses. Maize has a high extractive power for K, but is not suitable for microtests which are mostly made with cereals or grasses. Perennial grasses (e.g. *Lolium perenne* L.) are favoured for exhaustion experiments owing to their high rooting intensity and because several cuts can be taken for observing dynamics of K supply and soil exhaustion.

Microtests are easier to standardize than pot experiments and preferable for larger numbers of soils. Various techniques have been proposed: Neubauer (1923, 1936), Stanford de Menth (1959) and Chaminade (1964). They differ in detail. The test of Stanford de Menth is interesting in that it attempts to eliminate the effects of soil quality on germination and growth of the test plant for test series with different soils. The test plants are precultivated for a few days on quartz sand with a nutrient solution free of K and then, transferred with the rooted sand to the soil to be tested.

## 5.6. Multiple nutrient extractions

Extraction techniques which permit the determination of two or more nutrients in the one extract are particularly suited for routine soil analysis. By this means, considerable savings of time, chemicals and lastly money are possible. Obviously, the less specific empirical extractants are more suitable to multiple nutrient measurement. Examples are the calcium lactate extractant proposed by Egner and Riehm (Riehm, 1943) enabling the extraction and measurement of K and P, the EUF technique and also techniques with mixed resins. Extractants like NaTPB do not allow the extraction and measurement of other nutrients due to their high specificity. It is self-evident that for each of the nutrients measured in multiple extracts, an individual evaluation algorithm must be elaborated for each nutrient.

## 6. Interpretation and evaluation of parameters of soil K status

### 6.1. Aims, requirements and possibilities

The measurement of K parameters provides quantified data with an inherent information about the K status of the soil. The numeric data *per se* do not reveal this information. The latter has to be decoded. Two preconditions are set for getting the information:

1. We should know what we have measured in terms of the K system of soil.
2. We must have a reference system which allows comparison and classification of the parameter measured with regard to the aims of interpretation.

As explained in Chapters 4 and 5, empirical extraction methods do not precisely measure categories of K as defined in the K system, the boundaries between the categories are blurred but, it is still helpful to attempt classification and comparison of the available data to assist interpretation. This can be done by investigating how a parameter compares with values obtained for other related soils. There are at least two possibilities to refer measured parameters to other data in order to evaluate them and to transform them into an assessable information:

1. Comparison of the measured value with other values of the same K characteristic obtained by testing other soils.
2. Comparison of the measured value with K uptake and yield of crops or with the efficiency of fertilizer.

The evaluation of K parameters by comparison with the corresponding parameters of other soils needs a number of data allowing to construct a reliable histogram. This histogram is valid only for the group of soils from which it was derived and the soil to be evaluated should be a member of this reference group. In most cases, the range of possible figures of the parameter is divided into classes for qualification of the measured parameter. For some characteristics or parameters of the K system only rating algorithms of this kind are disposable, e.g. for the fixation capacity or the quantity parameters of  $K_{ier}$ . This manner of data evaluation is helpful, but insufficient for reliable management decisions.

A management oriented evaluation of parameters demands that we need to know how a parameter affects crop K uptake and/or response to K fertilizer. Evaluation algorithms must be derived from K supply to a crop in a soil/plant system in operation for which purpose pot and/or field experiments are essential. Two approaches are possible:



1. Growing test crops under defined conditions on different soils, or on one soil showing a range of values for a K parameter, and relating the latter to crop K uptake or yield. From the data obtained in this way, only relative estimates of the K parameter are possible referring to the yield expectation of the test crop or to the maximum value of K uptake or yield measured in the experiment.
2. Cultivation of a test crop on one soil under defined conditions and with increasing K fertilizer dressings. Comparing soil test value with response curve allows to establish the value of the soil parameter corresponding with optimum crop performance and/or fertilizer efficiency. Soil test rating related to these criteria becomes possible.

## **6.2. Quantity, intensity and rate in the assessment of K status**

The interest in assessing the K status of a soil results from its K supply function to plants. This function can be assessed by biological soil tests. In effect, this is to treat the soil as a "black box", leaving out of consideration the soil processes which control the delivery of K to the plant. Most of the empirical tests for the quantity of "available K" or for general fertility assessment are the outcome of this approach. Agronomically satisfying results have been realized in this way. However, only quantity information is obtainable and all data suffer from the following defects:

- no perfect relation of soil test value and K uptake by plant can be reached;
- with regard to a single soil the reliability of interpretation based on statistical relationships becomes the less the greater the variation of the properties of soils used to derive statistics;
- the possibility to transfer the evaluation algorithms to soils with properties differing from those the statistics have been taken from is restricted;
- soils occur for which the given extraction technique fails to give correct and interpretable information.

Besides search for better empirical test methods, the reaction to these limitations of empirical quantity measurement was the development of the quantity-intensity-rate concept. Many researchers have contributed to this concept, which is founded upon all findings referring to the nutrient system of soils and its dynamic response to K demand of crops as outlined in Chapter 3. The idea is that the K supplying capacity of soil is not only controlled by quantity characteristics, but also by intensity and rates of K transformation. The nutrient demand is realized at the soil/root interface and

nutrient mobility is involved in covering this demand, which is defined by:

- a total amount of K needed for the yield to be reached and,
- a time function of uptake rates, because the daily uptake of K changes according to growth stages.

It is evident that for the assessment of the K status considering of intensity and rate in addition to quantity should provide more reliable information about the K supplying capacity and its dynamics. All intensity and rate data need an evaluation as the traditional quantity parameters do, but it must be stated that our possibilities to evaluate single intensity, rate or buffering parameters are still less developed than those for quantity data. Nevertheless, the quantity-intensity-rate concept is very helpful in improving interpretation of measured parameters and soil test/crop response findings.

### 6.3. Interpretation and evaluation of individual K parameters

#### 6.3.1. Labile potassium ( $K_{lab}$ )

##### 6.3.1.1. Adsorbed and exchangeable potassium ( $K_{ads} + K_{ex}$ )

$K_{ads}$  is the main pool of soil K which is rapidly deliverable to the plant; its measurement has therefore always been, and still is, most important. Measurement of  $K_{ex}$  is a standard method to assess labile K content used in many countries.  $K_{ex}$  in soil is a conventional quantity parameter. For this reason, it has to be related to the quantity of K withdrawn by a crop. As with other quantity parameters, a rough estimate can be made comparing the amount of K contained in the rooted soil volume with the estimated K demand. For instance, in a soil with an apparent density of  $1.5 \text{ kg dm}^3$  a content of  $1 \text{ cg kg}^{-1}$  corresponds to  $15 \text{ kg ha}^{-1}$   $K_{ex}$  in a 10 cm layer. Taking into account the rooting depth, a comparison of the stock of  $K_{ex}$  with the K demand of the crop is possible.

However, the stock of  $K_{ex}$  will never be completely exhausted by one season's cropping and even after exhaustive cropping by densely rooting crops, residual  $K_{ex}$  may amount to 3 to 20  $\text{cg kg}^{-1}$  (Mutscher, 1983). There are two possible reasons for this:

- the residual  $K_{ex}$  is the level maintained by buffering through release of  $K_i$ ,
- the rooted soil volume is unevenly exhausted because K mobility (diffusion and mass flow) is too low to compensate the local lowering of  $K_{ex}$  near active roots.

The level of residual  $K_{ex}$  differs greatly between soils depending on variations in content and mineralogical composition of the clay fraction, particularly in the content and nature of its micaceous constituents. In a soil sample of a few grams, the determined value of  $K_{ex}$  is an average masking variation between microvolumes of soil. This applies even in samples from densely rooted pots in exhaustion experiments, the effect should be still more important in less densely rooted field soils. Hence, in order to make allowance for this variation, the quantity of  $K_{ex}$  required to cover completely crop demand must be a multiple (3 to 10 times) of the measured mean value. The multiple is the higher the lower K mobility and the higher the yield level. The outlined effects are reflected by rating scales for  $K_{ex}$  derived from experiments. Table 4 shows examples of a rough classification of  $K_{ex}$  content into three classes.

**Table 4.** Class boundaries for rating of the  $NH_4$  acetate extractable exchangeable potassium ( $K_{ex}$ ).

High values	$K_{ex}$ cmol kg <sup>-1</sup>		Comments	Source
	Medium values	Low values		
0.8 ... 0.4	0.4 ... 0.2	0.2 ... 0.03	Based on Malawi soils	Young and Brown, 1962
>0.5	0.5 ... 0.25	<0.25	From a general appraisal of USA soils	Thomas, pers. data unpubl., 1966
>0.8	0.8 ... 0.5	0.5 ... 0.3	New Zealand	Metson, 1961
>0.6	0.6 ... 0.15	<0.15	UK soils	Maff, 1967

Source: Landon (1984).

In Chapter 2, it was outlined that  $K_{ads}$  does not represent a homogeneous K form, but a pool of K adsorbed with variable binding forces. This is visualized by the curved part of Q/I graphs. The effects of binding strength of  $K_{ads}$  upon K uptake are mediated by K intensity and K mobility: the higher the binding strength the lower the intensity and mobility and, hence, K supply to roots. This is most important at low concentrations of  $K_{sol}$  when intensity may be the rate limiting factor for K supply. Low concentration of  $K_{sol}$  is common if intensity is controlled by e-positions on micaceous clay or by low or very low values for  $V_K$ . Intensity is scarcely rate limiting at values beyond 0.5 mmol.l<sup>-1</sup> K equilibrium concentration corresponding with the straight or weakly curved portion of the Q/I curve. This range of intensity is controlled by p-positions of clay. They become rate limiting only at very low levels of K saturation.

The need to comprise differentiated binding forces in the evaluation of  $K_{ads}$  depends on clay content, clay composition, level of  $K_{ads}$  content, technique of measurement used and intensity level of cropping for which the assessment of K is made. Since the amount of tightly bound  $K^+$  increases with clay content, it seems generally recommendable to introduce classes of clay content in the rating system for K. Table 5 shows an example taken from Zimbabwe.

**Table 5.** Assessment of  $NH_4$  acetate extractable potassium ( $K_{ex}$ ) referring to soil texture classes for Central African soils.

Rating	Exchangeable K cmol kg <sup>-1</sup>		
	Sands	Sandy loams	Typical red-brown clays
Deficient; response to K likely	<0.05	<0.1	<0.15
Marginal; some response likely	0.05 ... 0.1	0.1 ... 0.2	0.15 ... 0.3
Adequate; response unlikely, but maintenance usually desirable	0.01 ... 0.25	0.2 ... 0.3	0.3 ... 0.5
Rich; no K required	>0.25	>0.3	>0.5

Source: Ministry of Agriculture, Zimbabwe (according to Landon, 1984).

There are still more sophisticated algorithms in use. This can be demonstrated by the system applied for the labile K extracted with the technique proposed by Egner and Riehm (see Table 8 in Section 6.3.1.3.). However, the necessity to take clay content into consideration varies according to the circumstances:

1. The occurrence of high binding forces and strong differentiation of binding strength is restricted to soils with illitic clays. Therefore, for illitic soils the introduction of texture classes in the rating system for labile K is imperative. It is different for soils with kaolinitic-oxidic clays because the binding of  $K_{ads}$  is weak and the immediate buffering low (see Fig. 6, Q/I graph for kaolinite). Nevertheless, Boyer (1982) proposed a rating of  $K_{ex}$  in textural classes similar to that in Table 5 for ferralitic soils (see Table 6). It is questionable whether in this case the texture classes are necessary or helpful. If so, then the reason for is seemingly rather the influence of clay content on rooting conditions and soil moisture dynamics than on binding of  $K^+$ .

**Table 6.** Evaluation of exchangeable K in ferralitic soils (according to Boyer, 1982).

Rating	Exchangeable K cmol kg <sup>-1</sup>		
	Sandy soils	Medium soils	Heavy soils
	clay+silt <15%	clay+silt 15...45%	clay+silt >45%
Strong to very strong deficiency	<0.05 ... 0.07	<0.10	<0.20
Weak to medium deficiency	0.07 ... 0.14	0.10 ... 0.20	0.20 ... 0.40
Weak or no deficiency	>0.14	>0.20	>0.40

2. The various techniques disposable extract  $K_{ads}$  more or less completely. The more completely  $K_{ads}$  is extracted the more binding sites with high binding forces are involved, if there are such in the soil tested. Consequently, more complete extraction of  $K_{ads}$  increases the necessity to consider the possible differentiation in binding strength in the rating system.
3. The higher the cropping intensity and K demand the more the soil is depleted from  $K_{ads}$  during the vegetation period. Hence, the probability that K adsorbed on e-positions is involved in the seasonal K supply increases with K demand of the crop and this must be considered in rating.
4. In the same time, the high uptake rates to be covered in the phase of the most intensive growth make the crop particularly sensitive to low intensity values as induced by lowering the  $K_{ads}$  content up to the range of intensity values controlled by e-positions. This regardless the absolute amount of  $K_{ads}$  contained in the soil. For this reason, evaluation algorithms considering clay content and clay quality are more important in intensive agriculture and for crops with high K demand (sugar beet, sugar cane, banana, cassava, pineapple and others) than in case of medium or low yield levels.
5. Many old cultivated soils regularly receiving fertilizer dressings differ from freshly reclaimed and cropped soils in that they enable good rooting and frequently are enriched with K. In this case, crops use soil K more efficiently. The accumulation of K stemming from fertilizer raised the K saturation in the range of planar sites with the corresponding high intensity. So far, the stock of K bound at planar sites suffices to cover the K uptake between two fertilizer dressings there is no urgent necessity to consider binding forces as differentiating factor in  $K_{ads}$  evaluation.

### 6.3.1.2. EUF extractable labile potassium

The standard 35 min extraction in 5 min intervals (see Section 5.1.2.) extracts only a fraction of  $K_{ads}$  and provides virtually a quantity parameter, but it allows further assessment:

1. It is assumed that  $K_{lab}$  extracted in 35 min comprises loosely bound  $K_{ads}$  mainly on planar sites of silicate clays (Wanasuria *et al.*, 1981) and thus, the influence of selective binding sites is largely eliminated.
2. There is a close correlation between 10 min EUF-K (x) and K concentration in the saturation extract (y) (Grimme and Nemeth, 1979).

$$y \text{ (mmol.l}^{-1}\text{)} = 0.01 x \text{ (cg.kg}^{-1}\text{)} - 0.06; \quad r = + 0.93$$

Therefore, 10 min EUF-K can be used as a measure of intensity and the ratio 35 min EUF-K : 10 min EUF-K as an indicator of buffering (Q/I of loosely bound  $K_{ads}$ ).

3. The difference between  $K_{ads}$  measured by percolation with  $NH_4$  acetate and 35 min EUF-K provides a measure of  $K_{ads}$  tightly bound on e-sites of micaceous clays.

Table 7, applying only to soils with three layer silicates, shows Nemeth's (1979) estimates of the amounts of K fertilizer needed to raise 35 min EUF-K to 150 mg.kg<sup>-1</sup> which he considered adequate for intensive agriculture.

**Table 7.** Quantity of K required to raise the level of EUF extractable K (35 min. standard procedure) to sufficiency level in intensive agriculture (Nemeth, 1979).

Test value of EUF 35 min. K (cg kg <sup>-1</sup> )	Fertilizer K required (kg ha <sup>-1</sup> )			
	Clay content of soil %			
	10	10 - 20	20 - 30	30 - 40
1	600	1200	1600	3000
2	560	1050	1300	1800
3	480	900	1100	1400
4	420	800	900	1100
5	370	700	800	900
6	330	600	700	800
7	270	450	550	650
8	240	300	400	500
9	210	250	300	350
10	190	150	150	200
12	120	120	120	150
13	90	90	90	90
14	60	60	60	60

### 6.3.1.3. Empirical methods for estimating "available K"

K extracted by these methods (4.2.3. and 5.1.4.) is essentially  $K_{lab}$  but the proportions of  $K_{ads}$  and  $K_{str}$  involved differ between different extractants. Hence interpretation of the data is specific to the method used and any technique of extraction requires its own evaluation algorithm for the parameters measured. The number of classes distinguished for rating and the factors considered affecting the relation between soil test value and crop response can vary. For instance, Kerschberger *et al.* (1986) classified intensively cropped soils in Eastern Germany on the basis of texture and organic matter content and used 5 categories for "available K" (Table 8). The rating algorithm is based on numerous medium-term and long-term field trials in various cropping systems of a high intensity level. The definition of classes of K content was made in a way that crop response to K level in soil and required fertilizer application became an inherent element of the system. Kerschberger *et al.* defined the medium K class (class 3) as containing sufficient available K to satisfy crop demand in intensive systems provided crop removal of K was compensated by K fertilizer application. The classes 1 and 2 with higher contents of soil K render possible reduced fertilizer application as compared with K exportation by crop. In class 1, K application can be omitted for years in order to reduce the unnecessarily high K content in the soil. The classes 4 and 5 with soil test values below optimum (class 3) require increased amounts of fertilizer in order to raise the soil K level. Class 5 comprises soils with low K levels causing serious yield losses if no K fertilizer is applied.

### 6.3.1.4. Degree of K saturation ( $V_K\%$ )

In some countries  $V_K$  is used for the assessment of the K status. While  $V_K$  indicates intensity (4.3.), it is also a measure of quantity and:

- additional information is needed to estimate intensity and quantity separately;
- in soils with equal values of  $V_K$ , difference in capacity to supply K increases as  $V_K$  decreases.

Clay content and clay quality must be known. Soils differing in these respects are not comparable. The only way to obtain sufficiently reliable evaluation is grouping of soils according to clay content and clay quality and the delimitation of K classes according to these groups.

**Table 8.** Rating of the K content measured according to the technique of Egner and Riehm (0.02 M Ca lactate + 0.02 M HCl extractant) in texture classes for soils with three layer silicate clays and for intensive cropping systems (Kerschberger *et al.*, 1986).

Soil groups based on texture and organic matter content		K supplying capacity / content of "available K" (cg kg <sup>-1</sup> )				
		Very high	High	Medium	Low	Very low
Clay+silt %	Org. matter %					
8	<15	≥16	15 - 11	10 - 7	6 - 4	≤3
8 - 15	<15	≥20	19 - 12	11 - 8	7 - 4	≤3
16 - 25	<15	≥23	22 - 24	13 - 9	8 - 5	≤4
26 - 38	<15	≥27	26 - 16	15 - 11	10 - 6	≤5
38	<15	≥40	39 - 23	22 - 16	15 - 10	≤6
all	>15	≥25	24 - 17	16 - 13	12 - 7	≤6

Note: The class boundaries for pasture land differ from those for crop land given in this table.



$V_K$  was recommended as a measure of K availability for highly weathered tropical soils. Pagel *et al.* (1982) rated soils as follows:

$V_K < 1.2\%$	Low K; response to K fertilizer certain.
$V_K 1.2 - 2.3\%$	Medium K; response to K fertilizer probable.
$V_K > 2.3\%$	High K; response to K fertilizer unlikely.

Boyer (1982) specified somewhat higher thresholds for the same soils saying that for high yielding or high K demand crops, the desirable range is 3 - 5% K saturation. Unnecessarily high values of  $V_K$  should be avoided as they increase the risk of leaching.

#### 6.3.1.5. Q/I isotherms and derived parameters

Q/I graphs express the exchange behaviour of a soil with regard to K. They permit to estimate fluctuations of K intensity in dependence on changes of the content of  $K_{ads}$  and vice versa. That means they are suitable to forecast the effects of K fertilizer application or of K withdrawal by plants. In distinction to  $V_K$  which always reflects only a single point of the Q/I relationship, the graph comprises all possible situations within the limits of measurement made.

The evaluation of Q/I relationship may pursue two objectives:

1. a comparison of different soils with regard to their sorption/desorption behaviour,
2. a prognosis of the K supply to plants and of the effect of K fertilizer on K transformation in the soil.

The graphs of the Q/I relationship of different soils allow a rapid judgement of their differentiation with regard to the dynamic behaviour of  $K_{lab}$ . Because the dynamic behaviour of  $K_{lab}$  depends largely on clay content and clay quality, the isotherm can give a qualitative estimate of the clay fraction (Figure 6). It is permissible to compare only graphs obtained by identical methods and plotted on the same scale. Table 9 shows normal ranges of the chief parameters derived from isotherms.

Assessment of K supply from Q/I graphs rests on the fact that the higher the equilibrium concentration and the higher the immediate buffering capacity at the intersection of the plot with the abscissa the better will be K supply. But it should be noted that as intensity increases, so will the likelihood of leaching. The following estimates can be made:

- K status as indicated by  $K_{lab}$ ;
- the necessity for supplementary K dressings to improve K status;
- how fluctuations in K supply depend on the K balance;
- whether it is permissible to reduce K dressing to lower an unnecessarily high level of  $K_{lab}$ .

**Table 9.** Evaluation of parameters derived from Q/I graphs<sup>1)</sup> based on 5 classes within the variation range observed for soils with all possible clay qualities.

	Class boundaries				
	Very low	Low	Medium	High	Very high
Equilibrium concentration (intersection graph/abscissa)(mmol.l <sup>-1</sup> )	<0.05	0.05 - 0.30	0.30 - 0.70	0.70 - 1.20	>1.20
Immediate buffer capacity in the range of intersection cg.kg <sup>-1</sup> /mmol.l <sup>-1</sup> <sup>2)</sup> (kg K per 0.1 mmol.l <sup>-1</sup> )	<30 (<90)	30 - 75 (90 - 225)	75 - 125 (225 - 375)	125 - 300 (375 - 900)	>300 (>900)
Desorption against 0.002 M CaCl <sub>2</sub> , 1:10 (cg.kg <sup>-1</sup> )	<1.0	1 - 5	5 - 12	12 - 25	<25
Maximum adsorption from 0.002 M CaCl <sub>2</sub> + 0.002 KCl, 1:10 (cg.kg <sup>-1</sup> )	<10	10 - 30	30 - 50	50 - 70	>70

- Notes: 1) Conditions of measurement and depiction: soil:solution 1:10; solution 0.002 M CaCl<sub>2</sub> + maximal 0.002 M KCl; equilibration 1 hour shaking; scales of the coordinates of the graph 5 mg kg<sup>-1</sup> K<sub>ex</sub> = 0.1 mmol l<sup>-1</sup>
- 2) "In the range of intersection" means an arbitrarily fixed section of the abscissa on both sides of the point of intersection graph/abscissa, e.g. ±0.1 mmol l<sup>-1</sup>. This section is used to calculate the actual buffer capacity. The more the graph is bent at the point of intersection the narrower should be the fixed section of the abscissa in order to obtain correct values of actual buffering
- 3) Transferred to the topsoil (0-20 cm depth) of 1 ha land; the data are useful to estimate the practical significance of immediate buffering, but the range of intensity for which the value of buffering is valid must be considered: this range may be less than 0.1 mmol l<sup>-1</sup>

The desirable level of  $K_{lab}$  is that which optimizes K supply for given conditions of target yield, cost of fertilizer and risk of leaching.

There is as yet insufficient data from cropping experiments to allow full and detailed evaluation of parameters derived from Q/I relationships. This persisting shortcoming is linked with the difficulties in calibrating the data with regard to K supply or K uptake, because none of the parameters (equilibrium concentration, immediate buffering, desorbable K) is alone in close correlation to yield or supply parameters. Correlations between  $AR_O$ , LBC, BC, K desorption and yield or crop K uptake were investigated in the sixties and seventies without entirely successful results. This, and the high cost of determining Q/I isotherms are reasons why the method has not been adopted for routine soil testing. On the other hand, Q/I isotherms, yielding as they do information on K transformations in the soil, are valuable for characterizing benchmark soils.

#### 6.3.1.6. K concentration in the saturation extract

Frequently, the K concentration of the saturation extract has been used to estimate K intensity. Because of the short-term fluctuations of K concentration and of the role of immediate buffering for K supply, the K concentration is not suitable to routine soil testing. However, the measurement of K concentration in the saturation extract has been useful in studying the functions of K concentration in K release and mobility.

Pagel *et al.* (1982) devised a rating system based on K concentration in the saturation extract (Table 10).

**Table 10.** Rating of the K concentration in the saturation extract according to Pagel *et al.* (1982).

Rating	K concentration mmol l <sup>-1</sup>	
Very low	<0.05	(~ < 2 mg l <sup>-1</sup> )
Low	0.05 - 0.10	(~ 2 - 4 mg l <sup>-1</sup> )
Medium	0.10 - 0.50	(~ 4 - 20 mg l <sup>-1</sup> )
High	0.50 - 1.00	(~20 - 40 mg l <sup>-1</sup> )
Very high	>1.00	(~ >40 mg l <sup>-1</sup> )

At levels up to 4 mg l<sup>-1</sup>, K mobility is estimated very low even when soil moisture content is high and it can be growth limiting though this may be moderated by high buffering capacity. Within the range 4 to 40 mg l<sup>-1</sup> which indicates normal K supply, an increase in K concentration may, in intensive agriculture, improve K supply and yield. Increasing K concentration above 40 mg l<sup>-1</sup> may be justified in some circumstances: K demanding crops, poor rooting conditions, very dry soils.

## 6.3.2. Structural K and its release

### 6.3.2.1. General remarks

Conventional procedures extract both  $K_{str}$  and  $K_{lab}$  hence, in assessing K status two approaches are possible: evaluation of total K extracted ( $K_{str} + K_{lab}$ ) or of  $K_{str}$  alone, obtained by subtraction of  $K_{lab}$  determined separately from the total figure. It is unfortunate that many publications fail to state whether or not  $K_{lab}$  is included. It is doubtful if the separate measurement of  $K_{lab}$ , which increases costs, can be justified. In relation to the NaTPB procedure, Mutscher (1980), in pot experiments, found the following values for correlation of K uptake with the different methods:

$K_{ex}$	$r = 0.807^{+++}$
K-NaTPB minus $K_{ex}$	$r = 0.760^{+++}$
K-NaTPB including $K_{ex}$	$r = 0.950^{+++}$

The closest correlation for the total K extracted with NaTPB results from the implication of short-term buffering. Obviously, for practical purposes, the potassium supplying capacity can be assessed without subtraction of  $K_{lab}$ . But principally, for an analysis of the K supplying behaviour of a soil, it seems to be disadvantageous to use data of the bulk quantity extracted. Such figures do not allow to separate the role of  $K_{lab}$  and of replenishment and they obscure compensation effects. Evaluation loses accuracy and reliability. Replenishment data are more difficult to interpret than data for  $K_{lab}$  because:

1. Replenishment affects K supply in different ways:
  - buffering of  $K_{lab}$  near active roots during intensive uptake,
  - compensation of removals of  $K_{lab}$  when the cropping system is in negative K balance;nominally equal test values may have distinct significance with regard to both functions.
2.  $K_{lab}$  represents the main pool for K supply to roots. Replenishment plays a complementary role which is difficult to separate from the supply of  $K_{lab}$ , particularly if the dynamic link between both K forms is considered. Long lasting vegetation experiments are necessary in order to assess replenishment by the help of comparisons between balance data and repeated measurement of soil parameters for getting the change in the K status.
3. Factors controlling replenishment are more complex and variable than those for transformation of  $K_{lab}$ . They are affected by mineralogical composition, distribution of K bearing minerals between particle size fractions, unlimited variation in spatial arrangement of soil solids and conditions of weathering. In practice, it is virtually impossible to disentangle the web of internal environmental factors controlling amount and rate of replenishment.

In spite of these difficulties, it is generally accepted that assessment of replenishment would be useful. Data from  $K_{str}$  extraction are plentiful but there are few from cropping experiments to allow unambiguous interpretation on a plant-related basis. For this reason, evaluation of test data refers in most cases to the less meaningful classes of frequency distribution for the given extraction technique. Generally, the evaluation of replenishment data is only qualitative or semi-quantitative and related to a replenishment potential, the involvement of which in K supply to crop is difficult to forecast. The best conditions for interpretation give the  $K_i$  specific test data. This is due to the role of short- to medium-term buffering by  $K_{ier}$  not depending on weathering.

### 6.3.2.2. $K_i$ specific quantity parameters

#### *NaTPB extractable K*

The most frequently used method specific to  $K_i$  is NaTPB extraction (Duthion and Grosman, 1970 and 1971; Cabibel, 1972; Quemener *et al.*, 1974; Mutscher, 1980). It is the only such procedure for which plant-related data are available and good correlations with plant uptake have been reported:  $r = 0.955^{+++}$  (Wenworth and Rossi, 1977);  $r = 0.963^{+++}$  (Quemener *et al.*, 1974);  $r = 0.825^{+++}$  (Mutscher, 1979 and 1980). But the method has been so modified from time to time that quantitative generalization for evaluation is impossible. Mutscher (1980) proposed an evaluation table for Cabibel's (1972) method (Table 11). The ratio  $K\text{-NaTPB}/K_{ex}$  gives a measure of short to medium term buffering. For soils with three layer silicates, it is assumed that at values for this ratio  $>1$ , buffering is high, at values  $<0.5$  low.

**Table 11.** Rating of the NaTPB/NaCl extractable potassium (method Cabibel) according to Mutscher (1980).

Rating	Reserve K, cg kg <sup>-1</sup> *
Very low	<5
Low	5 - 15
Medium	15 - 40
High	40 - 75
Very high	$\geq 75$

\*) Note: Labile K subtracted from the total quantity extracted  
 Extractant 0.05 N NaTPB + 1 N NaCl  
 Extraction soil:solution 1:20; 24°C, 1 hour.

Workers differ in their opinion as to the value of this NaTPB test for routine purposes but, it is generally accepted that it differentiates well between soils as regards  $K_i$  release and identifies soils with a high capacity for  $K_i$  release. Generally, the NaTPB technique is the most suitable among the  $K_i$  specific extractions. However, a standardization is hardly needed and with new data the evaluation algorithm should be improved.

### *Thermic digestion*

This method has been little used and there are few data from cropping experiments. Table 12 gives classes of test values related to the frequency distribution of parameters measured. Legg and Axley (1958) found a close relationship between soil test data from the first thermic digestion and K uptake by plant. Later studies made by Mutscher (1980) with illitic soils could not confirm this ( $r = 0.528^+$ ).

**Table 12.** Rating of the potassium reserve as measured by a single thermic treatment (method Kolterman and Truog, 1953) referring to the observed variation range as proposed by Mutscher (1980).

Rating	Reserve K, cg kg <sup>-1</sup> *
Extremely low	< 5
Very low	5 - < 15
Low	15 - < 30
Moderate	30 - < 60
Medium	60 - <100
High	100 - <140
Very high	140 - 200
Extremely high	>200

\*) Note: Labile K subtracted from the total amount of K extracted.

Between the amounts of K extracted by NaTPB and after thermic digestion, only a loose correlation exists ( $r = 0.33^+$ ; Mutscher, 1980). Obviously thermic digestion, being an aggressive technique, touches some  $K_i$  in primary silicates which have no influence on short or medium term  $K_{lab}$  buffering. Richter (1975) proposed using single thermic treatment to estimate K replenishment for adjusting forecasts of fertilizer K requirement indicated by level of  $K_{lab}$ .

### 6.3.2.3. Parameters obtained from non-specific extracts

#### *Strong acids*

These methods, being easy and cheap, have been popular but results are difficult to interpret and there are no meaningful rating systems. The test data have been related to cropping experiments to assess replenishment but results were most contradictory (e.g. Oliveira *et al.*, 1971; Foster, 1972). The greater the variation in mineralogy and genetic character of soils, the less possible is any generalization. Modifications of the technique could not alleviate the shortcomings.

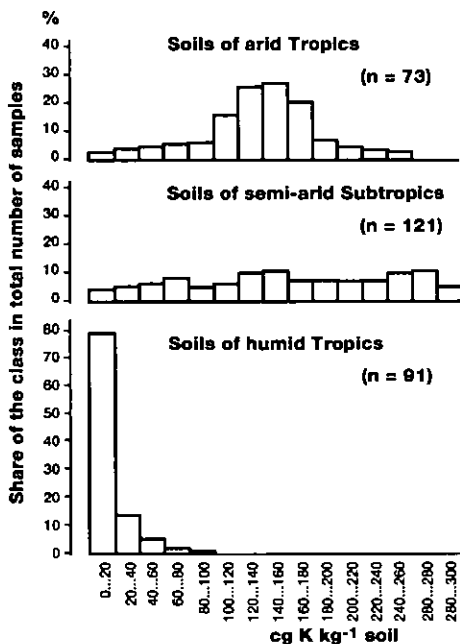
Only a few proposals have been made as concerns plant-related evaluation. That made by Haylock and Metson forty years ago (1956) for the step K has been trailed through many later publications without new checking and improvements or affirmation. These authors suggested the following ratings:

Step K	< 12 cg.kg <sup>-1</sup>	K deficiency following exhaustion of K <sub>lab</sub> ; high response to K fertilizer
	12-20 cg.kg <sup>-1</sup>	K fertilizer response by K demanding crops or on coarse textured soil
	> 200 cg.kg <sup>-1</sup>	No response to K fertilizer, high supply capacity.

In the light of our present-day knowledge about the functioning of the K system and the action of strong acid extractions, this rating is highly questionable and not to be generalized. Schachtschabel as soon as 1961 pointed out that due to the modalities of interaction between strong acids and the various K bearing silicates in soils, a close correlation between soil test value and K uptake of crop could not be expected. Rating scales for acid extractable K should be based on the variation range of test values for the kind of soil to be tested and assessed. Figure 12 demonstrates to which extent the measured values depend on the kind of soil under test.

#### *K<sub>str</sub> extracted with EUF or other methods*

Extraction by EUF at 80°C has been used to test K<sub>str</sub> but this and other aggressive methods including exchange resins present the same difficulties as strong acids. No algorithm for their evaluation is known.



**Fig. 12.** Frequency distribution of reserve K ( $K_{lab}$  subtracted) extractable with 1 M boiling  $HNO_3$  for soils of different regions (Pagel *et al.*, 1982).

#### 6.3.2.4. Rates of K release

Rates of K release have been measured in the laboratory by leaching with water or salt solution, precipitation with NaTPB or using exchange resins as sink but the determination of rates is not a routine test. Data published mostly belong to in-depth studies of the K supplying behaviour of soils of particular interest. Absolute rate figures measured strongly depend on the extraction technique and for the same technique even on minute details of the conditions set.

No standardized technique of determination and no evaluation algorithm is available. One can compare rates of K release with K uptake rates of growing crops. But any such comparison should be interpreted with care, because the rates of K transformation in a soil/plant system in operation differ from those measured under laboratory conditions. Rate figures derived from measurements made in cropping experiments, e.g. in exhaustion experiments with perennial ryegrass, are more realistic. But to obtain such data is costly and time consuming, hence recommended in special cases only.



### 6.3.3. K fixation capacity

The effects of controlling factors make it unlikely that laboratory measurement of fixation capacity will correspond with fixation in the field. Values determined in the laboratory are usually higher than in the field because  $K^+$  is more uniformly distributed in the sample and there is better contact of  $K^+$  with clay particle surfaces. But laboratory data can be used for general comparison of soils and estimating the risk of fixation.

The fixation capacity has often been measured. However, techniques for measuring fixation capacity have varied greatly, so possibilities for comparison and generalization are very limited. Some authors refer fixation capacity to the whole soil, others to the clay fraction only. As fixation is centred in fine particles, the latter procedure in some cases allows better interpretation and more meaningful assessment.

Due to the lack of a standardized generally accepted technique of determination, no sufficiently founded evaluation algorithm exists. In Table 13, a proposal for rating is made derived from data measured with the technique proposed by Schlichting and Blume (1966) frequently used in Europe.

Table 13. Proposal for rating wet fixation.

Rating	Wet fixation of $K^+$	
	soil $cg\ kg^{-1}$	Clay $mg\ g^{-1}$
Very low	< 5	<0.1
Low	5 - <10	0.1 - <0.4
Moderate	10 - <20	0.4 - <0.8
Medium	20 - <30	0.8 - <1.2
High	30 - <50	1.2 - <1.5
Very high	50 - <75	1.5 - <1.8
Extremely high	>75	>1.8

Note: Technique of determination according to Schlichting and Blume (1966): 10 g soil; K load 1 g K/kg soil as 0.05 N KCl; exchange with 1 N  $NH_4$  acetate pH7.

## **7. Assessment and monitoring of the K status: approach to development of a case-oriented strategy**

### **7.1. Basic considerations**

The assessment and monitoring of soil nutrient status involves considerable expenditure and calls for investment in manpower, equipment and scientific support. Organization must be at the highest level so that this expenditure is used efficiently. The collection, critical analysis and generalization of scientific findings and practical experience - at both national and international levels - is a precondition to efficient work. One outcome of such activities should be the recommendation of standardized techniques of soil testing and the development of evaluation algorithms for the parameters measured. Private or administrative structures must be organized in order to respond to such tasks and a strategy of action must be developed and implemented. This strategy implicates structural, functional, territorial and subject-related elements. It is impossible to outline all these problems here, but some selected aspects of rational target-oriented measurement, assessment and monitoring of soil K are discussed.

In the foregoing chapters, factual and methodological fundamentals have been discussed. It follows from them that the assessment of the K status of soil is based on three conditions:

- measured parameters of the K status;
- evaluability of measured data with regard to crop response;
- interpretability of measured parameters in terms of the K system of soil.

However, to be aware of this is not enough to guarantee efficient work in soil investigation and routine testing for K. Questions which emerge are:

- Which characteristics or parameters should be used for soil testing?
- Is one test applicable to all soils to be tested and does it cover all the information needs for the given management requirements?
- If there are several techniques to measure a characteristic, which is the most appropriate?
- Is one single parameter sufficient and in which cases are complementary parameters useful?

Answering to these questions depend upon cropping targets, site qualities, and socio-economic conditions of agriculture and forestry. Before attempting to answer these questions, some observations should be made:

1. Soil investigation and routine testing for K are essential for the assessment of the K status and fertilizer efficiency, but they cannot supply all the information needed. Crop-related data are as important as

soil parameters. In particular, yield data, nutrient content of dry matter harvested, total nutrient uptake and nutrient removal are required. Such data provide an insight into the nutritional status of plants and permit the calculation of nutrient balances. Crop data and nutrient balances not only give information about the effects of a cropping system on nutrient stock and nutrient supplying capacity of soil, they are also valuable for developing and improving evaluation algorithms for measurable soil parameters. Moreover, full decoding of the information inherent in a soil parameter is impossible without referring to crop-related data. Therefore, soil analysis should never be planned, executed and interpreted in isolation from cropping experiments and study of plant growth.

2. Alongside countries having more than a century's experience of fertilizer use and with highly sophisticated and reliable soil testing systems, are others which are only now taking the first steps on this road. Consequently, approaches to the assessment of the nutrient status of soils (both in agriculture and forestry) and the structures and operations needed differ greatly. Mechanistic transfer of established policies or testing systems from developed to other countries is not to be recommended, differences in natural and socio-economic conditions speak against this. However, the general experience resulting from failings and successes of advanced countries is of outstanding interest. This experience together with the modern tools of remote sensing, separation and measurement of chemical elements as well as data handling generate a new basis for action in countries beginning this work: strategies for efficient soil nutrient assessment can more quickly be designed and realized, work and money can be saved and adverse environmental impacts of bad fertilizer use can be avoided.
3. Assessment of soil nutrients is not an end in itself, but it serves to support land use or management decisions. At the least, market-bound agriculture is an economic activity based on cost/benefit information. From the point of view of the farmer, but also from that of the country's administration in case of subsidized soil testing and delivery of information to farmers, the assessment of the nutrient status should be made at the lowest cost possible for the information needed. To minimize cost, we have to take into consideration the following: any assessment establishes a link between information represented by the measured parameters and their interpretation and the task to be resolved with the help of this information. Consequently, minimizing the cost of soil testing depends on two preconditions:

- precise definition of the aim of the assessment;
- delimitation of the information needed to realize this aim.

Any successful nutrient assessment and monitoring starts with reflection on these two requirements. This is the only way to reach a high level of efficiency in routine testing for advisory work and in investigation of K in benchmark soils. The principle should be: no measurement, if the resulting data cannot be transformed in a decision-supporting assessment and, consequently, does not contribute to the solution of a defined task.

## 7.2. Objectives of K assessment

Any categorization abstracts from reality. Nevertheless, it can be useful to typify the objectives of soil K assessment in order to comprehend differences in tasks and the resulting consequences with regard to sampling, measurement and evaluation of parameters. A possible classification of tasks may be the following:

1. First general assessments of the K status as part of the nutrient supplying capacity of soil and of its spatial differentiation in areas not yet evaluated for land use purposes (survey-related assessment).
2. Assessment and monitoring of the K status of soils in areas under agricultural or forestal land use with no or minimum external input systems (no use of fertilizer).
3. Assessment and monitoring of the K status in medium to high external input agriculture for soils regularly receiving K fertilizer.
4. Investigation of the K system and assessment of the K status of benchmark soils or of soils of field trials.

In Table 14, aims of the assessment for each of the tasks are listed for comparison. This table needs some comments:

Economically, by far the most important objective of the assessment of soil K refers to agricultural land where fertilizer is used. In this case, the assessment of the K status of soil has two objectives:

- to support highly efficient fertilizer use and,
- to prevent K supply becoming yield limiting and adversely affecting the efficiency of inputs other than K.

However, the intensity of cropping and the corresponding yield levels or K demands vary widely. This affects the kind of measurements to be made for K assessment. Where fertilizer is used the transformation behaviour of soil with regard to this fertilizer K assumes increasing importance and K supply from native stocks recedes into the background (7.3.1.).

Benchmark soils which are representative of a segment of the soil cover have special requirements as regards K assessment. Their investigation has three aims:

- improved understanding for land use related soil qualities and for process dynamics in main soil units;
- improved evaluation and interpretation of parameters measured for field-related routine testing;
- extrapolation of findings to a reference area with similar soil characteristics.

Benchmark soils provide a key link between research and crop management and so, justify more costly and in-depth investigation than is warranted for work on farmers' fields. Frequently, benchmark soils coincide with agricultural benchmark sites where long-term field experiments are located. The combination with field trials makes the investigation of the K system in benchmark soils an important tool for raising the efficiency of routine soil testing and fertilizer application. This case presents the ideal conditions for studying the soil/plant system as a whole and for complementary measurements of soil and plant parameters, as proven by the experience of countries with a well developed system of benchmark sites and long-term field trials. For all these reasons, in-depth studies of such soils are well justified: the more we know about them the better. Nevertheless, the cost/benefit problem still exists and has to be solved by careful planning of experiment design and measurements as well as thorough interpretation of data obtained.

There is one difficulty to be considered with regard to the choice of benchmark soils for K: the K system and the K status are controlled by mineralogical composition of parent rock and degree of leaching and weathering. Hence, the selection of benchmark soils for studying this soil quality should refer to that criterion. But K supplying capacity is only one factor of soil productivity and agronomists have to select their benchmark sites for field experiments optimizing all requirements (site qualities, land use and management practices, socio-economic conditions and infrastructure). Their choice is not necessarily the best for investigation of soil K. Moreover, benchmark soils are often selected according to higher categories of genetic soil classification. Frequently, soils chosen on this basis are not ideally suited for the identification of agronomically important differentiations with regard to the K status. One possible solution is to select some additional reference soils for work on soil K, referring to soil mineralogy, thus complementing the benchmark soil system based on more general targets.

**Table 14.** Aims of the assessment of the K status of soil.

Assessment of soil K in areas not yet evaluated for land use purposes (land surveys)	Assessment of soil K for no or low external input cropping systems	Assessment and monitoring of soil K in intensive agriculture	Investigation of the K system and assessment of the K status of benchmark soils
<ol style="list-style-type: none"> <li>1. Evaluation of the K supplying capacity and its spatial differentiation for land units based on site-related information.</li> <li>2. Characterization of the K status within land units, preferably based on a limited number of parameters of reference profiles in genetic soil units.</li> </ol>	<ol style="list-style-type: none"> <li>1. Field- or farm-related assessment of the K supplying capacity.</li> <li>2. Proposals for improved spatial land use pattern.</li> <li>3. Improvement of soil and crop management.</li> <li>4. Control of K depletion of soils.</li> </ol>	<ol style="list-style-type: none"> <li>1. Guarantee of a K level in soil covering the K demand for the yield planned.</li> <li>2. Identification of long-term effects of the fertilizer policy on the K status of soil and deduction of timely corrections.</li> <li>3. Avoidance of useless fertilizer inputs and of nutrient losses.</li> <li>4. Identification of needs for improved routine testing (techniques of extraction or evaluation algorithms).</li> </ol>	<ol style="list-style-type: none"> <li>1. Characterization of the site specific K system.</li> <li>2. Improved interpretation of routine test data and soil test value/crop response findings.</li> <li>3. Provision of information for grouping soils according to the characteristics of their K system.</li> <li>4. Development of optimum application techniques for K fertilizer.</li> <li>5. In connection with long-term cropping experiments improvement of the cropping system and of crop management practices in the reference area.</li> </ol>

Generally, first-step-assessments of the nutrient supplying capacity of soils including the K status have to be made against the background of land evaluation tasks. The objective is the delimitation of land units or a project-related evaluation of an area. Tasks of this type are mostly set in developing countries in connection with attempts to improve land use though countries with developed economy face similar tasks so far as they still possess land reserves. The general assessment to be made basically refers to general information about landscape and soil cover, only supported by a few measured soil parameters mostly originating from samples of reference profiles for mapping.

There is still much agricultural land in the world which receives no fertilizer or other external input and though, for socio-economic reasons, this situation may be expected to persist for many years, it is unfortunate that research has tended to neglect this field. Only recently, has any effort been made to reverse this trend. The devising of sustainable low intensity farming systems which do not rely on external inputs demands specific information about nutrient cycles and the part played by the soil therein. This is also true for K. Because low or no external input systems for sustainable farming in developing countries are mostly needed for highly weathered soils, the open question as concerns principles and techniques of K assessment for those soils hinder the solution of actual tasks in tropical countries (see Chapter 8).

### **7.3. Information needs and parameters to be measured**

The kind of information required can be derived from the decision-related aims of K assessment. It is clear from the discussion above that the kind of information (both qualitative and quantitative) needed for assessment of the K supplying capacity of the soil differs according to the situation. The question then arises as to which parameter(s) should be selected.

Following definition of targets of K assessment by far the most important step to assure meaningful information and efficient work is the selection of appropriate parameters for measurement. Another consideration in making the choice is that of cost. Appropriate selection of parameters may contribute to optimizing cost/information quality relationship. Figure 13 shows the place of selection of parameters in the procedure of information provision and decision making with regard to soil K assessment.

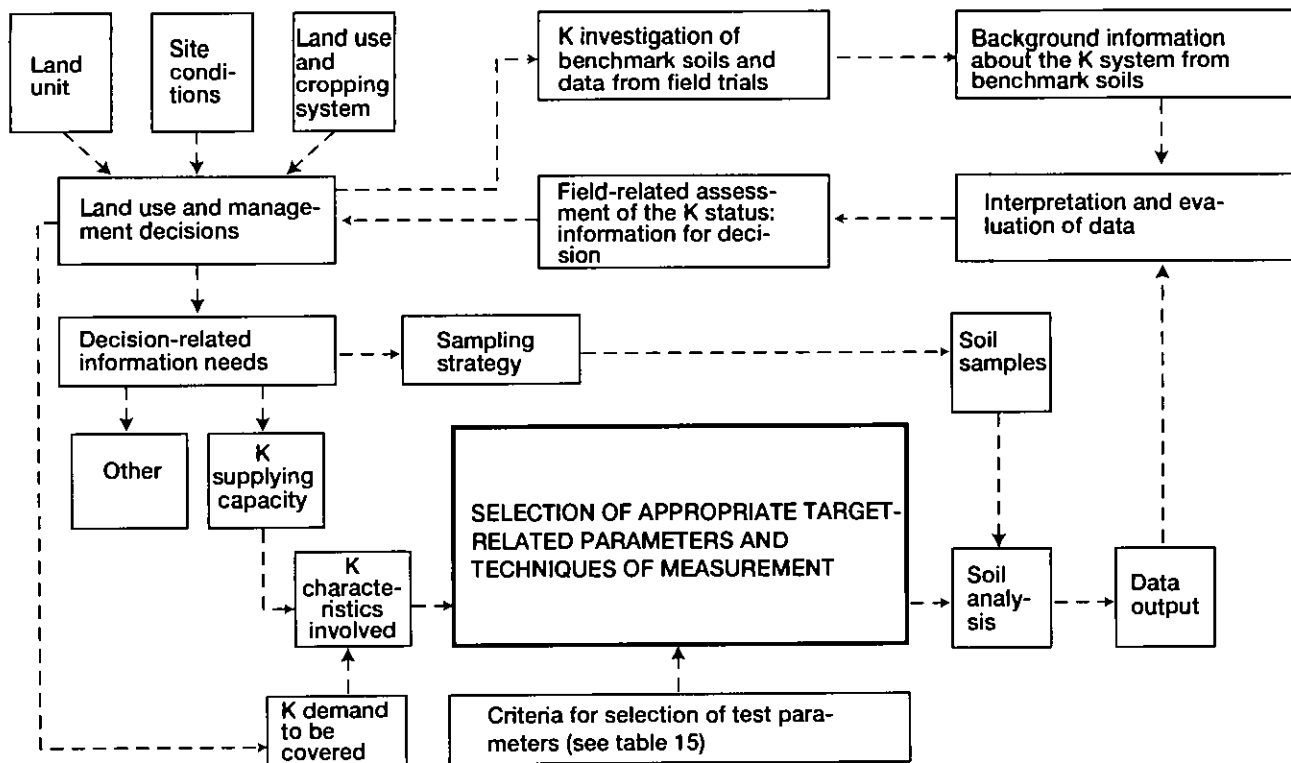


Fig. 13. Selection of parameters to be measured for field-related K assessment: place in the strategy.



There are several ways to obtain improved target-related information about soil K:

1. Selection of the most suitable single parameter and of the most appropriate technique of measurement with regard to the specific information we need.
2. Complementation of a basic parameter measured by additional parameter(s), e.g. quantity by intensity or rate data.
3. Improvement of the evaluation algorithm for a measured parameter by grouping soils in more appropriate homogeneous groups and differentiation of algorithms, e.g. according to clay content and clay quality.
4. Improvement of the understanding of the K system in the soil by in-depth studies of K in benchmark soils and again improvement of the evaluation algorithm or its interpretation.

The measurement of several parameters increases cost. Generally, extended laboratory capacity, more staff and more equipment are needed for this purpose. It is evident that this solution is applicable to a limited number of selected soils only, preferably to benchmark soil(s) of a land unit or soils from field experiments. For routine testing, single measurement is preferred. The most appropriate soil test has to be selected from the numerous tests proposed and outlined in Chapter 5. However, we can conclude from items 3 and 4 that correct selection of parameters is only one of our instruments for improving K assessment.

It is evident that single parameter measurements for routine testing should refer to the pool of  $K_{ads}$  since this quantity information is of overriding importance in assessing the K supplying capacity of the soil. But, clearly, skillful selection of the soil test enables us to obtain more than just simple quantity information from a single soil test (see Section 6.3.1.1.). Knowledge about the K system and its relation to the plant enables us better to select the test which provides the most appropriate information. In the long run, improved interpretation of the single test in the light of this knowledge is cheaper than multiple measurement. Other criteria for selection of soil test method are listed in Table 15 and discussed in the following.

**Table 15.** Criteria for selection of parameters and related techniques of measurement with regard to assessment of soil K.

Criteria for K parameters	Criteria for related techniques of measurement
<ol style="list-style-type: none"> <li>1. Evaluability that means availability of evaluation algorithms and their qualitative level.</li> <li>2. Suitability for the soils to be tested.</li> <li>3. Interpretability of the parameter in the terms of the K system.</li> <li>4. Cost of measurement and data interpretation.</li> <li>5. Informative value with regard to K supply according to the level of K demand attended.</li> </ol>	<ol style="list-style-type: none"> <li>1. Suitability for the soils to be tested.</li> <li>2. Reliability and reproducibility of measurement.</li> <li>3. Practicability of the technique that means ease of its execution and equipments required.</li> <li>4. Feasibility of the technique under local conditions (infrastructure, staff, equipment).</li> </ol>

### 7.3.1. Cropping intensity and selection of parameters

In Chapter 6, cropping intensity was discussed as a factor to be considered in development of rating systems for labile K. The selection of the most appropriate parameter for routine testing must also refer to cropping intensity, because the role of the various K characteristics with regard to K supply to crops changes with increasing K demand of the crop and the amount of K fertilizer applied.

In any case, the soil test has to provide quantity information since the stock of K ( $K_{lab+ier}$ ) contained in the soil before seeding or planting must cover the K demand quantitatively. The relation between quantity measured by the soil test and the satisfaction of K demand of a crop can be found in cropping experiments (see also Section 6.3.1.1.). As long as K demands of single crops or of the crop rotation as a whole remain low, quantity information, preferable about  $K_{lab}$ , provides the information needed for K assessment. All techniques extracting  $K_{lab}$  nearly completely are convenient, regardless of small amounts of other K forms contributing to the test value, as for instance some empirical methods for "available K".

However, with increasing K demand and high to very high daily uptake rates in the main growth phase, transformation processes assume increasing importance for sufficient K uptake. Therefore, intensity, buffering and mobility may become rate limiting for K supply to roots, even in soils quantitatively well supplied with K. Consequently, the higher the K demand the more realistic assessments of the K supplying capacity require intensity and rate information to complement quantity measurement. If no additional measurements are possible to obtain this information directly, then the selection of a test technique fitting the information need can help to solve the problem.

In soils with three layer silicates, techniques extracting preferably the  $K_{ads}$  from planar sites of silicate clays are, for several reasons, superior to techniques extracting  $K_{ads}$  more completely. The  $K_{ads}$  loosely bound at planar sites controls intensity at a level ( $>0.5 \text{ mmol l}^{-1}$ ) sufficiently high to assure high mobility and high uptake rates for K. In addition to the quantity information (amount of  $K_{ads}$  loosely bound), the test value indicates high intensity levels. High test values express additionally high capacities for immediate buffering and prove that high daily uptake rates can be covered. Water extracts, as used for instance as standard techniques in the Netherlands and Switzerland, or the 35 min. standard extraction by EUF, in loam and clay soils, also the  $K_{ex}$  techniques, are methods which measure K on planar sites.

In intensive cropping, soil test/crop response is still affected by a second factor. In soils with micaceous clays, plants have access to easily releasable  $K_i$  as soon as K concentration, in the immediate vicinity of active roots, drops to a level allowing appreciable  $K_i$  release ( $<0.05 \text{ mmol l}^{-1}$ ). Thus, translocation of  $K_{\text{sol}}$  towards roots along concentration gradients and  $K_{\text{ier}}$  release near root surfaces are concomitant processes. This is contrary to the former belief that the release of  $K_i$  becomes important only after exhaustion of  $K_{\text{ads}}$  in the bulk soil to levels below a critical threshold. Release of  $K_i$  takes part in K supply to intensively growing crops even in soils with high levels of labile K. The more the K diffusion is restricted, for instance by low moisture content or low intensity values, the more the importance of  $K_i$  release increases. Extracts of loosely bound  $K_{\text{ads}}$  in no way reflect the short and medium term buffering by  $K_{\text{ier}}$ . But, the  $K_{\text{ier}}$  needs not necessarily be measured separately. The capacity for  $K_i$  release is reflected by techniques extracting  $K_{\text{ads}}$  including that from e-positions, because there is generally a close correlation between the quantity of e-positions and the amount of  $K_{\text{ier}}$  in soil. An example of such a technique is, for instance, extraction with percolating  $\text{NH}_4$  acetate solution.

Recently, it was proposed (Grzebisz and Oertly, 1993) to use K extractable by boiling nitric acid as routine test for intensively cropped soils. In principle, this method may have some advantages for testing soils in which layer silicates dominate reserve K. But, for testing soils differing in the mineralogical quality of reserve K (share of weatherable K bearing tecto-silicates) and low in micaceous clay, the proposal presents more problems than advantages. This is a good example for the role of grouping soils and the complementary functions of soil test selection and soil grouping for improved K assessment.

### 7.3.2. Site qualities and selection of K parameters for testing

The parameters capable of furnishing the information we need for K assessment depend also on site qualities, particularly on soil qualities other than the nutrient supplying capacity. The most important soil quality of concern is the degree of leaching and weathering of inorganic soil constituents (DLW). Most of our present knowledge about soil K accumulated over the years refers to soils with a low DLW, i.e. with three-layer silicates in the clay fraction and permanent charge of clay. This is demonstrated by the facts reported in the foregoing chapters. It is often overlooked that the K system of highly weathered soils differs considerably from that of soils with a low DLW. With regard to the K system, there are at

least three important distinctive features of soils with a high DLW:

1. The instable pH dependent equilibrium  $K_{ads} \longleftrightarrow K_{sol}$  and the equally pH affected intensity dynamics. Both are due to the variably charged soil clays (kaolinitic-oxidic soil clay).
2. The loss of a large part of the primary K containing silicates, especially those with a higher weatherability.
3. The receding significance of  $K_i$  release, short-term buffering and K fixation owing to the disappearance of layer silicates caused by their weathering.

The peculiarities of the K system of highly weathered soils have to be taken into account in assessing their K supplying capacity. All techniques for K extraction or characterization and most algorithms for evaluation of measured parameters have been developed for soils with low DLW containing K-bearing layer silicates and permanently charged clay. These cannot be mechanically transferred to variable charge soils. Unfortunately, deficits in K research with regard to soils of high DLW (see also Chapter 8) result in considerable uncertainty in K assessment of such soils. A few hints of what the problems are, shall be given here:

1. The pool of  $K_{ads}$  should be extracted by methods which extract it completely and for this, percolation methods are preferred. When, for general characterization of soils, the percolation technique is used for determination of  $CEC_{eff}$ ,  $K_{ads}$  is also measured, but leaching with unbuffered salt solutions is also appropriate for a separate routine testing of K.
2. The pH dependence of the relative binding strength for K makes it difficult to estimate K intensity from absolute values of  $K_{ads}$  measured and from  $V_K$  % as well. Fluctuations in pH induce important changes in saturation, binding strength and competition with other ions, e.g. Al ions.
3. For the same reason, the Q/I graphs are not reliable for characterizing the transformation behaviour of  $K_{lab}$ . Actually, no appropriate standardized technique is available for determination of Q/I graphs in variable charge soils.
4. In variable charge soils, generally low in K, it is interesting to get information about reserves of  $K_{str}$ . Owing to the advanced stage of weathering, only very resistant K bearing silicates remain. In extracts with strong acids, frequently recommended and used for highly weathered tropical soils, a part of this residual silicate might be dissolved indicating a reserve present. But, in the natural soil environment, particularly after liming or incorporation of ash, the rates of weathering and K release from these resistant residual K silicates are very low. The

practical significance of the K extracted. e.g. by boiling nitric acid, is different from that in soils with medium or low DLW. Nonetheless, the reserve measured is important at least for all long fallow systems in the tropics. During fallow periods, low rate K release enables the build-up of new K stocks in the biological cycle.

5. Highly weathered variable charge soils usually do not contain noticeable quantities of layer silicates with easily releasable  $K_i$ , at least in the topsoil and upper subsoil. Therefore, the application of  $K_i$  specific extraction procedures seems to be useless. However, it is still questionable to what extent estimates of residual  $K_i$  may contribute to a meaningful differentiation of highly weathered soils with regard to K status. This is similar with K fixation. Generally, highly weathered soils do not contain enough three layer silicates in clay to produce an appreciable fixation capacity. But recently (Poss *et al.*, 1991), slight fixation has been observed in such soils, obviously due to residual three layer clays. Whether the small amounts of K fixed after fertilizer application improve buffering to an extent practically significant for K supply to crops has yet to be investigated.
6. In weathering crusts and soil profiles developed *in situ*, the DLW of inorganic material decreases with increasing depth. This makes studies of depth functions of the K parameters interesting, particularly for the widespread cropping systems with tree or bush fallow or for agroforestry systems.

The role of other site-related factors for the selection and evaluation of parameters can be demonstrated by the following examples:

- It is not necessary to measure K fixation capacity for all soils with low DLW, hence containing three layer silicates in clay. Only loams and clays may have a high fixation capacity. In such soils, the fixation capacity should be tested, particularly if the  $V_K$  is low to very low (<1.5%) or whenever vermiculitic clays are present (clays with very high CEC).
- The high neutralization potential of calcareous soils modifies the extractive power of any acid solution. For this reason, extraction techniques based on  $H^+$  effects must be avoided. Whenever they are applied to that soils, ratings deduced from tests with non-calcareous soils should not be used.
- Under site conditions with frequent dry spells in the growing period or generally low soil moisture levels, Q/I graphs are useful for estimating possibilities for improving K mobility by raising the level of  $K_{ads}$ .

### 7.3.3. Evaluability of parameters measured

Essential aspects of evaluability of measured parameters are outlined in Chapter 6 where it was stressed that there are distinct qualitative levels of evaluation. The principle for selection of parameters is that:

The only such parameters suitable for routine testing are those for which there are evaluation algorithms relating the parameter value to decision making.

As mentioned elsewhere, the same parameter is not equally interpretable and evaluable in all circumstances and for all purposes, e.g.  $K_{cx}$  in soils dominated by permanent or variable charges, respectively.

The problem of evaluability is somewhat different for soils from field trials or benchmark soils. In this case, the availability of evaluation algorithms is not a precondition to selection of a parameter for measurement. The interpretability in terms of the K system is sometimes more important and often data obtained are destined only to generate a meaningful evaluation algorithm. Moreover, the parameters serve frequently for support of spatial extension of findings.

### 7.4. Soil sampling for K assessment

An essential part of soil testing is sampling and sample treatment. Its effect on reliability and reproducibility of measurement and assessment is often underestimated. Errors due to sampling mistakes are later difficult to identify and it is mostly impossible to offset them. This is particularly the case if the whole procedure of testing is divided in the steps: sampling - sample treatment and storage - laboratory test - data handling and interpretation and the steps are allocated to different administrative units and/or different staff. Usually, the interpretation of data is done by specialists who cannot know whether the sampling has been made correctly or not.

#### 7.4.1. Soil sampling in the field for measurement of K

For correct field sampling, several factors are important:

- sampling pattern,
- depth of sampling,
- time of sampling,
- volume of the sample.

Main sampling-related problems are caused by the variability of soil in space and time.

#### 7.4.1.1. Horizontal variability of soil and sampling for K

Like other soil qualities, the K status shows a horizontal variation. Therefore, data obtained from point samples are generally not representative of an area as large as is appropriate for soil management considerations. For this reason, mixed samples are used in soil testing for nutrients like P and K: smaller subsamples of equal size are taken from different points of the field or area and thoroughly mixed. Mixing eliminates differences in the state of the soil between sampling points. The bigger these differences masked by the mixed sample, the more the real K status of points in the area represented may deviate from that of the mixed sample. Mixing of samples is justified only within certain limits of variability. Therefore, the area for a mixed sample is not constant, its size changes with the degree of variability of the K status. Generally, mixing should not mask point deviations of more than 10 to 20% from the mean value of the mixed sample. If the deviation surpasses this limit, the sampling area should be subdivided.

Within a sampling area for a mixed sample, a defined spatial pattern for taking subsamples should be fixed and used for each sampling. There are various possibilities for such a standard sampling pattern. In sloping areas, catenary differentiation across the slope must be taken into account.

Normally, the horizontal spatial variation in K status is not known before sampling. The techniques of geostatistics are too costly to describe spatial variability of a soil characteristic for agricultural routine purposes. Therefore, general knowledge about factors related to spatial variation of the K status have to be used for delimitation of sampling areas. These are factors like parent material, relief, internal drainage, erosion, texture, humus content, etc.

#### 7.4.1.2. Vertical variability of soil and sampling for K

The K status not only varies horizontally, but also vertically. As concerns  $K_t$ , the vertical changes show no general pattern in soils of low DLW. Frequently, the stratification of parent material dominates the vertical differentiation. This changes with progressing leaching and weathering. In highly weathered soils, developed *in situ*,  $K_t$  increases with depth, the top layers being largely depleted of K.

The vertical changes in K concern not only  $K_t$  but also the K forms and their proportion. Usually, the A horizon of a soil profile shows the highest values for  $K_{lab}$ . This is due to biological accumulation of K or - on agricultural land - to the use of fertilizers. In the deeper horizons, the relationship between K forms shifts towards a higher share of  $K_{str}$  compared with  $K_{lab}$ . This pattern may be modified by erosion/sedimentation processes.



Mixed sampling for routine testing on agricultural land generally refers to the plowed layer or topsoil, in most cases to the top 15 to 20 cm. Since the topsoil contains the most of the roots of a crop, its K status controls the K supply to the crop and a test value from topsoil samples satisfies the information need. But sometimes, sampling from deeper layers is useful. Crops withdraw K from subsoil if there are deep roots. The share of subsoil K in total K uptake increases if topsoil dryness restricts the K mobility in this layer or if the topsoil is very poor in K. The proportion of topsoil to subsoil K in uptake depends also on the geometry of the root system, which is partly genetically fixed, partly the result of physical, sometimes also chemical soil properties. Subsoil K testing for routine purposes can be made referring to layers or horizons and at longer intervals than topsoil testing. Sampling of genetic horizons is occasionally advantageous because it allows the extrapolation of findings by means of genetic soil maps. For in-depth studies of benchmark soils, sampling of horizons and subhorizons is recommended.

#### 7.4.1.3. Sampling time

K status varies in time. The time-related variation is caused by factors like K withdrawal by plants, K input from litter fall or leaf outwash, root decay, application of manure or fertilizer, soil pH and moisture dynamics, erosion/deposition impacts, etc. For monitoring of the K status, periodically repeated sampling is required and comparability of samples should be given. Sampling immediately after manuring or fertilizer dressings should be avoided. The best sampling time is between main harvest and new cropping season.

In any case, the date of sampling has to be noted and the interpretation of test results must refer to this date. Sampling time is important, especially for a periodic sampling for comparison of test values in order to quantify changes in the K status of the same soil.

#### 7.4.1.4. Size of the sample

Transport, storage, treatment of the sample need labour and cause cost. Hence, the tendency to work with samples as small as possible. No general rule can be made because sample size depends on the measurements to be made on the sample. But fixing a sample size should take into account that the smaller the sample size, the more possibilities exist for accidental effects and non-representativity.

### 7.4.2. Sample treatment

There is a long road between sampling in the field and extraction in the laboratory: transport, drying, grinding, sieving, storage. The kind and manner of treatment and the conditions in each of the steps may have effects on the parameters measured. These effects are different according to the kind of soil.

The best known effect of sample treatment is that of drying on soils with three layer silicate clays. Changes in the measured values of  $K_{ads}$  or  $K_{ex}$  resulting from drying have been reported by numerous authors. The observations are conflicting as concerns the sense of change: sometimes the values were lowered, sometimes increased after drying. Obviously, the equilibrium  $K_i \longleftrightarrow K_{ads} \longleftrightarrow K_{sol}$  and the hydration of ions and clays are involved. It seems that in soils low in  $K_{ads}$ , drying increases the measured content of  $K_{lab}$ , whereas in soils high in  $K_{ads}$  drying lowers it. These effects are not particularly important for routine testing as long as the samples are always treated in the same manner. The only problem is a possible overestimation of  $K_{ads}$  in soils poor in  $K_{lab}$ . However, effects of drying must be taken into account with all time-related comparisons for the same soil and with comparisons of treatments in field trials. Unfortunately, no reliable information is disposable as concerns effects of drying on measurements of  $K$  with samples from highly weathered soils rich in free oxides. Such effects should be supposed, particularly in soils with hydrated amorphous forms of oxides. Any rigorous drying should be avoided for such soils.

Besides drying, grinding and sieving are important treatments. They can modify particle surfaces important for adsorption/desorption processes and for  $K_i$  release. The finer the soil is ground, the less realistic adsorption/desorption data measured become. These effects are more important for highly weathered soils with strong oxidic particle coatings on silicate and quartz grains and/or with high contents of free oxides forming individual grains. There has not yet been sufficient study of the extent to which treatments like sieving and grinding affect  $K$  measurements in highly weathered soils but it must be assumed that this would be considerable and should be considered in data interpretation. For these soils, no grinding or only soft physical treatments (ultrasound) seem to be better for getting realistic information.

Duration of sample storage is important in that it allows establishment of a more perfect equilibrium  $K_i \longleftrightarrow K_{lab}$ , long-term fixation of  $K$  and changes due to crystallization or aging of free oxides.

## 7.5. Conclusion

Any strategy for soil K assessment must be tailored to the local or regional conditions. At the technical level, no general procedure is possible. The most reliable basis for appropriate decisions allowing efficient and reliable K assessment is the understanding for the functioning of the soil/plant system in K uptake and fertilizer K transformation. Many factors must be taken into consideration to ensure efficient work and it is essential for success that the decision on what information should be sought should be related to the purpose for which it is required. Tables 16 and 17 give some orientation for the development of a target-oriented strategy in K investigation for agronomic purposes and field-related K testing.

Table 16. What can we measure and which techniques are possible? A synoptic summary of Chapters 4 and 5.

Characteristics Parameters	Techniques	Parameter qualification*		
		Suitability	Interpretability and assessability	Importance
QUANTITY CHARACTERISTICS				
$K_t$	complete dissolution in acids; digestion in an alkali melt	B	1b/2a/3a	xxx
$K_{sol}$ , concentration	saturation extract	A?	1a/2a/3b	0
$K_{lab}$	a) pure exchange techniques	A	1b/2b/3b	xxx
	b) electrodialysis	A	1b/2b/3b	xxx
	c) desorption by resin sink	A	1a/2b/3b	xx
total content of $K_{lab}$	percolation with $NH_4OAc$	B	1b/2b/3b	xxx
fractions of $K_{lab}$	water extracts	A	1a/2b/3b	xx
	EUf 10 or 35 min.	A	1b/2b/3b	xx
	short term extraction with resin	A?	1a/2b/3b	xx
"available" or "supplyable" K	isotope exchange	B	1b/2a/3a	x or 0
	numerous empirical tests with various extrac- tants based on exchange and dissolution	A	1a/2a/3b	xx
$K_{ier}$	a) long duration percolation with salt solution	B	1b/2b/3a	x
	b) extraction with NaTPB	B	1b/2b/3a+b	xxx
	c) thermic treatment	B	1b/2a/3a	x

\* For legend, see page 94.

Table 16. Continued.

Characteristics Parameters	Techniques	Parameter qualification		
		Suitability	Interpretability and assessability	Importance
Fractions of reserve K, non-specific with regard to K forms	a) extractions with strong acid	A	1a/2a/3a	x?
	b) EUF 80°C	A	1a/2a/3a	0
	c) long duration extraction with H <sup>+</sup> resin	B	1a/2a/3a	0
K fixation capacity	wet or dry fixation under lab. conditions; no generally accepted technique	B	1b/2a/3a	x
<b>INTENSITY CHARACTERISTICS</b>				
Equilibrium intensity	K concentration in the saturation extract	A	1b/2b/3a	0
	derivation from Q/I graphs	B	1b/2a/3a	x
V <sub>K</sub> %	derived from CEC and K <sub>ex</sub>	A	1b/2a/3a	xx
Estimated intensity	from K EUF 10 min.	A	1a/2a/3a	xx?
<b>Q/I RELATIONSHIPS</b>				
Q/I graph and derived parameters	indirect measurement	B	1b/2b/3a	xxx
single point parameter	measurement of K conc. in the saturation extract and K <sub>ex</sub>	B	1a/2b/3a	0
<b>RATES AND RATE DYNAMICS</b>				
Rate of K <sub>i</sub> release	a) NaTPB extraction	B	1b/2b/3a	x
	b) resin extraction	B	1a/2a/3a	x
	c) extraction with salt solution	B	1b/2a/3a	x

Table 16. Continued.

Characteristics Parameters	Techniques	Parameter qualification		
		Suitability	Interpretability and assessability	Importance
Rates of release of $K_{str}$ by dissolution	simulation of acid attacks	B	1a/2a/3a	0
<b>BUFFER CAPACITIES</b>				
Immediate buffering	derived from Q/I graphs	B	1b/2b/3a	xxx
long to medium term buffering	a) NaTPB extraction	B	1b/2a/3a	xxx
	b) thermic treatment	B	1b/2a/3a	x
	c) derivation from data obtained in field or pot experiments	B	1a/2b/3a	xxx

Legend: Suitability A = for repeated routine testing of a large number of soils,  
B = for selected soils, preferably benchmark soils and soils from field experiments.

Interpretability and assessability

1a = difficult or imprecise in terms of the K system,

1b = good in terms of the K system,

2a = difficult in terms of K supply to crops,

2b = good in terms of K supply to crops,

3a = preferable relative evaluation in comparison to parameters of other soils,

3b = evaluation with regard to crop response or fertilizer efficiency possible; evaluation algorithms available,

Importance xxx = basic information for the complex assessment of the K status; important,

xx = useful for routine testing,

x = useful as complement to basic parameters,

0 = little or no importance for agronomic purposes.

**Table 17.** Orientation for a task-related sampling and selection of test parameters or techniques of measurement for assessing soil K.

Soil survey	K related studies of benchmark soils	K related studies of soils from field experiments	Field-related routine testing in soils of low external input cropping systems	Field-related testing and monitoring of K in intensive agriculture	Special cases
<b>Sampling</b>					
Profil samples in main soil units with reference to parent materials	Horizon-related sampling	Preferably layer-related sampling	Mixed topsoil samples, few subsoil samples; systematic subsoil sampling in highly weathered soils	Periodic sampling of mixed topsoil samples; few subsoil samples for orientation	Topsoil and subsoil sampling; mixed samples in most cases not suitable
<b>Soil testing principles</b>					
Reference to landscape units and catenary differentiation	Measurement and assessment as detailed as possible; description of the K system is recommended	Repeated sampling for discovery of changes of the K status and involvement of reserve K in supply is useful	Selection of simple and cheap tests with reliable evaluation algorithms	Selection of tests according to K demand; only tests with reliable evaluation algorithms	Problem-related selection of appropriate parameters; comparison of soil test with nutrient balances; control of geological conditions and parent material
<b>Appropriate parameters and/or techniques</b>					
$K_{ads}$ : quantity and degree of saturation; K reserve: acid extraction	$K_{ads}$ : with leaching technique ( $NH_4$ acetate);	$K_{ads}$ : with leaching technique	$K_{ads}$ or $K_{ex}$ ; K reserve: boiling $HNO_3$ for initial orientation	All tests extracting basically $K_{ads}$ are suitable.	1. No response to fertilizer K contrary to soil test indication: - fixation capacity

Table 17. Continued.

Soil survey	K related studies of benchmark soils	K related studies of soils from field experiments	Field-related routine testing in soils of low external input cropping systems	Field-related testing and monitoring of K in intensive agriculture	Special cases
K fixation: in heavy loams and clays with three layer silicates	<p>Q/I graph: indirect measurement;  <math>K_f</math>: any technique            Amount of <math>K_{ier}</math>: NaTPB extraction, 1 h;            Common soil properties required:            - CEC or <math>CEC_{eff}</math>            - texture            - pH;            Special tests: exhaustion experiment in pots, rate dynamics of <math>K_{ier}</math> with NaTPB</p>	<p>The locally common routine test(s) for comparison:  <math>K_f</math>: in bulk soil and clay + fine silt, any technique;  <math>K_{ier}</math>: NaTPB 1 h or thermic treatment;            K reserve in general: with strong acid extraction;            Special tests as with benchmark soils</p>	<p><math>K_{ier}</math>: if micas or micaceous clay is supposed; NaTPB or thermic treatment</p>	<p>With increasing K demand, preference should be given:            a) in soils with three layer silicate clay to weak extractions seizing planar K (EUF, water); additional testing for <math>K_{ier}</math> useful (NaTPB)            b) in highly weathered soils to <math>K_{ads}</math> extracted with unbuffered salt solution and by leaching technique</p>	<p>- Ca:K and Mg:K checking            - checking of the intensity level            2. Checking fertilizer policy:            - comparison of balances (field trials, farmer's field, region) with soil test value changes            3. Discrepancy balance/development of soil test level:            - fixation capacity            - release of <math>K_{ier}</math>            - K content of subsoil            4. Poor stand and/or deficiency symptoms contrary to soil test indication:            - checking intensity level            - checking Ca:K and Mg:K            - checking possibility of toxicity impacts</p>



## 8. Research problems

A critical review of K research over the past decades with special reference to the applicability of findings to improved K assessment for land use and management decisions shows that considerable progress has been made but that there are still questions to be answered.

Particularly during the sixties and seventies, successful work enlarged and deepened our understanding for the soil K system and enabled the development of new approaches to assessing the K status quantitatively:

1. Improved concepts and techniques for investigation of silicate clays and the application of thermo-dynamic approaches to the transformation of labile K generated a more precise idea about the adsorption/desorption relationship of labile K in soils with three-layer silicates.
2. The application of new techniques, particularly the use of NaTPB for the extraction of  $K_i$  from standard and soil clays, brought forth considerable progress in the understanding of the significance of  $K_i$  release from micaceous clays.
3. Both realizations resulted in a clearer idea about buffering in the system  $K_i \longleftrightarrow K_{ads} \longleftrightarrow K_{soil}$  and its role in K supply to crops.

It was mainly the versatile K related research in the period 1960-1980 which produced the facts and interpretations for describing the K system of soil as we understand it today.

Significant contributions to a better insight in soil/plant relationship with regard to nutrient supply and nutrient uptake came from researchers investigating processes in the soil/root contact space. Their findings enabled us to interpret the K system more dynamically and complexely.

However, regardless of all progress made, gaps and weak points in K research cannot be overlooked. Some of the resulting research requirements concern the following problems:

1. Characteristics and dynamics of the adsorption/desorption equilibrium of labile K and the buffering behaviour of inorganic variable charge soils.
2. Peculiarities of K transformation in wetland soils, especially inorganic, but also organic ("paddy soils").
3. Relationship between K supply to soil solution and K translocation in the solution with regard to improved K assessment by (semi-) quantitative mobility assessment.
4. Interactions between the K system of soil, soil moisture dynamics and fertilizer K in areas with strong moisture fluctuations and their impact on fertilizer K efficiency.

Actually, the weakest point in the state of the art seems to be the onesidedness as concerns the kind of soils studied. Our findings and the modern understanding of the K system refer almost exclusively to soils with silicate clay, mainly three layer silicate clay. The number of studies reported dealing with the K system of highly weathered soils with oxidic clay is relatively small. This is especially true with regard to studies using modern approaches and techniques. As was repeatedly indicated in the foregoing chapters, our knowledge about the K system of highly weathered tropical soils and our ability to consider their specificities in measuring and assessing soil K are significantly less developed than those for soils with silicate clays.

As compared with the boom in K-related research in the sixties and seventies, a certain hesitation of researchers to tackle the problems of K in highly weathered soils must be noted. There are understandable reasons for (e.g. priorities of nutrient research in developed and developing countries; unfavourable location of well equipped research centres; low level of purchase of K fertilizer in underdeveloped regions, etc.). However, the proportion of highly weathered soils in agricultural land in the tropical countries and the role of K in developing sustainable cropping systems adopted to these soils require enhanced research activities. Some urgent needs in K research for highly weathered soils are listed in Table 18.

**Table 18.** Research needs to improve the understanding of the K system of highly weathered variable charge soils and the assessment of their K status.

1. Elaboration of techniques to measure and to assess the adsorption/desorption equilibrium of labile K.
2. Quantification of effects of pH fluctuations, liming, organic matter inputs and impacts of anions on the adsorption/desorption equilibrium of K.
3. Clarification of the importance of residual primary and secondary micaceous minerals for the fixation and buffering behaviour with regard to K and  $\text{NH}_4$ .
4. Study of peculiarities of water storage and water movement in highly weathered soils according to their spatial organization and to their impact on nutrient storage and leaching losses.
5. Quantification of effects of sample treatment on measured K parameters.

More generally and with a view to improved K assessment, it seems to be necessary to devote more work to improve interpretation of measured parameters and their evaluation instead of searching for new extraction techniques. More diversified rating systems based on differing soil qualities and levels of nutrient demand are needed.

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