Proceedings of the 20th Colloquium
of the International Potash Institute
held in Baden bei Wien/Austria 1987

METHODOLOGY IN SOIL-K RESEARCH

International Potash Institute
Bern, Switzerland

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Chairman of the 20th IPI-Colloquium

Prof. Dr. *O. Steineck*, Director, Institute of Crop Husbandry and Plant Breeding, Agricultural University, Vienna/Austria; member of the Scientific Board of the International Potash Institute

Opening Session

Welcome address

Dr. N. *Celio*, Former President of the Confederation of Switzerland; President of the International Potash Institute

Ladies and gentlemen, distinguished guests,

I extend to you on behalf of the Board of the International Potash Institute a hearty welcome to this 20th Colloquium in the charming atmosphere of Baden bei Wien.

As the official languages of the Colloquium are English and German you will perhaps allow me to pronounce this welcome also in the language of Shakespeare, which I do in the knowledge that our interpreters will be well able to make good any errors in my pronounciation. I am confident that two working days with a third day set aside for the technical excursion will be spent in the congenial atmosphere of an international family gathering and that this will help us to clarify some of the fundamental problems of methodology in potassium research.

We are indeed fortunate that our Austrian friends, led by Professor *Otto Steineck*, member of our Scientific Board and President of this Colloquium, invited us to hold this meeting in Austria where we last met in a Congress 30 years ago. This country's fundamental research into agricultural problems has for long occupied a leading position in Europe. Austria and the Austrian people have for centuries exercised a magnetic power on account of their prominence in the fields of art, science and technology. This country was the centre of the great Austro-Hungarian Empire with its many different peoples. Now much smaller in area, Austria and her capital city have lost none of their importance as a bridge between East and West Europe; on the contrary, it seems that this role has become even more important and indeed indispensable.

The choice of venue, on the advice of Professor *Steineck*, fell on Baden bei Wien and there were several reasons for this. The subject of the colloquium embraces fundamental problems which will tax your intellectual concentration. It is possible to concentrate only in a quiet and restful atmosphere and this is certainly to be found here; Baden bei Wien offers a creative atmosphere for scientific discussion.

We also thought that Vienna with its pulsating life and many cultural attractions is already well-known to many of you, or, if not, this is an omission that will sooner or later be corrected, while the essentially Austrian small town of Baden offers attractions which are no longer easy to find.

The topic of this 20th Colloquium «*Methodology in Soil K Research*» is of worldwide importance. On this occasion we are not confined within the limits of a particular climatic zone or type of agriculture. Scientific research into the problems of soil potassium is being persued worldwide but there are plenty of uncertainties as to the most efficient methods. The *International Potash Institute* is not concerned with the current methodological strife but rather hopes, as the programme demonstrates, to clarify fundamental principles.

Thanks to the wide contacts of the members of the Scientific Board it has been possible to find truly authoritative and internationally recognised contributors to deal with the interlocking problems of our theme. We are indeed grateful to our speakers.

A main aim of the *Scientific Board* is that the Colloquium proceedings will be a reference source for all engaged in the relevant fields of study.

One further point: we originally intended to restrict attendance at this specialised meeting to 70 or 80 specialists. This we failed to achieve. Although the Colloquium received minimum publicity, we find ourselves welcoming today 138 participants from 24 countries. We have no regrets – «Nothing is here for tears, nothing to wail or knock the breast».

And so to work. I wish you all a fruitful Colloquium!

Chairman of the 1st Session

Prof. Dr. *H. Laudelout,* Dept. of Soil Science, Catholic University of Louvain-la-Neuve/ Belgium; member of the Scientific Board of the International Potash Institute

1st Session

Mineralogy of Soil-K

Current Aspects of the Mineralogy of Clays and Soils

G. Pedro, Soil Science Station, INRA, Versailles/France *

Summary

The aim of this paper is to present the new look of soil mineralogy, and especially soil clay mineralogy, so as somewhat to redefine the relationships between the mineral constituents of the soil and potassium.

The standard method for characterising separated soil minerals is reviewed. Despite recent improvements in the study of structure and polycrystallinity, this has its limitations. Current problems are then discussed under:

- Mineralogical characterisation of undisturbed soil samples in the dry state: optical and electron micromorpholgy in association with X-ray diffraction and electron probe micro-analysis.
- Mineralogical characterisation of undisturbed hydrated soil samples: the significance of electron-microscopy (SEM and HRTEM) and of small angle scattering (SAS).

The results of current research concerning the different levels of organisation (structure, texture and plasmic fabric) are then presented as they relate to the chief characteristic clays of soils.

Dénominations des Méthodologies / Names of Methods

(see also paper by *Tessier*, page 45)

Diffraction des rayons X	= X-ray diffraction (XRD)
Diffraction interparticulaire	= Interparticle diffraction
Diffusion aux petits angles	= Small angle scattering (SAS)
Microscopie électronique à balayage	= Scanning electron microscopy (SEM)
Microscopie électronique à transmission	= Transmission electron microscopy (TEM)
Microscopie électronique à haute résolution	= High resolution transm. elect. microscopy (HRTEM)
Microscopie électronique analytique à balayage	= Scanning transmission electron microscopy (STEM)

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Spectroscopie infrarouge = Infrared spectroscopy (IR)
Résonance paramagnétique électronique (RPE) = Electron spin resonance (ESR)
Résonance magnétique nucléaire (RMN) = Nuclear magnetic resonance (NMR)
Spectromètre à dispersion d'énergie = Energy dispersive spectrometer (EDS)
Spectromètre à dispersion de longueur d'onde = Wavelength dispersive spectrometer (WDS)
Spectroscopie d'absorption optique = Optical absorption spectroscopy
Spectroscopie d'absorption des rayons X = X-Ray absorption spectroscopy
EXAFS: Extended X-ray absorption fine structure.

1. Introduction

Soils are dominated by the mineral components (some 90% by weight and 45% by volume) and it is certain that improved understanding of the minerals must lead to improved understanding of soil properties. Soil mineralogy remains a fundamental part of soil science; soil potassium relationships must be approached from the standpoint of mineralogy. This is not an easy field of study because soil is a special kind of material.

- First, the soil is an *unconsolidated* system, a «divided» solid; it is not just made up of different mineral species, but each species identified occurs as a great number of particles of varying size, often extremely small ($<0.1\ \mu m$). Actually, it is a population. Illustrative of this point is that 1 cm^3 clay plasma contains from $200 - 400 \times 10^9$ particles.
- Second, it is a *hydrated* solid, water normally being adsorbed to the solid phase. This adsorbed water, which corresponds to water of crystallisation or subjected to surface tension ($\varnothing < 1\mu$), should be considered an integral part of the solid constituents, and is therefore concerned in the characterisation of soil minerals. This is true to the extent that *Millot [1964]* defined the clays as «the most typical representatives of the hydrosphere silicates».
- Finally, it is an *organo-mineral* system – a medium where there are interactions between organic compounds and mineral units.

All this means that soil mineralogy cannot be understood just by simple application of the methods of classical mineralogy but that soils occupy a special position. However, ideas and methodology in the study of soil minerals have made great progress in recent years.

Discussion will fall under the following headings:

- the use of classical mineralogy,

- a review of progress in the study of soil minerals after extraction and separation,
- recent *in situ* studies (undisturbed moist samples),
- finally, some applications and perspectives concerning present knowledge.

2. Review of classical methods in mineralogy

The classical approach is concerned only with the characteristics of the minerals themselves quite independent of other considerations (location, distribution, environment ...). Since the soil is made up from an arrangement of crystalline mineral elements of variable size, it is necessary to obtain reasonably homogeneous (type and dimensions) samples to work on which; they can be sorted first on size (particle size separation) and then on other properties, *e.g.* density (heavy minerals).

Two main groups can be distinguished:

a) Large particles (macro-crystals) which can be examined in the same way as *individual* crystals (individually and in isolation).
b) Small particles (micro-crystals) in the study of which the heterogeneity and polycrystallinity of samples must be taken into account.

2.1. Study of macro-crystals relies on familiar methods

Such as: the study of crystal form (geometric crystallography), optical properties, chemical composition. These can be observed with the naked eye (macroscopic), or by binocular magnifier (sub-macroscopic); use of the polarising microscope on thin sections which renders the minerals transparent (*Sorby [1845]*); normal chemical analysis.

Such a procedure is usually enough to describe the mineral; but it can be taken a stage further by more detailed work using X-ray diffraction on individual crystals to indicate the atomic structure. Precise identification is possible using reference tables.

2.2. The characterisation of samples made up from small particles is a much more delicate matter

This is the usual situation with the clay fraction. Here we are dealing with samples of mixed mineral composition (several mineral species in association) and which are always polycrystalline (numerous crystals within a given species).

Up to 1930 the problem was virtually insoluble. The optical microscope had insufficient resolution to yield useful information. Chemical composition reflected only the average.

Progress became possible first with X-rays and then with the electron microscope.

The favoured method uses the powder method of Debye-Scherrer – diffraction of monochromatic X-ray by polycrystalline samples. The diffraction is characteristic of the nature of the substance and in particular of its atomic structure (application of Bragg's law).

Measuring the X-ray diffraction pattern the peaks (001) and (hkl) gives information on the crystalline constituents of the powder.

The method has played a major role in the study of soil clays (Ø‹ 2 μm), which have been shown to be phyllosilicates made up of layers 7, 10 or 14 Å thick, with fixed or variable inter-layer spacing. However it is limited because the individual clay particles cannot be «seen» in isolation and it does not indicate the diversity of particles within the same species. The morphological study of small particles had to await the availability of transmission electron microscopy (TEM) (*Beutelspacher and van der Marel [1968]*) used with the electron microprobe to obtain information on the chemical composition of isolated small particles.

All this opened the way for a standard methodology for study of microcrystalline elements of the soil and it is worth recalling the main lines which have been followed and their limitations.

2.3. Value and limitations of the standard method for characterising the constituents of the clay fraction of soils

Here we refer to the application of X-ray diffraction to air-dried soil samples, either pre-treated or not, and, in some cases, to the same samples impregnated with poly-alcohols and/or dried at high temperature (300–500° C).

The method is valued for its simplicity in use and for the results it gives. It described the main types of clay minerals (*cf.* the international nomenclature AIPEA [Table 1]). Main points can be summarised:

- the data obtained result from the X-ray properties and relate to the *elementary structural units* of the layers and interlamellar space of which the degree of expansion is given by the equidistance (001). It throws no light on the structure of larger particles such as crystallite.
- It can only distinguish the main groups (chlorite, vermiculite, smectite); it rarely defines the mineral species.
- Because the minerals examined in this way are *anhydrous or only weakly hydrated* (Figure 1), the data are not applicable to real soil conditions. For the non-expanding minerals (kaolinite, illite ...) this is of little consequence, but in others (vermiculite, smectite) it is.
- finally, this approach is *global*, reflecting only the average of a large number of crystals, and so gives a mean value both as regards geometry (spacing, type of stacking, degree of organisation ...) and chemistry (composition).

All properties except the thickness of the structural units, *i.e.* those relating to stacking, are difficult of access though they can be understood in macrocrystals (polytypes)[1]. Because of this, ideas about interstratification deriving from the superposition of different layers (interstratification) or about crystallinity (as in illites *Kubler, [1966, 1968])* can only be approximate.

To conclude, the standard method has been of great service in relation to the small mineral particles, but being relatively easy in use and having acquired reputation and some prestige, it has resulted in a picture which is both *simplistic* and *incomplete* and which distorts the true facts. It has led to a very restrictive picture of the mineralogy of soil constituents:

- It is an essentially typological approach based on characteristics of the mineral species without taking account of questions of form, arrangements and associations within the whole system;
- It is a concept based exclusively on crystallography, that is «mean» characterisation of the layers present in the sample (interlamellar spacing and crystal-chemical constitution).

  This was the state of affairs for fifty years or so. It is only since 1975, thanks to the availability of new apparatus and new methods that there has been development, at least in some research laboratories. There have been two main avenues of progress:
- the first, further study of separated minerals, refining previous work;
- the second entirely different approach attempted to study the constituents in situ *in the natural environment.*

Table 1. General scheme for classification of phyllosilicates (AIPEA, 1966 – 1980)

Type and spacing of layer	Interlayer constitution			Spacing of structural unit d (001)	Layer charge* z	Group
2/1 Te-Oc-Te (10 Å)	Interlayer empty		without cations	10 Å	0	Pyrophyllite-Talc
	Interlayer occupied	Cations	Hydrated cations	(10 + Δ) Å Δ variable	$\sim 0{,}25 < z < \sim 0{,}6$	Smectites
					$\sim 0{,}6 < z < \sim 0{,}9$	Vermiculites
			Cations not hydrated	10 Å	$z \sim 1$	Micas
					$z \sim 2$	Brittle micas
		Hydroxide sheet		14 Å	z variable	Chlorites
1/1 Te-Oc (7 Å)	Interlayer empty	without cations		7 Å	0	Kaolinite Serpentines

(*) Corresponding to formula T_4O_{10} for phyllosilicates.

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[1] Only totally disorganised stacking of layers, known as turbostratic can be recognised: disappearance of lines (hkl) and the appearance of wide bands (hk).

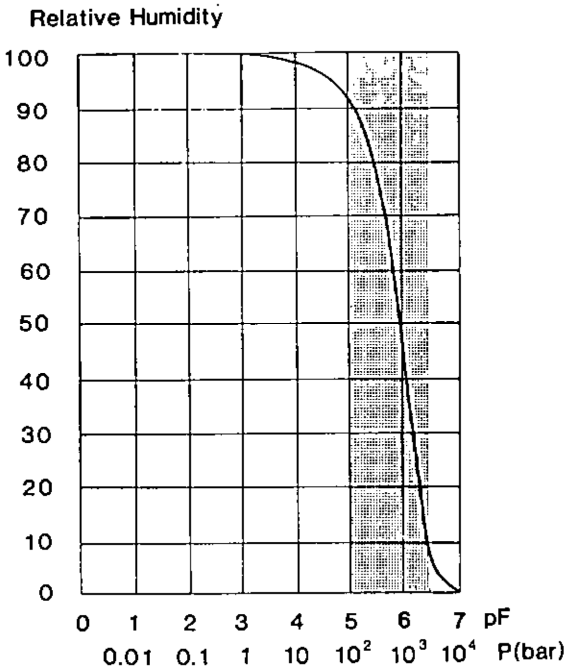


Fig. 1. Variation in constraint (suction) on water in the soil system related to relative humidity of the air.
The shaded area represents normal conditions of clay study. The pF range 0-5 corresponds to the biological activity.

3. Recent progress in the study of separated soil minerals (clays)

Two aspects are mentioned:

- Refined study of the structure of the elementary unit of the mineral and of the layer in particular in the case of clays; this concentrates on the typology of the mineral species.
- Attempts to elucidate structure of *particles* (of the same species) present in a sample aiming at a populational view of the various minerals.

3.1. Improved knowledge of structure

Improvement has come about with the development of new methods in solid physics: infra-red spectroscopy (IR) – X-ray absorption spectroscopy – absorption spectroscopy (optical 400-1700 mm) – high resolution transmission electron microscopy (HRTEM) – nuclear magnetic resonance (NMR) – paramagnetic electron resonance (PRE) – Mossbauer effect ...

We confine ourselves to presenting some examples to show that things are not as simple as formerly thought; whether it be at short or moderate distance: 2-5 Å (atomic absorption spectroscopy) or at larger separation: ~ 10 Å (EXAFS and HRTEM).

a) Without debating the nature of a phyllosilicate, it appears that homogeneity of structure is not always the rule. Thus *Bonnin [1981]* has shown by considering magnetic properties, that in nontronite (ferriferous smectite) the actual structure of the layer consists of islets of ordered zones of small dimensions dispersed in a random manner in a disordered whole (Figure 2). Similarly *Manceau [1984]* in a study of mixed Mg-Ni clays showed that the distribution of nickel in relation to magnesium in the octahedral layer was not random but that there was always «segregation». This segregation is shown (Figure 3) at the level of the individual layer by zones or domains enriched in Ni, such is the case with 7 Å clays (Lizardite-Nepouite); or at the level of different layers in a particule of a given species: some, entirely nickeliferous, are distributed in an assemblage of magnesian layers; *e.g.* 10 Å clays (Kerolites-Pimelites).

In another direction, HRTEM using high voltages has a resolution of the order of 1 – 1.5 Å (atomic range) and makes it possible to obtain «pictures» of the atomic structure of minerals (lattice imaging).

This has led for example to:

- looking into the structure of minerals (Figure 4) and even in some cases defining the position of interlayer K^+ ions in a micaceous clay (so-called «canal» structure).
- direct description of the different types of stacking (polytypes) even showing up faults in the stacking (Figure 4).

b) Also, with the aid of these new methods (notably HRTEM) evidence of abnormal structures and phenomena of intergrowth have been discovered. We may mention:

- the existence of different types of serpentine minerals (7 Å): lizardite, chrysotile and antigorite having the same general composition ($Si_2O_5Mg_3(OH)_4$); the wavy appearance of antigorite resulting from the presence of «abnormal» layers (Figure 5).
- The discovery of constituents whose structure partakes at the same time of pyroxenes, amphiboles and trioctahedral micas and for which a special designation has been coined: *biopyroboles (Thompson [1978]; Chisholm [1981])*. The existence of such structures results simply from the presence in the 3 types of silicates of apparent beam-modules (Figure 6) which can be associated in varying proportions in the building of *hybrid* units. *Martin Vivaldi and Linares Galego [1962]* had already postulated the possibility of intergrowth between two fibrous clays: palygorskite and sepiolite.
- Finally, phenomena of intergrowth of layers of differing type, like talc (T), chlorite (Chl), lizardite (S) have been observed in the same particle *(Busek and Veblen [1981])*.

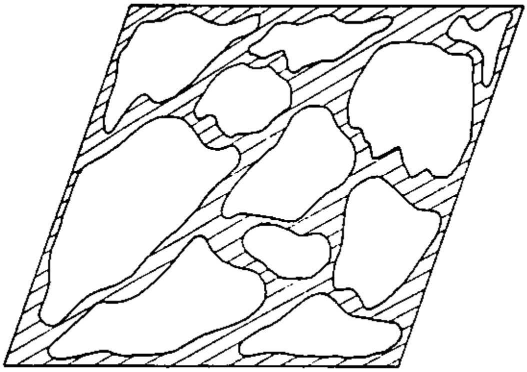


Fig. 2. Actual structure of nontronite layer seen perpendicularly (001) after *Bonnin [1981]*. Clear areas are well crystallised, hatched areas poorly crystallised.

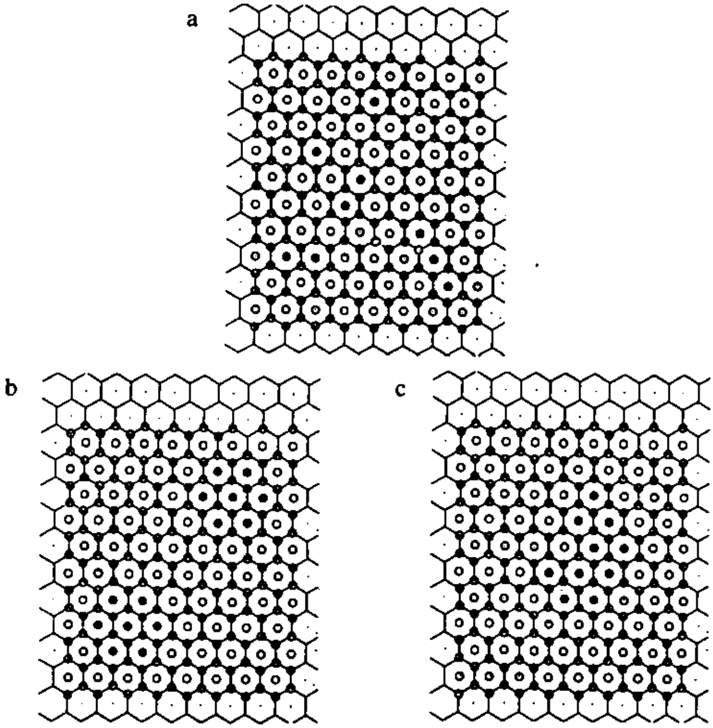


Fig. 3. Model distribution of nickel atoms (black circles) and magnesium (empty circles) with Ni/Ni+Mg = 0.12. After *Manceau [1984]*.
a) random distribution
b) and c) two types of segregation

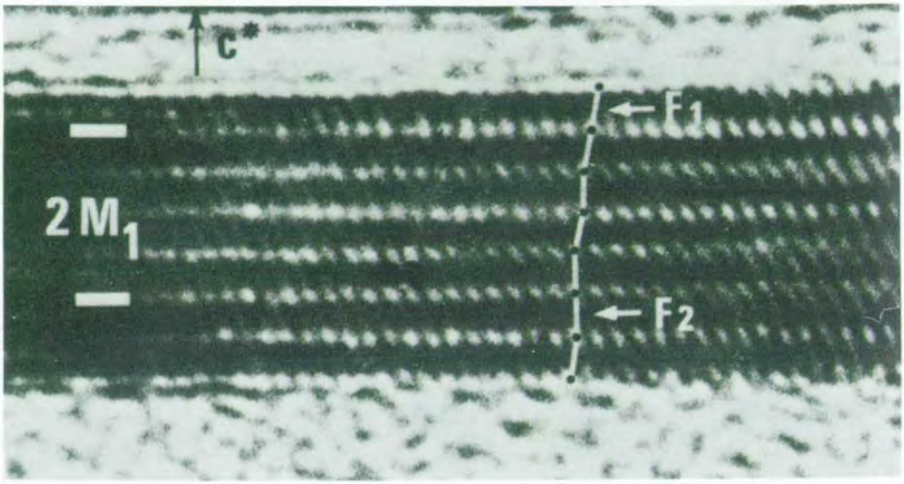


Fig. 4. Structural image of muscovite crystal 2M$_1$ seen at (100) by HRTEM. Open points are lacunae between interlayer K$^+$ ions. Note the 2 stacking faults F1 and F2. After *Amouric [1981].*

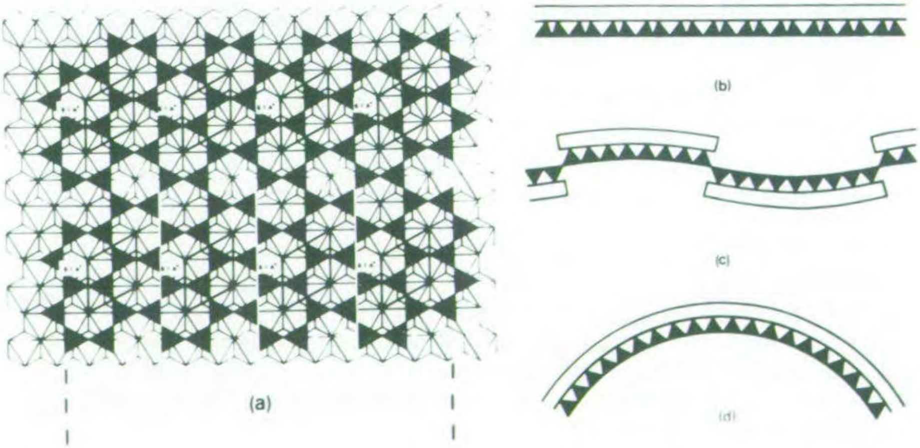


Fig. 5. Structure of serpentine (a) layer in plan (b) typical lizardite with flat layers (c) antigorite with wavy layers (d) chrysolite with rolled layers.

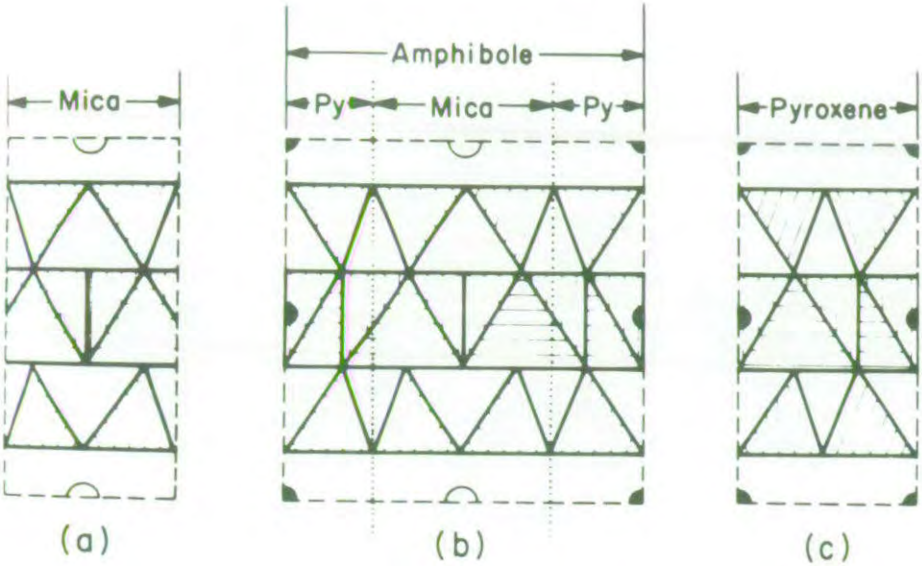


Fig. 6. Beam-modules of biopyroboles seen in section. After *Thompson [1978]*

3.2. Improvement in recognition of polycrystallinity

The study of entities larger than the layer became possible with the introduction of electron microscopy which could show them up in dispersed samples. We mention two aspects:

- The search for the existence of an elementary particle characteristic of each type of clay (electron microscopy);
- Study of the chemical homogeneity of the various particles constituent in the same mineral species (electron microdiffraction and electron probe).

a) So far as concerns the former, attempts have been made to identify the elementary particle of various minerals *(primary particle (Mering and Oberlin [1971])* or *fundamental particle (Nadeau et al. [1984])*. According to this concept, each clay would be made up by face-to-face aggregation of these elementary particles.

Also, when the particles are very small (<50 Å) the indications of X-ray diffraction actually result from disordered stacking of particles (interparticle diffraction; *Nadeau et al. [1984, 1985]*); the width of coherent diffusion then being greater than the thickness of the particle.

Thus according to *Nadeau*, the illites are distinguished by the thickness of their fundamental particles (Figure 7) on which basis they can be divided into two groups:

- $e > 50$ Å – well crystallised illites showing intraparticle diffraction;

- $e < 50$ Å – weakly crystalline illites of smectitic type showing interparticle diffraction.

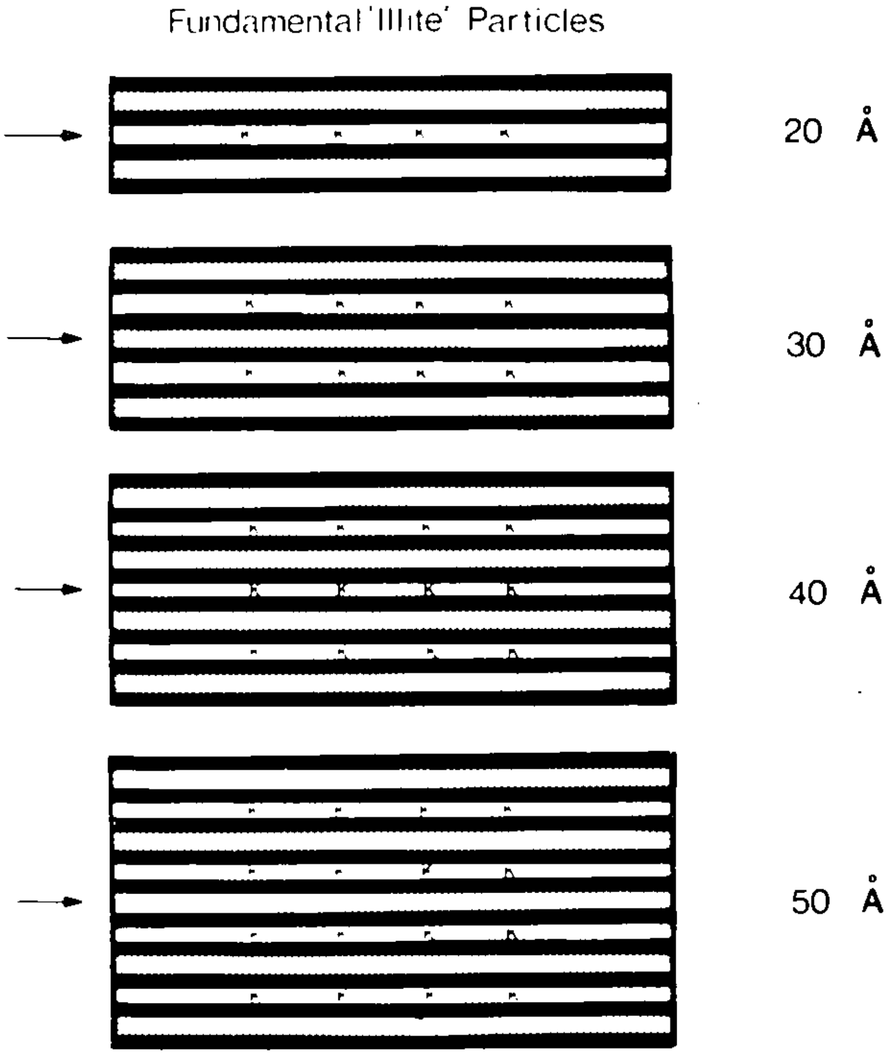


Fig. 7. Model of section through fundamental particle of illite – after *Nadeau et al. [1984]*. Black areas represent tetrahedral layers, grey the octahedral and K position of interlamellar cations.

Table 2. Distribution of cations among tetrahedral and octahedral sheets and K amount (on the basis of 22 negative valencies) for particles of 4 minerals taken for example, *i.e.* glauconite, stevensite, nontronite, illite

	Tetrahedra	/	/	Octahedra		/	
	Si	Al(tetr.)	Al total	Al(oct.)	Fe^{3+}	Mg	K
Odin glauconite							
6	3.65	0.35	0.54	0.19	1.40	0.31	0.85
20	3.70	0.30	0.655	0.355	1.17	0.485	0.72
23	3.69	0.31	0.72	0.41	1.12	0.485	0.69
26	3.88	0.12	0.93	0.81	0.75	0.43	0.52
29	3.55	0.45	0.57	0.12	1.485	0.40	0.79
39	3.80	0.20	0.655	0.455	1.24	0.20	0.67
Ibel Ghassoul stevensite							
4	3.945	0.055	0.15	0.095	0.09	2.70	0.07
15	3.83	0.17	0.35	0.18	0.08	2.63	0.11
16	3.95	0.05	0.78	0.73	0.30	1.40	0.15
18	3.97	0.03	0.32	0.29	0.01	2.51	0.09
25	3.92	0.08	0.10	0.02	0.06	2.89	0.03
33	3.92	0.08	0.62	0.54	0.17	1.93	0.08
43	4.00	—	0.20	0.20	0.03	2.55	0.06
Galapagos nontronite							
1	3.865	0.135	0.29	0.155	1.46	0.47	0.29
2	3.995	0.005	0.17	0.165	1.47	0.26	0.53
3	3.84	0.16	0.16	—	1.70	0.23	0.66
5	3.88	0.12	0.16	—	1.67	0.17	0.66
7	3.92	0.08	0.35	0.27	1.23	0.44	0.67
8	3.95	0.05	0.51	0.46	1.31	0.21	0.31
16	3.65	0.35	0.35	—	1.43	0.76	0.58
29	3.86	0.14	0.22	0.07	1.48	0.64	0.16
Trias illite from the Pyrénées							
3	3.13	0.87	2.55	1.68	0.18	0.40	0.44
7	3.17	0.83	1.70	0.87	0.315	1.31	0.60
12	3.13	0.87	2.27	1.40	0.24	0.77	0.41
14	3.215	0.785	2.515	1.73	0.10	0.34	0.58
27	2.995	0.005	2.32	2.315	0.28	0.69	0.805
30	2.94	0.06	2.08	2.02	0.31	1.21	0.63
33	2.855	1.145	2.235	1.09	0.35	1.05	0.70
53	2.89	0.11	2.12	2.01	0.49	1.055	0.47

The value of this kind of approach is in having shown the need to introduce parameters relating to the dimensions of the crystalline entities in describing fine minerals (not confined to the layer). Its value is limited as it is confined to measurements on samples obtained by vigorous dispersion and it is not known whether this simply separates the original units or whether it also results in artificial fragmentation. In any case, we are here dealing with conditions very different from those in the natural soil.

b) The second aspect concerns the chemical homogeneity of clay crystals (Ø < 2 µm). Here we can cite the work of *Duplay [1982, 1984]* on chemical analysis by electron microprobe of 15 – 20 particles of pure clay. These analyses showed that each «species» is made up of a population of particles of different chemical composition (Table 2); thus classical analytical methods give only a mean of dispersed point values.

Two general conclusions can be drawn:

- At least in the case of typical clay particles the concept of species should become one of a *population*.
- Secondly, most of the time there is continuous variation in chemical composition between extreme values. Because of this, it appears as though the various layers of a 2 : 1 clay make up a continuum of variable composition like a solid solution.

Such results are most instructive in that they call for reconsideration of results which have been accepted up to now. Nevertheless they result from work on clay suspensions which do not necessarily correspond to conditions in the soil. Hence it has been essential to initiate mineralogical studies of undisturbed and undispersed soil materials.

4. Present status of the knowledge of soil minerals; importance of the «ecological» approach to mineralogy

The great progress made in this area over the past ten years has been made possible by being able to make studies of mineralogy directly on natural soil samples. This goes beyond the usual methods using separated minerals and takes into account the environment of the mineral, its degree of hydratation, its situation, and its relationships with its neighbours. Work has been done both on air-dried materials and on hydrated samples, *i.e.* in their field state of hydratation or hydrated to varying degree.

4.1. Mineralogical characterisation of undisturbed dry soil samples.

4.1.1. Methodology

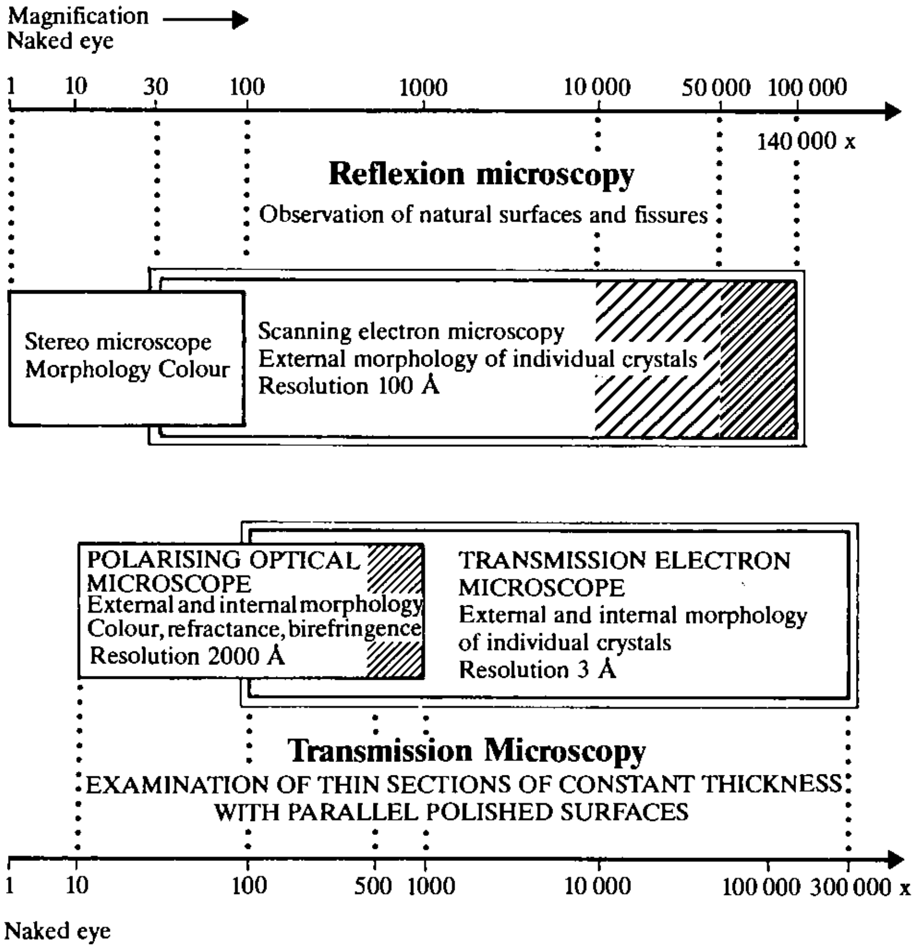
Progress became possible when the advantages of impregnating the soil with synthetic resins were realised for the preparation of thin sections for microscopic examination of soil samples ... Following the early work of *Delage and Lagatu [1904]*, *Kubiena [1938]* developed this research before the war and it was carried further by

Brewer [1964] and then by *Bullock et al. [1985]*. Nowadays it is called «soil micromorphology».

All *in situ* work comprises several operations: morphological description, diffraction studies, X-ray microanalysis.

a) The morphology can be studied in various ways:
- in natural light for submacroscopic examination by reflectance (stereo microscope) and by transmitted light with the microscope.
- submicroscopic examination by reflexion with the scanning electron microscope (SEM) and/or microscopic and ultramicroscopic by transmission (TEM and HRTEM). This is summarised in Table 3.

Table 3 Comparison of various methods for microscopic examination



b) In using X-ray diffraction (XRD) to study fine minerals *in situ*, two procedures have been used: direct diffraction on thin sections *(Wilson and Clarke [1978])*, which is difficult; diffraction on small samples taken from thin sections *(Meunier and Velde [1982], Beaufort et al. [1983])*. The latter involves very small amounts of material (10^{-1} – 10^{-2} mg) tedious to prepare, using micro-sampling apparatus *(Proust [1983])* (Figure 8), and diffraction analysis along with a proportional detector or preferably a linear detector *(Proust [1986])*.

c) Micro-analysis can be achieved easily with the electron microprobe [1949]. This analyses the X-ray spectrum emitted by the sample under a beam of electrons using energy dispersive spectrometer (EDS) or wavelength dispersive spectrometer (WDS). The volume of the sample analysed is of the order of several μm^3. The localisation of the zone examined has been improved with the introduction of scanning transmission electron microscopy (STEM) along with the X-ray spectrometer *(e.g. Rautureau and Steinberg [1985])*; in effect this is nano-analysis.

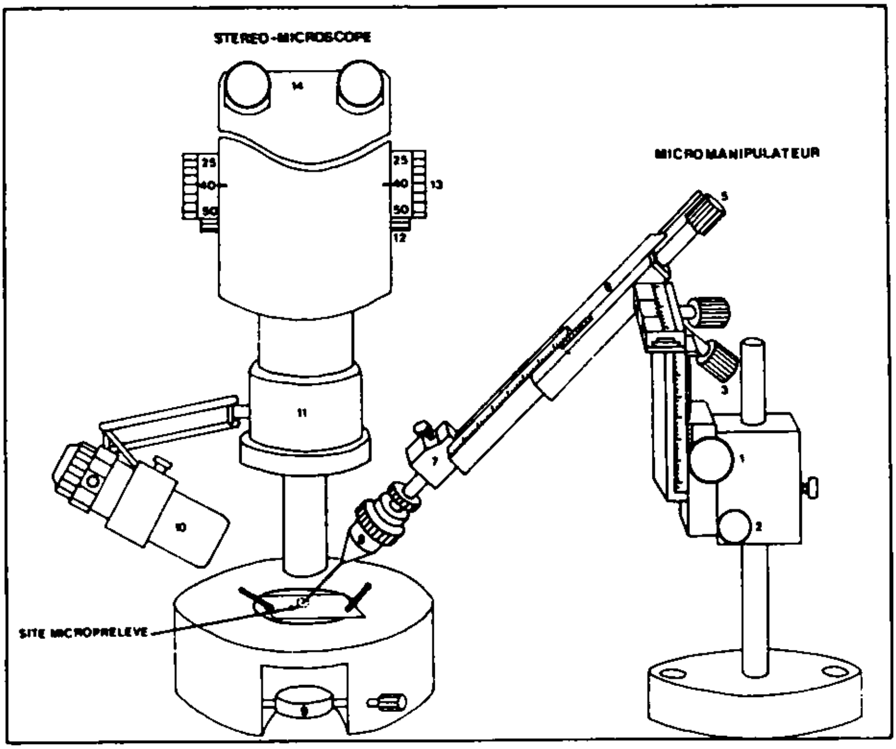


Fig. 8. Apparatus for taking thin sections. After *Proust [1983]*.

4.1.2. Present-day in situ *mineralogical studies*

It is not enough to know the general mineralogical composition of a soil sample however precise it may be; it is also necessary to include other aspects such as mineral dimensions, their respective arrangement, origin and location in the system to complete the picture. Minute examination *in situ* (submacroscopic, microscopic and ultramicroscopic) has confirmed the approach based on granulometric separation and a specific soil nomenclature has been established.

Thus we have:

- *Residual minerals* (primary minerals of the parent material) which make up the soil «skeleton» *(Brewer [1964])*
- *Weathering (or secondary) minerals* which arise by superficial pedological evolution and which are characteristic of soil (clays, oxides and hydroxides, carbonates ...). These take various forms *(Brewer [1964])*:
  - typically they are of colloidal dimensions (< 2μm) and are called *plasma* (clays, oxyhydroxides ...);
  - others are larger, either neoformed oxyhydroxides which are concentrated and form large crystals (cristallaria) or larger phyllites (kaolinite, micas ...)

  Supplementary descriptions apply to arrangement origin and location in the plasma.

a) Regarding arrangement, the plasma is characterised by its birefringence; thus we say:

- heterogeneous *(heteroplasma)* when there are anisotropic domains; it may then be *asepic* (no plasmic separation[1]) or *insepic* (with several plasmic separations isolated in islets);
- homogeneous where there are 3 types:
  - *isotic* when it is entirely isotropic;
  - *undulic* if the plasma is weakly anisotropic but shows a less distinct undulant extinction;
  - *cristic* when the plasma, in general anisotropic, is formed from optically identifiable crystals.

b) From the point of view of origin and localisation, it is observed that the nature and aspect of individual mineral species formed in pedogenesis is a function of their position and of the mode of formation. One can thus connect the transformation product with *microsite* and put forward the notion of «microsystem evolution» *(Meunier and Velde [1976]; Ildefonse et al. [1979])*. Thus in a soil developed on crystalline rock the secondary minerals formed in the course of weathering (on the large scale) can be associated with 3 kinds of microsystems (Figure 9):

- *Contact microsystems* which are concerned in all the early stages of alteration when the primary minerals are still contiguous.
- *Plasmic microsystems* which appear when the rock becomes friable and the endogenous minerals are degrading to give a clay plasma. Three stages can be distinguished here:

---

[1] Plasmic organisation exhibits striated extinction.

- *Destabilisation surfaces* along mineral fissures, cleavages and fractures,
- *Primary plasma* which develops within the primary mineral,
- *Secondary plasma* which results from redistribution of primary plasma in proportion to the progress of weathering of the rock and the resulting rearrangement (pedoplasmation).

– *The system of fissures* apparent when the pedoplasma develops structure with general enlargement of fissures and pores through which water can circulate rapidly.

Each of these microsystems can have a nature, a crystal chemistry and a sphere of influence of its own. This will be dealt with in the following for the micaceous clays (illites) for illustration, but we can here cite examples of differentiated primary plasma. Thus, according to *Proust and Velde's [1976]* results, the evolution of amphibolites made up in essentials from plagioclase and hornblende (La Roche l'Abeille – Haute Vienne, France) leads to uniformly smectitic alteration.

Microscopic and microanalytical procedures have shown that we are concerned in fact with 2 different smectites (Figure 10):

– smectite formed from plagioclase which is an aluminous beidellite;

– smectite formed from hornblende which is a ferriferous beidellite.

It is not surprising that smectitic clay in the evolving B horizon appears to be aluminium-bearing, though in fact it is a mixture of particles of different species of the same group *(Duplay [1982, 1984])*.

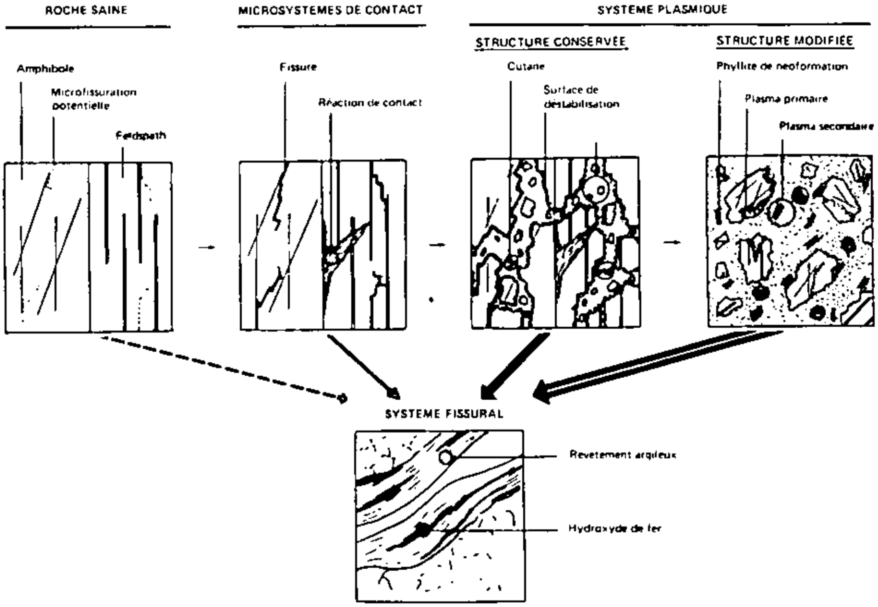
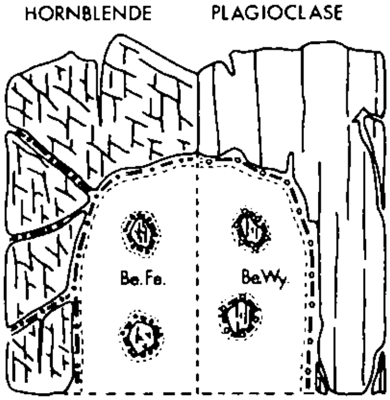


Fig. 9. Main pathways of weathering of crystalline rock. After *Ildefonse et al. [1979]*



Altération Hornblende	$[Si_{3,42}\ Al_{0,58}]O_{10}\ [Al_{0,96}\ Fe^{3+}_{0,79}\ Ti_{0,02}\ Mg_{0,23}](OH)_2\ Ca_{0,11}\ Na_{0,02}\ K_{0,03}\ Mg_{0,20}$
Altération Plagioclase	$[Si_{3,61}\ Al_{0,39}]O_{10}\ [Al_{1,35}\ Fe^{3+}_{0,34}\ Ti_{0,01}\ Mg_{0,30}](OH)_2\ Ca_{0,10}\ Na_{0,14}\ Mg_{0,16}$

Fig. 10. Localisation and composition of neoformed smectites during alteration of amphibolites at La Roche l'Abeille. After *Proust and Velde [1978]*

4.1.3. Application to a better knowledge of the micaceous clays (illites)

Granitic soils of the temperate regions are always characterised by the presence of micaceous clays of the type «illite», even if the crystal form is quite variable and the beginning of expansion is evident. The general term covers several «species». *Meunier [1977]* has shown in his research on the weathering of granite in the Vendée that there may be 4 categories of phyllites (Figure 11):

- The first 2 are microcrystalline (100 – 200 µm); these are small muscovites and sericites.
  - *Small muscovites* (100 – 150 µm) appear on perpendicular faces in cleavages of the large muscovites and are associated with fine strands of quartz. They become evident towards the end of the crystallisation process by pneumatolytic alteration of feldspars:

    $3KAlSi_3O_8 + 2H^+ \rightarrow (Si_3Al)\ O_{10}Al_2\ (OH)_2K + 6SiO_2 + 2K^+$
    orthoclase small muscovite quartz

    Their chemical composition is the same as that of the larger muscovites.
  - *The flattened or large sericites* (100 – 200 µm) also associated with fine quartz crystals appear sinuous. They are apparently formed in a similar way under somewhat different conditions (lower temperature and pressure). Their octahedral sheet is the same as muscovite though with less tetrahedral substitution; so the total charge is a little less. The reaction can be written:

$$\underset{\text{orthoclase}}{3KAlSi_3O_8} + 2H^+ \rightarrow \underset{\text{large sericites}}{(Si_{4-x}Al_x)\,O_{10}Al_2\,(OH)_2K_x} + \underset{\text{solution}}{(3-x)\,K + (1-x)\,Al}$$

– The other two are micaceous clays ($<2\mu m$) comprising sericites included in feldspars and in the so-called reactive micas.

- *Sericites included in feldspars (small sericites)* appear other than by retrodiagenesis or retrometamorphism *(Lelong and Millot [1966])*. They have octahedral substitution, the degree depending on the Si/Al ratio and have the general formula similar to phengites:

  $(Si_{4-x}Al_x)O_{10}\,Al_{2-y}(Fe,Mg)^{2+}{}_y\,(OH)_2K_{x+y}$ with $x+y \sim 1$

  In comparison with muscovite they have less tetrahedral Si – Al substitution and they are still dioctahedral but with some aluminium replaced by bivalent cations (Mg and Fe^{2+}).

- *Reactive micas* appearing preferentially on contacts between muscovite (and biotite) and feldspars in weathered granite. Very small, they are never associated with quartz like the above. Composition is very variable with both tetrahedral and octahedral substitution. Total charge is less than muscovite. Reaction of formation can be written:

$$3KAlSi_3O_8 + 2H^+ + y(Fe,Mg)^{2+} \rightarrow (Si_{4-x}Al_x)O_{10}Al_{2-y}(Fe,Mg)^{2+}{}_y(OH)_2K_{x+y}$$
$$+ (3-x-y)K + (5+x)Si + (1+y-x)Al \quad \text{with } x+y < 1$$

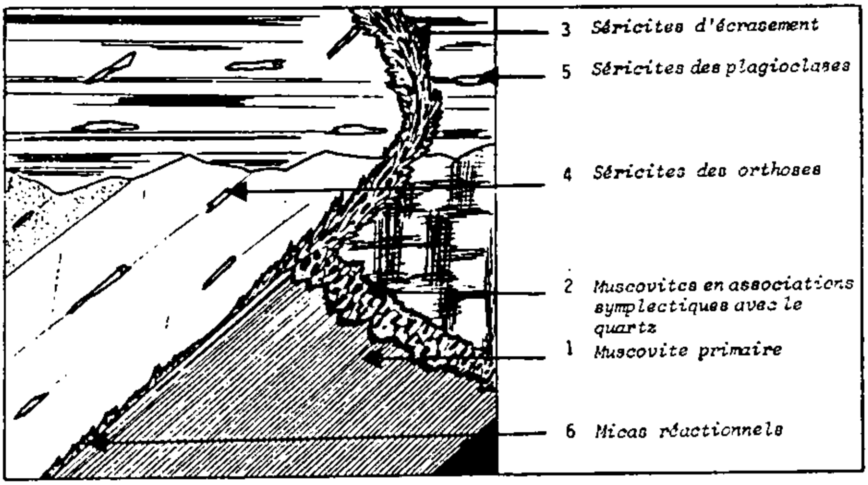


Fig. 11. Various types of micaceous clay («illites») encountered in superficial alteration of granite. After *Meunier [1977]*.

4.2. Mineralogy of natural soils (undisturbed and moist)

In general all soils are hydrated and even if the degree of hydration varies much with environmental conditions, it is always higher than in air-dried soil. This matter is of great current interest, especially in the case of the clay (‹2μm) and fine clay (‹0.1μm).

To enable the work to be done 3 things are required:

1. To know how to stabilise a sample in the existing state of hydration prior to controlled drying.
2. To know how to impregnate the fixed samples for preparation of ultrathin sections (ultramicrotome).
3. To be able to measure interparticular spacing up to 500nm, the hydrated particles being more widely separated than in dry samples.

1 and 2 will suffice for a particular, local, very precise but qualitative study using electron microscopy. 3 is indispensable for quantitative work and requires the use of X ray small angle scattering (SAS).

Brief complementary information on preparation and electron microscope examination follows, more detail is to be found elsewhere *(Tessier,* p. 45) but it is necessary to mention the SAS method here.

4.2.1. Preparation of moist samples.

A recent account has been given by *Tessier [1985].* In general two methods are used:

- *freezing-lyophilisation:* Samples are rapidly frozen to prevent the movement of water and formation of ice crystals; Freon 22 cooled in liquid nitrogen is used. During lyophilisation temperature is kept at -40°C and this can be done within the electron microscope using the Cryoscan procedure of Jeol *(Tessier and Berrier [1979]).*
- *Substitution method:* Methanol is the usual solvent which is replaced by liquid CO_2 which in turn is eliminated either by the critical point method for examination by SEM or by Spurr's resin to prepare thin sections by ultra microtome for examination by transmission (TEM and HRTEM) *(Tessier [1984]).*

4.2.2. Use of electron microscopy

There are two aspects:

- Using SEM it is possible to see the micro-structural arrangement of the plasmas *in situ,* which cannot be done with the optical microscope. This enables one to go beyond the particle (or to describe it in the lateral sense) and to obtain data on the spatial arrangement of units; this can be done for different hydric and geochemical situations (an example for the smectite network is given in figures 12 and 13).
- Using TEM one can visualise the particles in detail and even count the number of layers (by HRTEM) in the individual crystals (Figures 14 and 15). These results can be compared with those by SAS.

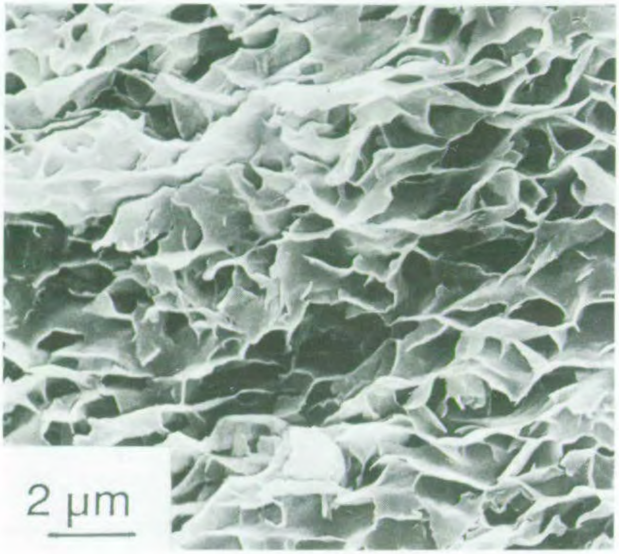


Fig. 12. General organisation of Na montmorillonite (Greek) 10^{-3}M NaCl – 1 bar – SEM (photo: *Tessier*)

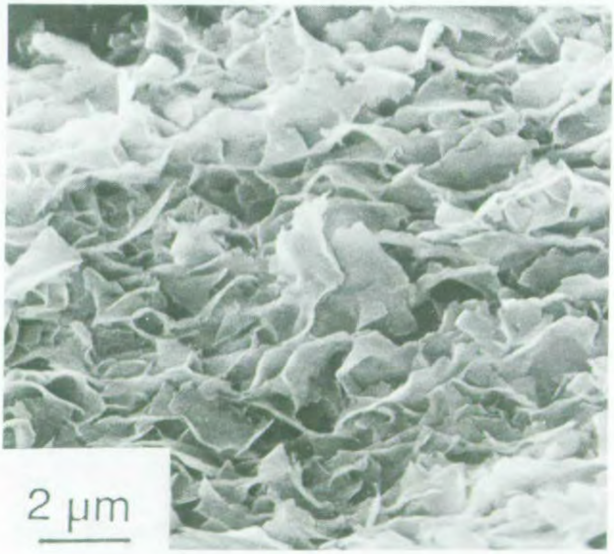


Fig. 13. General organisation of Ca montmorillonite (Wyoming) 10^{-3}M $CaCl_2$ – 1 bar – SEM (photo: *Tessier*)

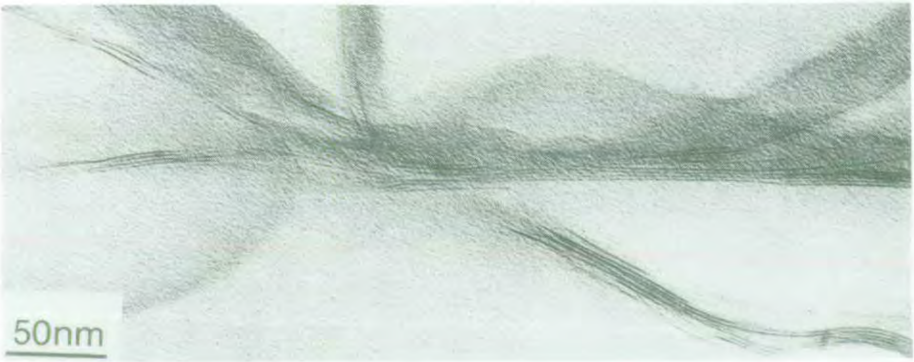


Fig. 14. Characteristic particles of a Na smectite (Hectorite) 10^{-3}M NaCl. – 0.032 bar – TEM (photo: *Tessier*)

Fig. 15. Characteristic particle of a Ca smectite (Greek) 10^{-3}M $CaCl_2$ – 0.032 bar – TEM (photo: *Tessier*)

4.2.3. Use of SAS

X-ray application on a powder sample produces a diagram with two components:

- One by diffraction with discrete lines (ool and hkl) representing the periodic mean of the structure; this has been used up to now for the characterisation of the various types of layers in the main clay groups.
- The other is diffuse and continuous not only in the zone of large angles (which indicate the deviations in relation to the average structure) but also small angles which correspond with *central diffusion*. This central diffusion can be most valuable in clay minerals to get a quantitative study of the arrangement above the

level of the layer – stacking of layers, thickness of particles, and finally microstructure.

Two conditions must be satisfied:

- use of X-rays having 3 essential properties: very intense beam, low vertical divergence of the source and a wide spectrum of wavelength (0.5 – ca. 3 Å). This will allow working in punctual collimation in the part examined (500 nm to 0.5 mm).
- to dispose of a method for quantitative interpretation of that part of the diagram arising from reflexion (ool) to the central area (node ooo of the reciprocal space). The most useful method at present *(Pons [1980])* compares the experimental curves with theoretical curves calculated from a model based on reference to the particle defined by its thickness and internal structure.

Hence it is possible to define for the smectites for example various parameters which aid description:

- M = *mean* number of layers per particle;
- M inf and M sup designate the number of layers corresponding respectively to the upper and lower boundaries;
- m is the number of layers within a particle with the same state of hydration, which is called «sub-stacking»;
- δ is the mean inter-layer spacing;
- $\frac{\delta_2}{d^2}$. is an order parameter, δ being the variance of spacing.

Table 4 gives information on some of the clay types discussed above (smectites) and shows the value of the method.

Table 4. Characteristic parameters of Wyoming montmorillonite under different conditions (after *Tessier [1984]* and *Rhaïem et al. [1986]*)

Samples		pF	$\overline{M}$	d (Å)	$\frac{\delta^2}{d^2}$
Montmorillonite Ca (10^{-3} M $CaCl_2$)	1st drying	1.5	55	20.09	0.046
		3	55	20.09	0.046
		4	225	19.97	0.058
		6	400	15.36	0.010
		6 → 3	170	20.15	0.066
Montmorillonite Na (10^{-3} M Nacl)		3	8	84.73	0.101
		6 → 3	20	46.55	0.085

5. Applications and perspectives

In concluding this review, it may be useful to summarise how ideas have developed and what further progress may be expected.

5.1. Principal stages in development

Knowledge of clay minerals has passed through 3 phases:

a) Colloidal or pre-mineralogical phase

Up to 1930, there were no means of understanding the real nature of clay minerals. Knowledge remained rather general and imprecise concentrating on the phenomena of dispersion (in water) and exchange, *i.e.* on colloidal properties. *Ignorance* and *confusion* dominated the scene.

b) Crystallographic or structural phase

X-ray diffraction showed up the micro-crystalline nature of most of the clay constituents and that they belonged to the layer silicates or phyllosilicates.

The basic structural unit was the layer characterised by its thickness (7, 10 or 14 Å), its atomic structure and chemical composition on the one hand and interlayer spacing measured on the dry or weakly hydrated material on the other.

There was considerable success but at the same time severe limitations because the information was really incomplete. While knowledge of the layer thickness and composition is an important determinant of species, it is by no means sufficient. There was a need to know more about larger aggregates, but time and again more or less unconciously one was led back to the basic layer (tens of Ångstroems). The main characteristics of this phase were great *success* but also excessive *simplification.*

c) Mineralogic and textural phase

The third phase which is now developing but has not fully replaced earlier ideas which are firmly embedded in our thinking is concerned with examining the minerals as they exist in the natural state (hydrated) and examining levels larger than the layer on the one hand and the structure of the layer in more detail (atomic and crystal chemistry scale) on the other. It is marked by *complexity* and *realism.*

5.2. Major aspects of the mineralogy of plasmic constituents

We are now occupied with several points of interest:
- the existence of several interlocking levels of organisation;
- variability of individual crystals in relation to clay species and environmental conditions (hydration in particular);
- the existence of levels larger than the layer, as in the case of the 2 : 1 minerals which are so important in the soil.

a) *Knowledge of a clay mineral sample* implies knowledge of individual crystal components at 3 levels:

- individual *elementary structure* at the level of the layer (nature and crystal-chemical composition) or better, of the structural unit (layer + interlayer);
- as to *texture* – constitution, dimension and morphology of individual hydrated crystals;
- the mutual arrangement of individuals, *i.e.* the *plasmic fabric.*

This involves not only characterising the solid portion (anhydrous) but at the same time taking account of water which to a substantial degree is found in the micropores (∅ ‹ 1µm) of the system.

Grosso-modo this can be diveded into 3:

- interlayer water (when present) for the structural level;
- intra-particle for the textural level;
- inter-particle for the plasmic fabric.

The first form of water is organised water which has always been considered outside the structural units. The two other forms, bound water but not organised, should also be taken into account because of the important influence they have on texture and disposition of individual crystals.

All this is of value no matter what the clay constituent. But when one wishes to treat things in more detail, one is compelled to define the clay type in advance.

b) *Variability of crystalline individuals in the main types*

The 3 clays encountered in soils are:

- Kaolinites (layer 7 Å, neutral, interlayer space empty)
- Illites (layer 10 Å charge z›0.6, interlayers occupied by non-exchangeable K)
- Smectites (layer 10 Å, charge z ‹ 0.45, interlayers occupied by hydrated and exchangeable cations).

According to the present state of knowledge, these clays are organised as in Figure 16:

- Kaolinites: layers are stacked in limited numbers to give a fixed *mono*-crystalline entity whose size depends upon origin (texture). These are elementary crystallites which are then arranged face-to-face to form larger aggregates.
- Illites: stacking is analogous to kaolinites. There is a supplementary level of organisation which is a fixed *poly*crystalline lens shaped unit. This is a *micro-domain* formed by a stable coupling of several crystallites. Here, the micro-domain is the fundamental crystalline individual.
- Smectite: in this case the problem is quite different. Four levels can be defined:
  1) the elementary layer (structural unit);
  2) ordered stacking of several layers corresponding to «crystallite» (substacking *[Pons, 1980]);*
  3) superposed overlapping of some of these crystallites yielding a *quasi-crystal (Aylmore and Quirk [1971])* (Figure 17)
  4) spatial arrangement of these quasi-crystals to give a 3-dimensional network which confers a sponge-like character (Figures 12 and 13).

The latter 3 are not constant for a given smectite because their existence and constitution depend much on environmental conditions and it is thus difficult to conceive of a single typical individual.

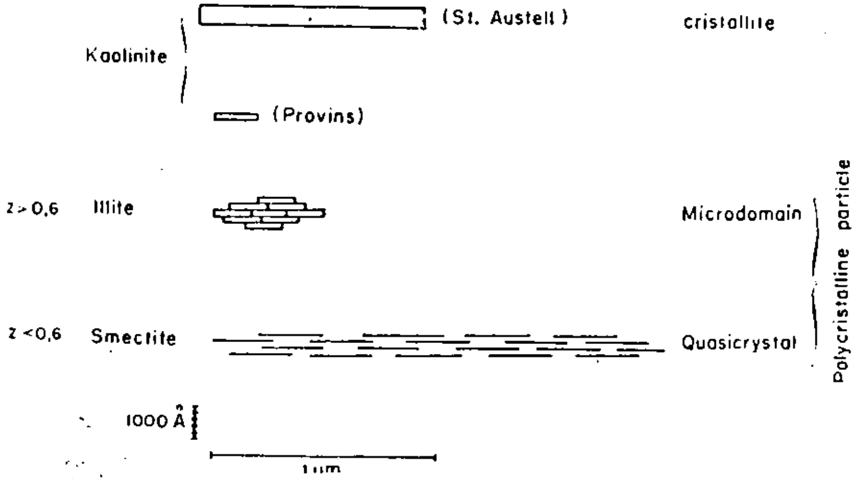


Fig. 16. Schematic representation of individual clay crystals. After *Pedro and Tessier [1983]*

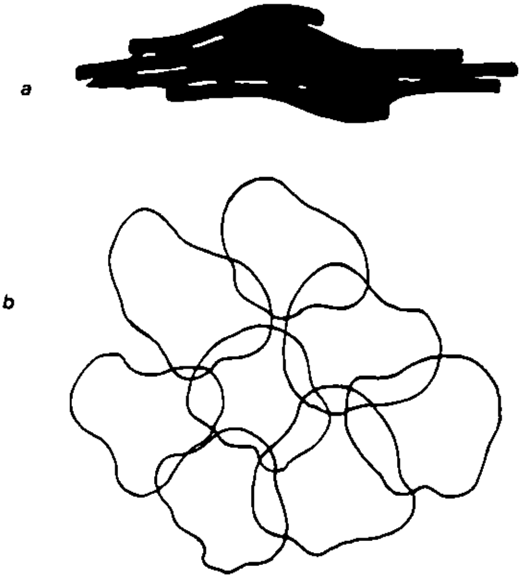


Fig. 17. Diagram of quasi-crystal of smectite in section (a) and surface (b). After *Tessier [1984]*.

c) Conclusions

First in this field, some points can be presented:

- Knowledge of the individual layer is by itself quite insufficient to conveniently characterise a clay mineral and to deduce its properties.
- Hence it is necessary to take account in future of the higher levels of organisation and particularly to take note of the crystalline individual corresponding, in common parlance, to the «particle».
- From this point of view, things are not uniform to the extent that it is rather an idle fancy to wish to define a characteristic particle for each individual clay. As we have seen, the situation with regard to the 3 mineral types is the following:

1) If water molecules cannot enter into the interlayer space (kaolinite and illite) the notion of the particle has a particular meaning. Structure and texture are then *constant* and can be defined. Only arrangement can vary with the environmental conditions. The particle is mono-crystalline for kaolinite and polycrystalline (microdomain) for illites (Table 5 and Figure 16).

Table 5. Levels of organisation of 3 main clays

Levels of organisation		Kaolinites	Illites	Smectites
Sructure (I)		Structural unit (layer+interlayer)	Structural unit	Structural unit
Texture	monocrystalline entity (II)	Crystallite	Crystallite	Crystallite (Sub-stacking)
	polycrystalline entity (III)	–	Microdomain	Quasicrystal
Plasmic fabric (IV)		–	–	Network

2) If the clays can hold water in the interlayer space the particle concept strictly no longer applies. There may be levels like substacking or quasicrystal but these are not fixed characteristics of the species because they are subject to continuous variation according to the types of exchangeable cations, the water status of the system and its hydric history. In other words, if the atomic structure is constant and the 3 dimensional network a characteristic state, the intermediate level (texture) is more *variable*. This is important because we now know that the physico-hydric properties of the plasmic phase depend in the first place on its texture. But, what about the other less well-defined 2:1 constituents?

3) *Problems of 2:1 clay minerals:* A recent study by *Tessier and Pedro [1985]* has shown that the different 2:1 clay minerals with $0 < Z < 1$ (Table 6, page 40) can be divided into 3 categories (Figures 18 and 19):

- The first category has charge $z < 0.45$ and consists of true smectites where all interlayer cations are exchangeable and in which the degree of hydration is inversely proportional to layer charge. These have all the structural and textural characteristics indicated above for smectites.

- The second category is defined by a charge $z > 0.6$. These are illites in which most of the interlayer cations are not exchangeable (100% for $z = 1$, 70% for $z = 0.6$). These minerals, always weakly hydrated, have all the structural and textural characteristics of illites and occur notably as micro-domains.
- The third group have intermediate charge ($0.45 < z < 0.6$). These are very common in soil and react to XRD like smectites though their interlayer cations are not all exchangeable (70 – 100%). Intraparticle hydration is weak and texture quite individual. From this point of view (Figure 20) while they appear as quasicrystals,

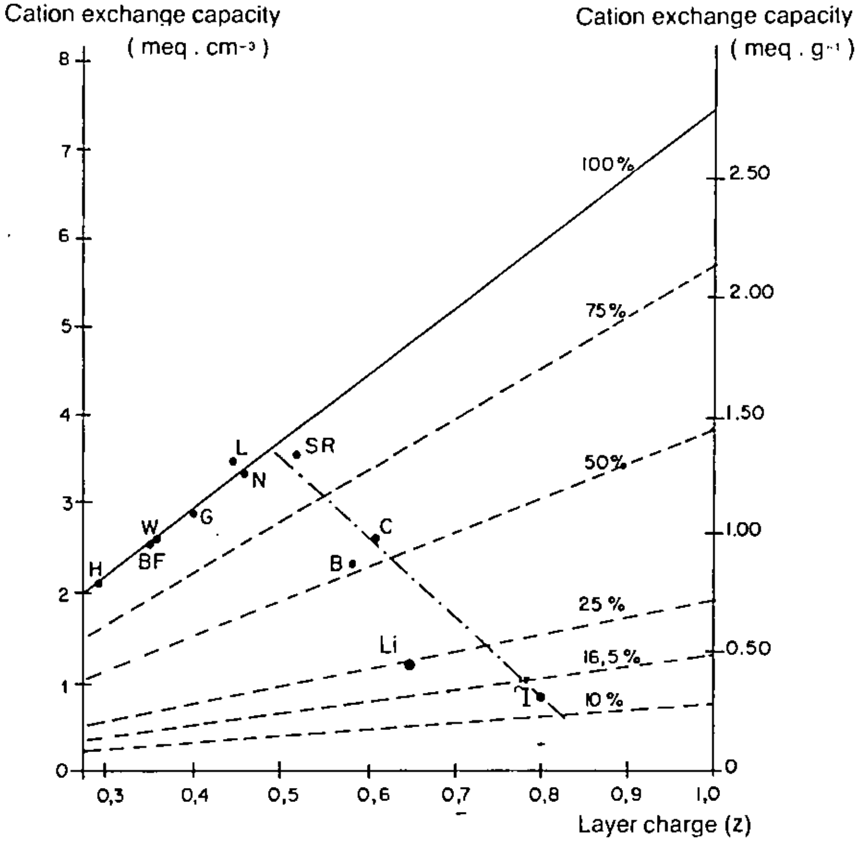


Fig. 18. Exchange capacity related to layer-charge for the 2 : 1 clays of Table 6. Diagonal lines indicate percentage of cations exchangeable. After *Tessier and Pedro [1985]*

they are in fact *heterogeneous* with smectitic units passing *continuously* to illitic microdomains, the ratio depending on layer charge with consequent effects on water characteristics.

Finally, the study of clay minerals has now assumed a new look which takes account of the nature of the layer structure but at the same time goes beyond that in attempting to characterise higher levels of organisation (texture and plasmic fabric). This approach will dominate the subject; it is only in thus that all the characteristics – physicochemical, physicohydric and rheological of such evolving minerals will be explained. The future will surely see strong development of research in this field.

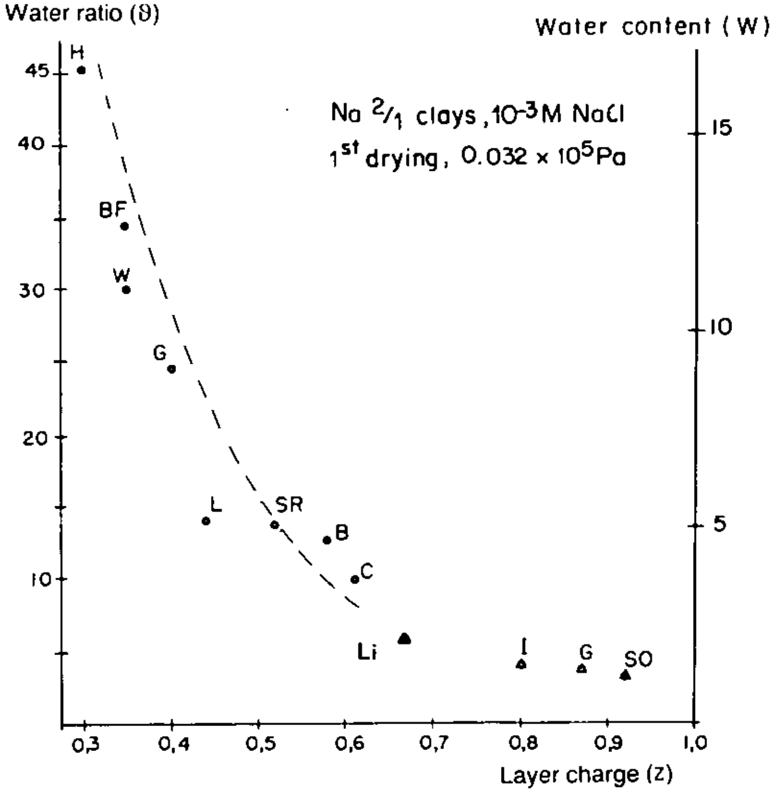


Fig. 19. Variation in water content in 2 : 1 clays (Table 6) related to layer-charge for identical conditions (10^{-3}M Na Cl and pF 1.5 [0.032 bar]). After *Tessier and Pedro [1985]*

Table 6. Cation formulae of the 2:1 clay minerals studied.

Sample and symbol	Formula
Hectorite (H)	
Hector, California	$Ca_{0.15}(Mg_{2.71}Li_{0.29})(Si_4)$
Smectite (BF)	
Belle Fouche, South Dakota	$Ca_{0.15}K_{0.03}(Al_{1.55}Fe^{3+}{}_{0.17}Fe^{2+}{}_{0.01}Mg_{0.29})(Si_{3.90}Al_{0.10})$
Smectite (W)	
Wyoming	$Ca_{0.17}K_{0.01}(Al_{1.53}Fe^{3+}{}_{0.18}Mg_{0.26}Ti_{0.01})(Si_{3.96}Al_{0.04})$
Smectite (G)	
Greece	$Ca_{0.18}Na_{0.03}(Al_{1.55}Fe^{3+}{}_{0.04}Fe^{2+}{}_{0.04}Mg_{0.38}Ti_{0.02})(Si_{3.92}Al_{0.08})$
Smectite (L)	
Lorena	$Ca_{0.22}K_{0.06}(Al_{1.54}Fe^{3+}{}_{0.20}Fe^{2+}{}_{0.02}Mg_{0.23})(Si_{3.82}Al_{0.18})$
Smectite (SR)	
Santa Rita, New Mexico	$Ca_{0.25}K_{0.01}(Al_{1.48}Fe^{3+}{}_{0.05}Mg_{0.45})(Si_{3.97}Al_{0.02})$
Smectite (B)	
Béthonvilliers	$Ca_{0.23}K_{0.11}Na_{0.01}(Al_{1.32}Fe^{3+}{}_{0.39}Mg_{0.23})(Si_{3.82}Al_{0.18})$
Smectite (C)	
Cameron, Arizona	$Ca_{0.20}K_{0.21}(Al_{1.36}Fe^{3+}{}_{0.42}Fe^{2+}{}_{0.02}Mg_{0.15})(Si_{3.70}Al_{0.30})$
Illite (Li)	
Lichères	$Ca_{0.14}K_{0.35}(Al_{1.48}Fe^{3+}{}_{0.33}Mg_{0.23})(Si_{3.47}Al_{0.53})$
Illite (LP)	
Le Puy	$Ca_{0.07}K_{0.66}(Al_{1.24}Fe^{3+}{}_{0.32}Fe^{2+}{}_{0.02}Mg_{0.38}Ti_{0.04})(Si_{3.48}Al_{0.52})$
Glauconite (CO)	
Cormes	$Ca_{0.08}K_{0.68}Na_{0.03}(Al_{0.45}Fe^{3+}{}_{1.14}Fe^{2+}{}_{0.04}Mg_{0.38})(Si_{3.63}Al_{0.37})$

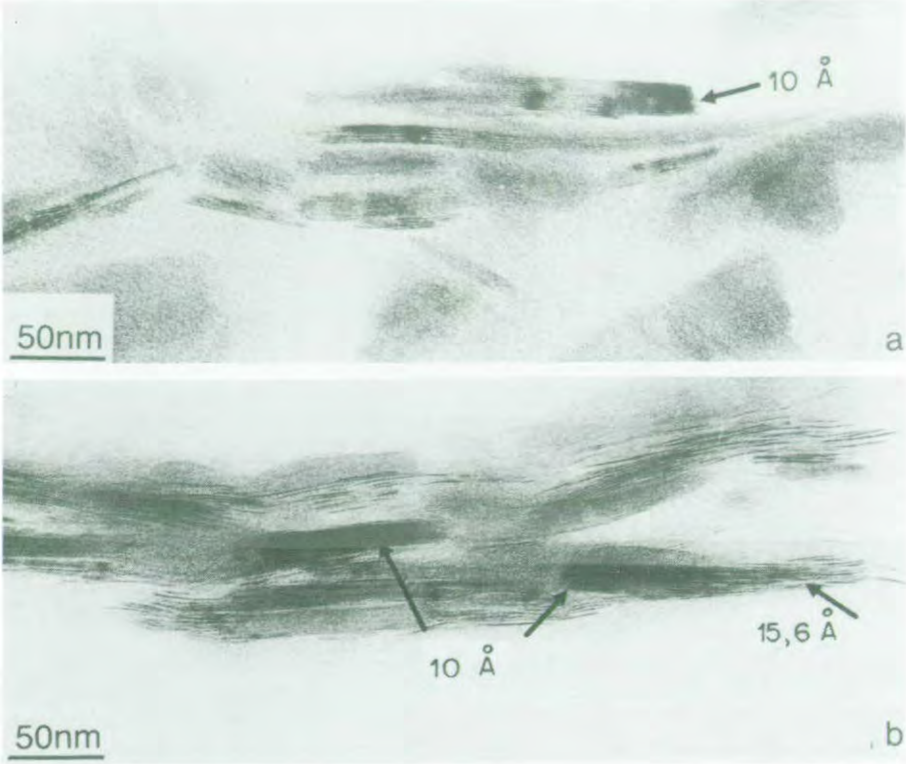


Fig. 20. Characteristic particles at 0.032 bar of Na clays – 10^{-3}M Na Cl – TEM – (a) illite from Le Puy (b) smectite in Bethonvilliers soil. (photos: *Tessier*)

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Identification of Clays – Data from Investigations with Strongly Hydrated Systems

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Summary

In conventional studies, clays are identified in strongly dehydrated samples (equilibrated at relative humidities < 90%). Under such conditions, their organisation is often very different from that in the natural soil. Clays can also be examined and identified in the range of biological activity (suction pressures < 16 bar). For this purpose, the behaviour of clays has been investigated under controlled matric and osmotic potential. Scanning and transmission electron microscopy and X-ray small angle scattering were used to characterise clay – water systems at various water content levels. It was then possible to identify clays not just by reference to properties of the interlayer space but also by description of the particles as they are found in well hydrated systems.

It was shown that, in the range of high moisture content, the interlayer hydration and particle characteristics of potassium smectites were comparable with those of sodium smectites. In this case, identification rests upon study of all states of hydration which is not possible with the classical methods (interlayer spacing ⩽ 2 layers of water).

1. Introduction

It is well-known that soil texture, clay content and type of clay mineral play a direct part in determining many soil properties including the dynamics of ions, especially potassium (Quémener [1986]). Quémener underlines the importance of climatic factors and cultural history and the need to study soils against the background of the energetic relationship of soil water. Work has shown that good water relations and, in particular, biological activity, in the soil require relatively low levels of soil water tension. The limit for the availability of water to plants is defined as the water retained at a suction pressure above 16 bar. This is the result of capillary and osmotic forces between clay surfaces and these forces are due to the presence of ions near the charged surfaces. This is also the range within which the clay constituents of the soil greatly influence structure in all its aspects.

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Most mineralogical, crystallographic and physico-chemical work on clay minerals has been done on relatively dry samples (water activity, $a_w < 0.90$) *i.e.* much drier than needed for biological activity ($a_w > 0.988$) [*Pédro,* this colloquium].

Most of the work has been limited to the study of the clay layer and inter-layer characteristics. This has taken no account of arrangements on a more microscopic level than the elementary units. While not ignoring the importance of the layer and interlayer, the characterisation of soil clays should also be concerned with the larger aggregates and their associations with the pore space.

In this paper which discusses the methods used and results obtained in the study of well hydrated clays, the accent is on the properties and microstructure of potassium clays.

2. Methods

2.1. Principles of the methods

The approach developed for the characterisation of clays describes the various levels of clay organisation and their influence on total water potential as well as their various components.

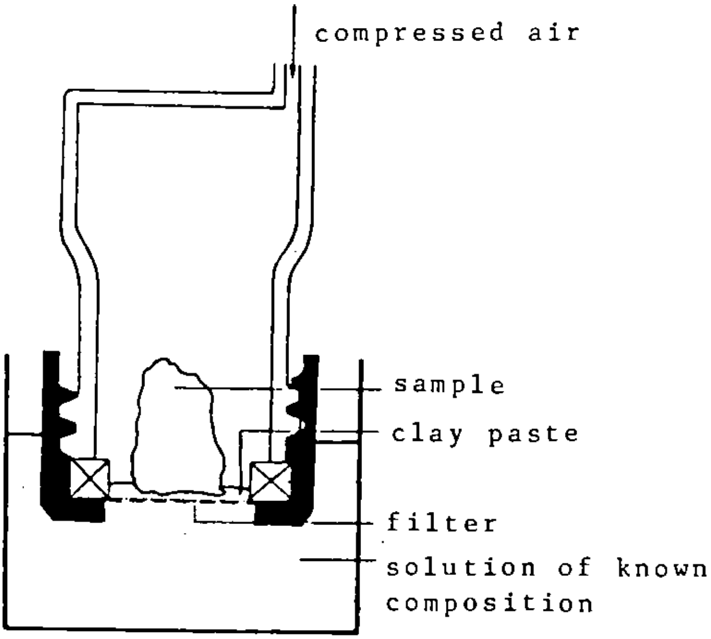

Figure 1. Apparatus for controlling water potential *(Tessier and Berrier [1979]).*

All precise work on clayey material, (hydration mechanism, mineralogical study) should be done on samples in which the exchangeable ions are accurately known. The method consists in particular in the elimination of excess salts from the interstitial solution during ion exchange so that clays can be studied at virtually nul osmotic potential. In well hydrated clays, as in many natural conditions, salt concentration of the solution directly affects the level of flocculation and consequently the microstructure of the soil and its structural stability *(Aylmore and Quirk [1962]; Tessier [1984])*.

To control the matric and osmotic components of water potential, we have used the method described by *Tessier and Berrier [1979] (Figure 1)*. This permits first fixing the suction pressure, *i. e.* the matric component (in the general sense) of water potential and secondly equilibrating the sample at a pre-determined salt concentration. The procedure can be used in both wetting and drying to obtain desorption and adsorption isotherms of water. Table 1 gives for various values of these parameters the equivalence between different methods of presenting the data, maximum pore size, according to Laplace's Law, and the change in water activity by lowering the temperature.

Tabel 1. Levels of energy and ways of expressing various states of water in the soil in relation to the external pressure applied and the maximum size of the corresponding pores.

Gas pressure applied (bar)	pF	Chemical potential of the water J. kg^{-1}	Water activity	Decrease in temperature °C	Maximum size of the pores filled with water (µm)
0.010	1	− 1	0.999993		150
0.100	2	− 10	0.999927		15
1	3	− 100	0.99927		1.5
10	4	− 1000	0.9927		0.15
15.8	4.2	− 1580	0.9888	− 1.1	0.009
100	5	− 10000	0.927	− 10	0.015
500	5.7	− 50000	0.695		
1000	6	− 100000	0.484	− 90	0.0015
Heated to 105 °C	≠ 7	—	≠ 0	—	—

2.2. Methods

Understanding of well hydrated clay systems in fact assumes the possibility of describing the solid phase and water sites over the range 1 Angström to macroscopic (*e.g.* several cm). Samples prepared at a know water potential are investigated by electron microscopy (SEM, TEM) and X ray small angle scattering (SAS).

2.2.1 Sample preparation

Only electron microscopy has sufficient resolution to enable study of the structure of clays. In this work it is not a matter of describing material whose particles have been separated by preliminary treatment (or which have been dried as in the classical methods). The freeze drying method and substitution of the interstitial solution by solvents have been used to preserve the microstructure as far as possible.

- For scanning electron microscopy (SEM) our microscope is equipped with means to observe small samples (≤ 1 mm) at low temperature (-100 deg · C) severely frozen in freon which is cooled by liquid nitrogen *(Tessier et al. [1979])*.
- For transmission electron microscopy (TEM), the interstitial solution is replaced by methanol, then by propylène oxide and finally by *Spurr*'s *[1969]* resin. After hardening, thin (500 Å) sections are prepared *(Tessier [1984])*. The replacement of water by solvents does not usually disturb the general arrangement of particles. When there is change in the interlayer spacing, this can be interpreted by reference to the properties of the solvent used *(Tessier [1987])*.

2.2.2 X-ray examination (SAS)

X-ray examination of clays is generally confined to the layer and interlayer. Interpretation of spectra is often essentially qualitative as it consists solely of identifying the position and intensity of the pick 001. The work is generally done on strongly dehydrated samples ($a_w < 0.9$). Because of this, the particles of the material are in very close contact. This does not give information on well hydrated particles because in the course of drying, many interparticular spaces become analogous to interlayer spaces in the dry state *(Ben Rhaïem et al. [1986])*. Further, well hydrated systems require a different approach to the X-ray patterns if it is wished to characterise the whole of the clay-water system. This involves the whole of the X-ray spectrum, *i.e.* the zone of central scattering as well as Bragg's diffraction.

2.2.2.1 The method in principle

The method used for quantitative interpretation of X-ray diagrams compares experimental curves with theoretical curves calculated from an appropriate model *(Pons et al. [1981, 1982]; Saez-Aunon et al. [1983])*. The models take into account the whole of the spectrum (central scattering and pick 001) because there is no discontinuity of intensity which allows the treatment of the central part of the diagram (small angle scattering) independently of the 001 peak. The model satisfying such conditions is based on the notion of particle and its internal order (Figure 2):

- a particle is defined first of all by the total number of layers $\overline{M}$
- internal particle structure depends on the degree of ordering of layers. It is well ordered when the interlayer distances are homogeneous (*e.g.* 7.14, 10, 15.6 etc.); it is not when the interlayer distance is irregular (*e.g.* 10, 15.6 and 50 Å)

In most 2:1 clays, packing in ordered particles is limited to 12 layers *(Tessier [1984])*. In many of the interstratified minerals, the limit is 2 or 3 layers *(Nadeau [1985])*.

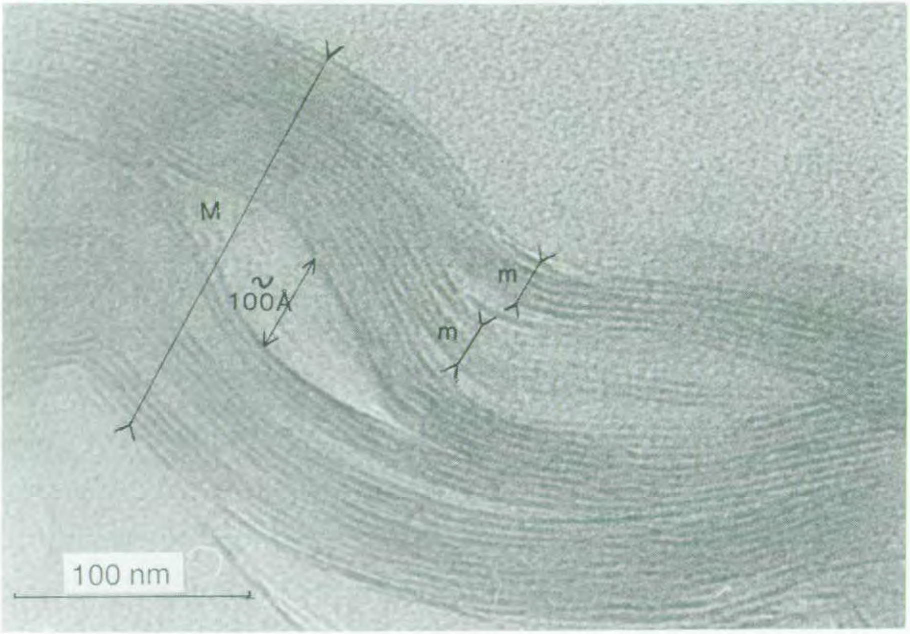

Figure 2. General arrangement of a clay particle (Ca montmorillonite at a suction pressure of 1 bar).

2.2.2.2 Significance of results

Figure 3 shows that the position and intensity of peak 001 are modified by the order *degree of stacking of the layers* (Figure 3a) but also by the number of layers per particle. The curve of small angle scattering is independent of disordered stacking of layers and depends only on the number of layers making up the particle (Figure 3b).

From a practical point of view, the comparison of the experimental trace on the whole diagram between central scattering and the first reflexion (001 peack) shows in each case the number of layers per particle and the extent of faulting in a direction perpendicular to the layers. It should be pointed out that in a case where the particle size diminishes and internal disorder increases, the two parts of the diagram (central and 001) become increasingly diffuse so that one has a quasi-continual decrease in small angle intensity up to angles corresponding with 001. In many cases it is impossible to interpret the diagrams. This is not the case if one uses the whole X-ray diagram with which the distribution of interlayer spaces within a particle can be described. These can be separated by layers of water for which one obtains discrete distances (*e.g.* 15.6, 18.6 Å) or by variable spacing between 35 and 100 Å separated by a diffuse double layer. Analysis of the diagram also gives information on the size of particles in different states of hydration.

In this paper, the two main methods we have described will be used to describe and identify clay-water systems at the particle level. First we shall describe such systems by reference to a fundamental characteristic of the system, that is the water absorption isotherm, mainly in the range of high water activity ($a_w > 0.5$).

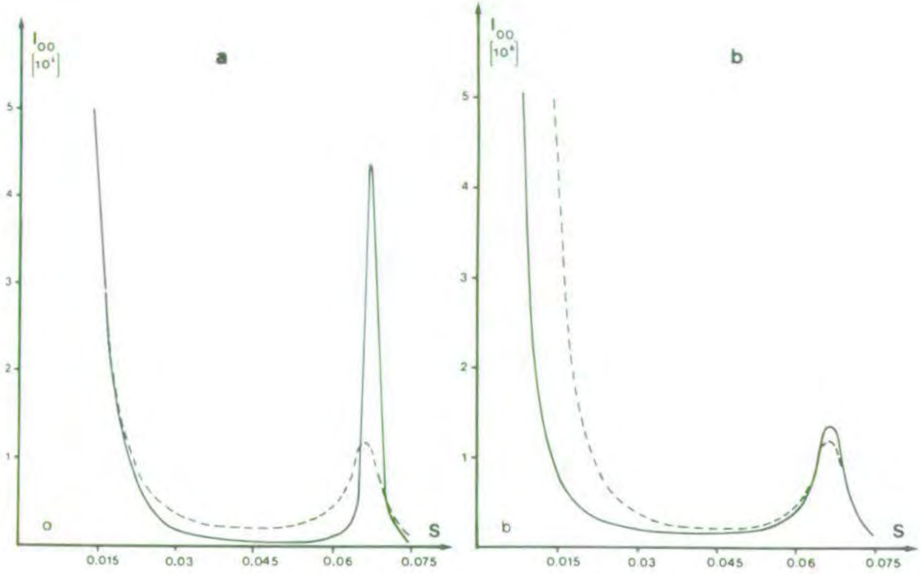

Figure 3. (a) Theoretical intensities for particles of ordered (—) and disordered (----) structure.

(b) Theoretical intensities for disordered particles made up of 20 (----) and 200 (—) layers *(Pons et al. [1981])*.

3. Behaviour of clays in relation to water

We shall show that drying – wetting curves and certain data relating to porosity of clays (like shrinkage limit) are characteristic of these materials. As for studies concerning low water activity it is necessary to distinguish between desorption (particularly during first drying) and absorption (wetting) curves.

3.1. Initial drying curves

To describe behaviour of a clay it is necessary to take into account a number of factors affecting this behaviour. Here, we refer to layer charge deficit, type of compensating cation and water potential.

3.1.1 Effect of layer charge

Layer charge distinguishes between the main types of 2:1 minerals in soils *i.e.* illites and smectites. Starting with different 2:1 clays whose layer charge (z) varies between 0.29 and 0.92 we have prepared gels or pastes in a 10^{-3} NaCl M solution. At a suction pressure of 0.032 bar (Figure 4) the results show a more or less steady evolution of water ratio. (ϑ) *i.e.* of the volume of water in relation to the volume of solid as the charge deficit increases *(ISSS [1976]; Tessier and Pédro [1987])*. One can say that for clays with charge < 0.6, *i.e.* smectites, the value for ϑ decreases strongly as the overall charge deficit increases. In contrast, for illites ($z > 0.6$) the values of ϑ varies or decreases slightly. These results agree with those of *Foster [1955], Dufey and Banin [1979]*. They show that clays belonging to the same general group (smectites, illites) have very different hydration properties on the macro scale which are themselves characteristic of the layer charge under the experimental conditions applying.

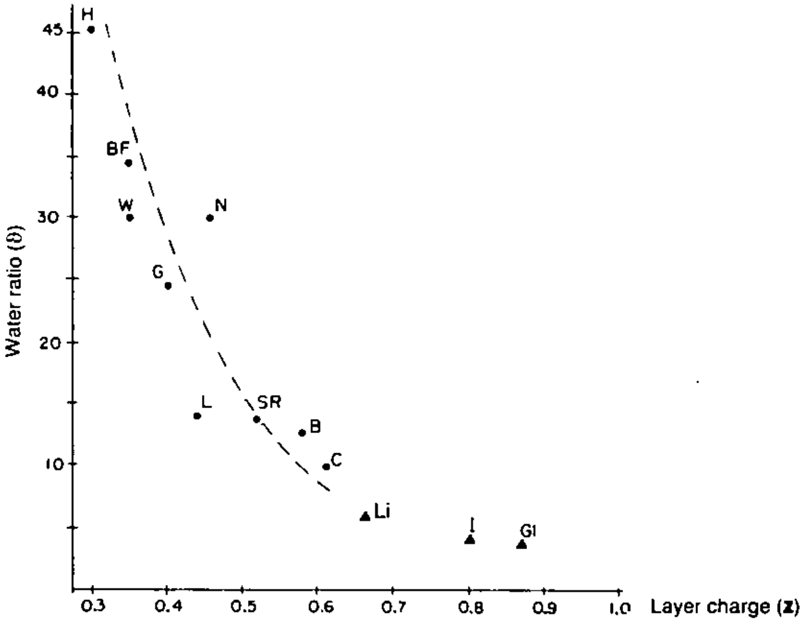

Figure 4. Water content of 2:1 Na-clays, 10^{-3} M NaCl related to layer charge at 0.032 bar.

3.1.2 Role of the exchangeable cations

The four most common cations in soil are: Na^+, K^+, Mg^{2+} and Ca^{2+}. The results of Figure 5 were obtained with Bethonvilliers (France) smectite saturated in turn with these 4 cations in a 10^{-3} M chloride solution. In the range of suction pressure $\leqslant 0.1$ bar, water content decreases in the order Na > K > Mg > Ca. In constrast at 1000 bar ($a_w = 0.5$) water contents are in the order Ca > Mg > Na > K.

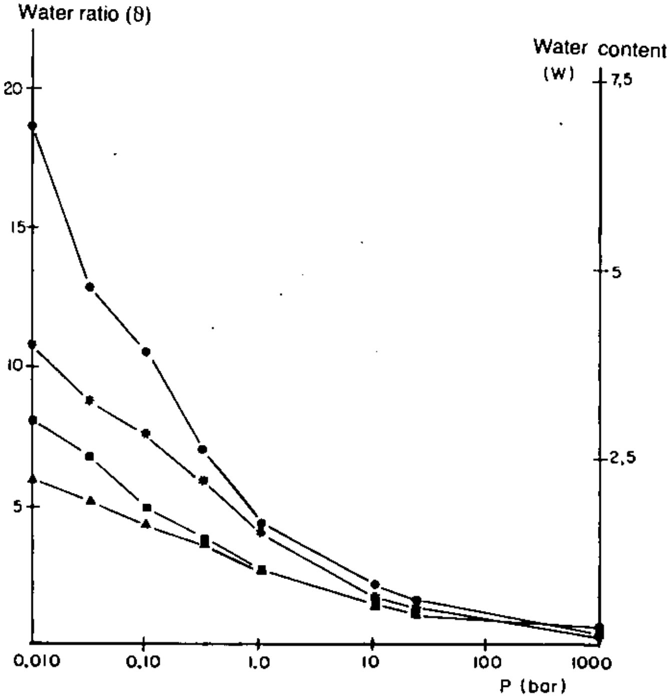

Figure 5. Water content of Bethonvilliers Na, K, Mg and Ca smectites – first drying.

This shows that in the range of low suction pressure where there is biological activity, Na and K smectites show similar isotherms and this distinguishes them from Mg and, more so, from Ca smectites. Results at high suction pressure (a_w = 0.5) confirm previous reports *(Monney et al. [1952]; Glaeser and Mering [1954]; Suquet [1968])*.

In contrast, with model illites (layer charge ~ 0.75) and kaolinites, it is virtually impossible to find evidence of difference in behaviour according to nature of the cation at low suction pressure. This shows that at high water activity it is the smectites and interstratified clays (*i.e.* with a major part of their compensating cations exchangeable) which show varied macroscopic hydration and as a consequence, have varied both swelling and structure.

3.2 Rewetting curves

In order to define the hydration properties of a clay, it is necessary to control water tension. Also, to understand the behaviour of clays it is necessary to define the extreme values for water potential and their consequences. Here, as an example, we compare potassium and calcium (the most abundant soil cations) smectites with illites (clays in which the interlayer K is non-exchangeable).

3.2.1 Potassic smectites

Samples of dehydrated K-smectite dried to two degrees, 10 and 1000 bar respectively, were re-wetted with a 10^{-3} M KCl solution. Figure 6 was the result with Wyoming K-montmorillonite. Even after severe drying (1000 bar, $a_w = 0.48$), when returned to 0.010 bar the clay recovered most of its initial water content at 0.010 bar. The Na clay behaves in the same way on re-wetting *(Tessier [1984])*.

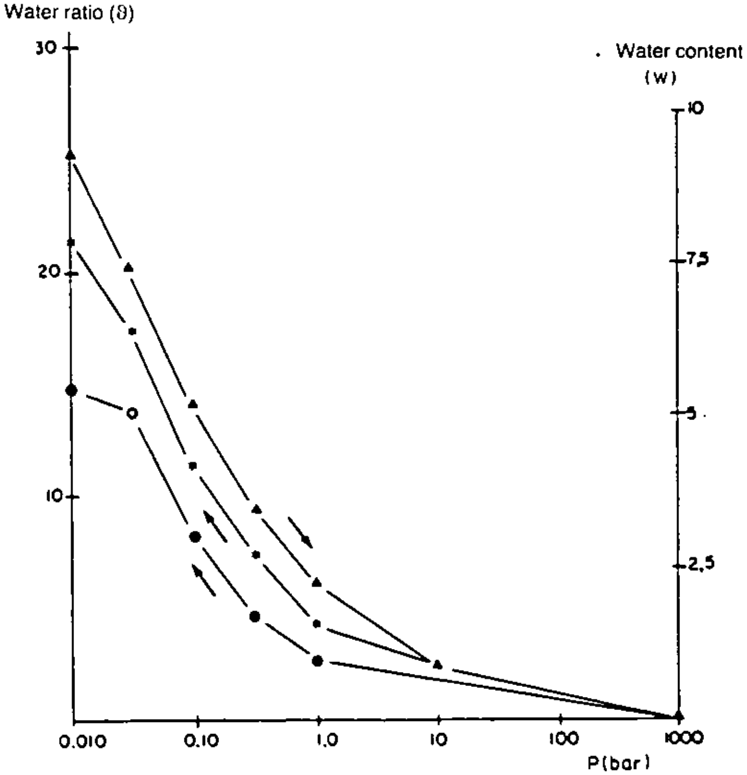

Figure 6. Change in water content on first drying and rewetting of Wyoming K-montmorillonite.

3.2.2 Calcium smectites

The same smectite saturated with Ca was subjected to the same treatment (Figure 7). The further it was dried the less it was able to take up water again. Thus after drying it regained 34% of initial water at 0.010 bar, 27% at 10 bar and 19% at 1000. The behaviour is fundamentally different from that of Na or K smectite. One drying is enough to change considerably its behaviour on wetting. The same has been found with all Ca and Mg smectites examined. It shows that soil-climatic conditions, geological history, *i.e.* all stresses to which the material is subject, play a direct part in its hydration properties and as a consequence in the development of soil structure.

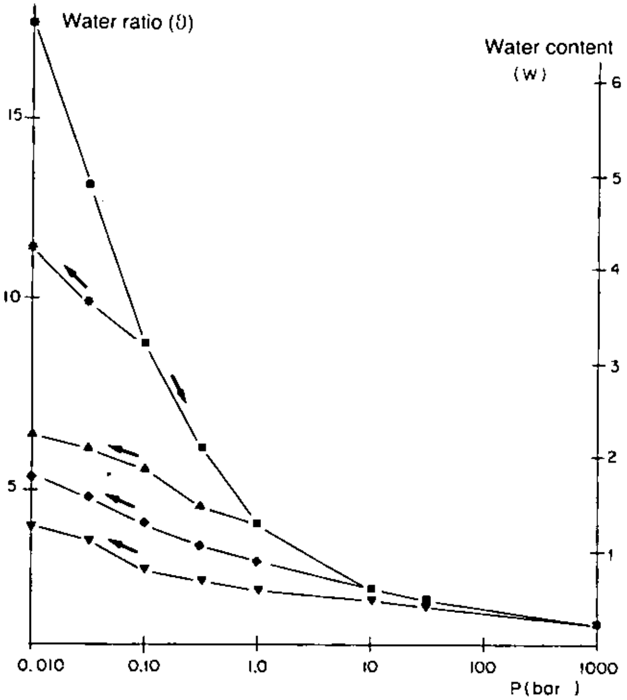

Figure 7. Change in water content on first drying and rewetting of Wyoming Ca-montmorillonite.

3.2.3 Illites

The isotherm for an illite from Le Puy is shown in Figure 8. As for Ca and Mg smectites, intensity of drying reduces clay water content but the difference in water loss at 0.010 bar between drying to 10 and 1000 bar is small compared with the smectites. Further on re-wetting, from 10 to 0.010 bar there is little increase in water content. Consequently the increase in volume does not exceed 20% while for Ca smectite it can exceed 150% *(Tessier [1984])*. This behaviour is characteristic of kaolinites and highly charged illites whatever the exchangeable cations (Na, K, Mg, Ca).

In thus appears that to analyse the hydration properties of clay-water systems, it is necessary to be aware of their nature and also of their energetic history. With clay materials it is not a case of classical hysteresis, as for a mass of rigid grains. The whole of the water potential curve depends especially on the maximum stresses suffered by the materials through their history *(Croney and Coleman [1954]; Tessier [1984])*. This must be taken into account in laboratory work.

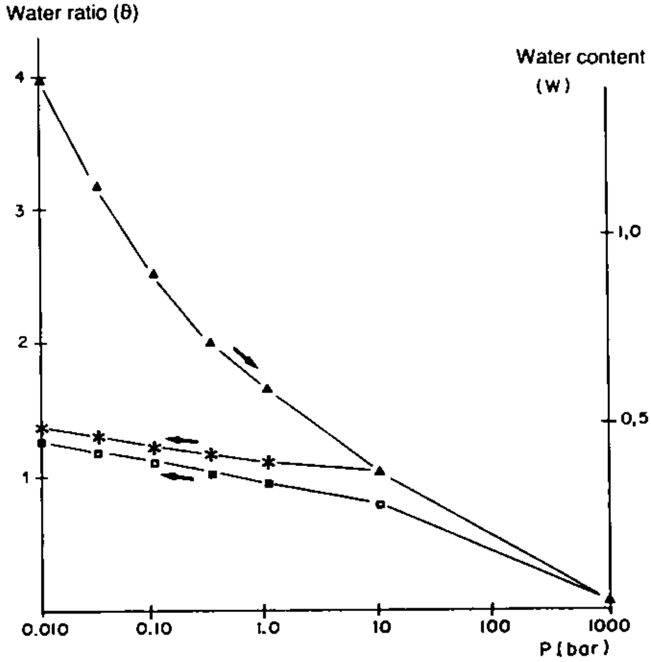

Figure 8. Change in water content on first drying and rewetting of K-illite from Le Puy.

4. Development of clay organisation

As we have seen, the curves relating water potential and water content are characteristic of clays. In proceeding to characterise the organisation of clay water systems in the range Ångstrom to submacroscopic, we shall show how knowledge of the microstructure of such systems aids in better identification. We shall also see how it is possible to describe the mechanism of hydration and swelling of clays in soil.

4.1 Smectites

First, take the case of a Ca smectite on first drying. Figure 9 shows how the interlayer spacing changes. For suction pressures < 50 bar the interlayer spacing at max. probability is 18.6 Å. Ca montmorillonite is very stable as regard layer spacing within this range *(Aylmore and Quirk [1971])*. Beyond 50 bar it changes to 15.6 Å. In other words, over a large range of suction pressure most of the elimination of water is from spacings greater than 18.6 Å, which are not taken into account in X-ray studies *(Mering [1946]; Emerson [1962])*.

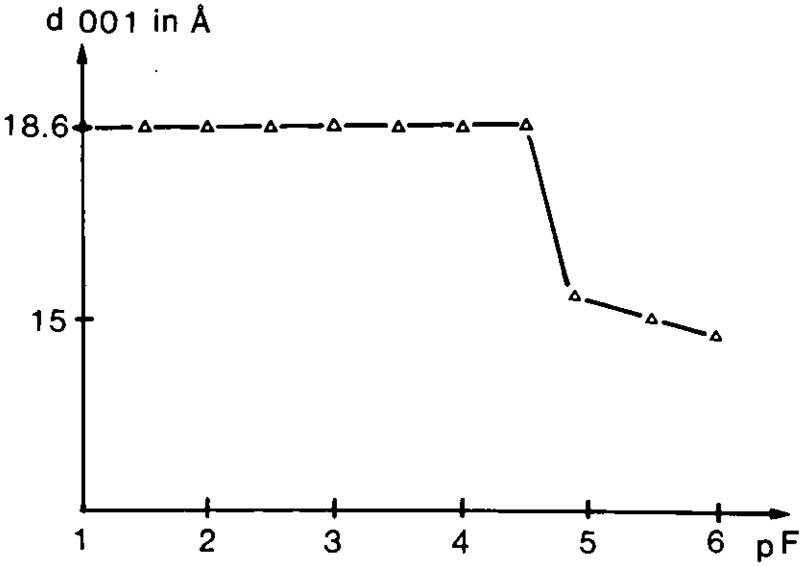

Figure 9. Interlayer spacing at maximum probability for Wyoming Ca-related to suction pressure (pF = log millibars).

In parallel, one can follow changes in $\overline{M}$, the mean number of layers per particle. From 0.010 to 1 bar, the best agreement of theoretical model with experimental results over the whole range of central scattering and 001 is given by $\overline{M} = 55$ layers (Figure 10). In this range water is eliminated just by closing up of the particles. At 10 bar on the other hand, $\overline{M} = 225$ and at 1000 bar 400 *(Ben Rhaïem et al., [1986])*. Between 1 and 10 bar water loss is simultaneously accompanied by a change in the arrangement and size of particles by face to face regrouping. Above 50 bar the interlayer space is also affected.

The results show also that particles thus defined (M layers) are not homogeneous, as the best agreement of theoretical and experimental data is obtained by taking into account homogeneous stacks of 10-12 layers separated by spacings from 50 to 150 Å spacings. The system ought then to be described as having in total M layers with homogeneous substacking (m) separated by greater distances of the order 50-150 Å (Figure 2). Note that in the range of low suction pressure (< 1 bar) most of the water is in the interparticle spaces, *i.e.* in pores ⩽ 1 μm diameter.

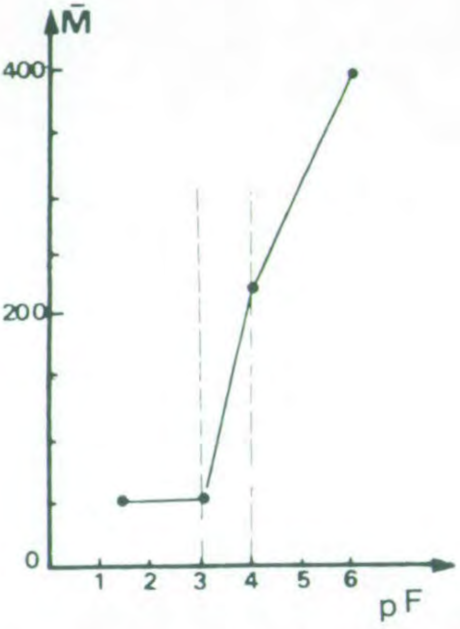

Figure 10. Change in number of layers in particles (M) during first drying of Wyoming Ca montmorillonite (data expressed as pF).

Such an arrangement is characteristic of Ca smectites both in the course of first drying and in rewetting. SAS shows in fact that the interlayer spacing is unchanged after severe drying (18.6 Å); in contrast, the number M of layers making up the particle increases and consequently the surface in contact with water in the pores. Even so, the size of smectite interparticle pores remains fairly constant and can reach 1 μm at 0.010 bar *(Tessier, 1984).*

From another viewpoint it is very interesting to compare the arrangement of a K smectite with the same Ca clay. For this we first used SEM and TEM. With SEM at 0.032 bar a K smectite appears as an isotropic network analogous with that of a Ca clay (Figures 11a and b). With TEM it is seen that the pore walls are made up of an average of ten layers (Figure 11c). Note that the number of layers is quite similar to that of the same clay prepared with Na at the same salt concentration. It is also pointed out that increase in salt concentration of the soil solution increases the size of the particles – an effect comparable with substituing Na or K with Ca or Mg *(Tessier and Pédro [1981]).*

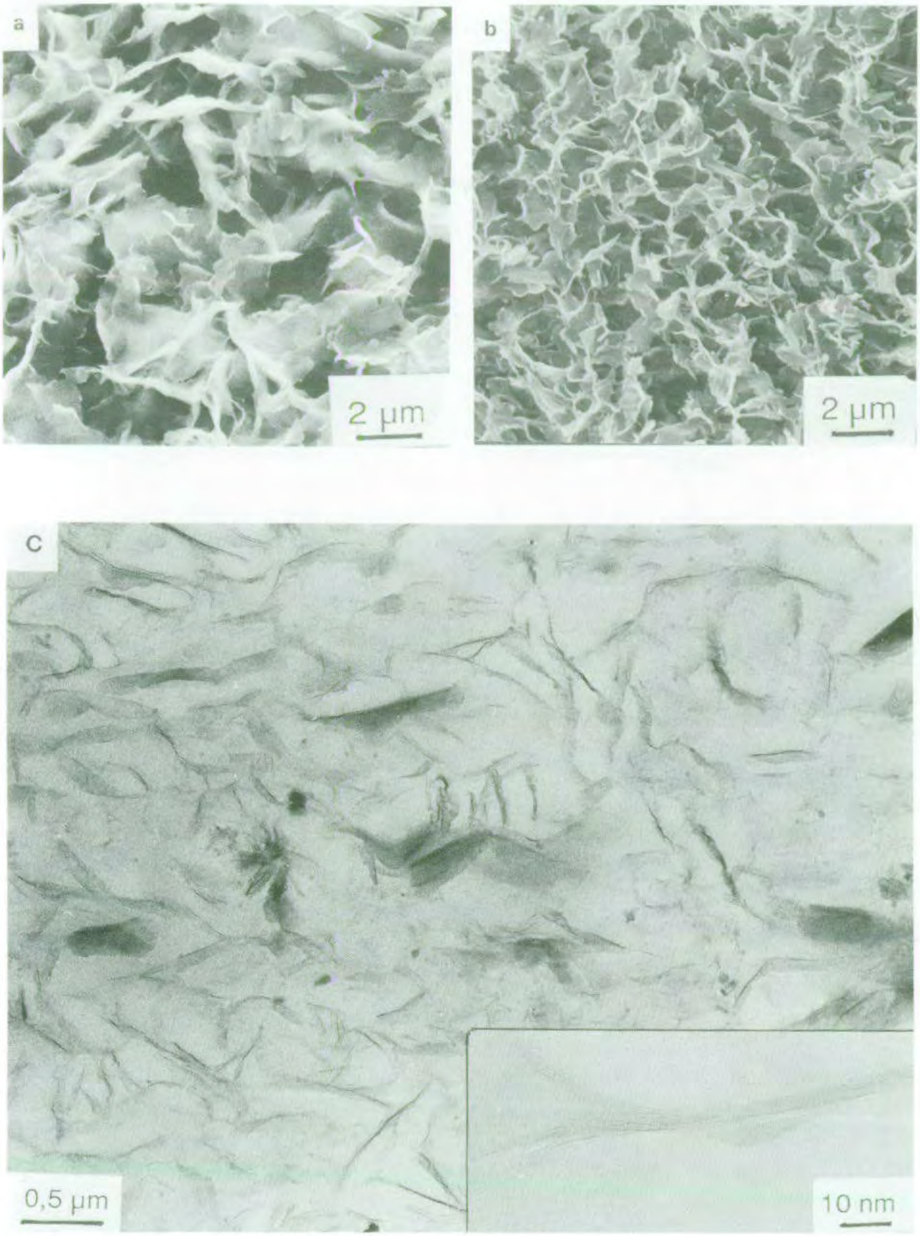

Figure 11. General arrangement of Wyoming montmorillonite 0.032 bar (a) Ca clay SEM (b) K clay SEM (c) K clay TEM.

It appears then that the network structure shown by microscopy is characteristic of smectites prepared initially in well hydrated form whatever the exchangeable cation may be. But what distinguishes the various clays studied is essentially the number of layers making up the particles. This varies with layer charge, the nature of the exchangeable cation, solution concentration and the energetic history (severe drying for example).

Thus for the smectites one cannot define a standard or unique particle characteristic of the clay water system. It should be noted that anything which increases cohesion forces between the layers increases the size of the particles and thus affects the surface area. In this matter, K at high moisture content behaves as a dispersing ion. *Pons [1980]* was able to demonstrate interlayer spacings from 35 to 100 Å, *i.e.* the presence of a double layer as in the Na smectites (Figure 12). The data confirm results showing that the K and Na smectites show similar hydration properties at high water activities.

Figure 12. SAS curve for K montmorillonite. Interlayer spacings essentially between 35 and 100 Å *(Pons [1980])*.

4.2 Illites and kaolinites

Here it is always possible to identify particles characteristic of the material. Thus Figure 13 shows changes in particle arrangement in the course of drying. In the case of St Austell Ca kaolinite, there is at 0.010 bar a face to face arrangement of crystallites. At 1 bar the particles are in contact. These results agree with data on the shrinkage of this clay which shows a limit around 1 bar. Note that the clay water system is made up of very rigid particles.

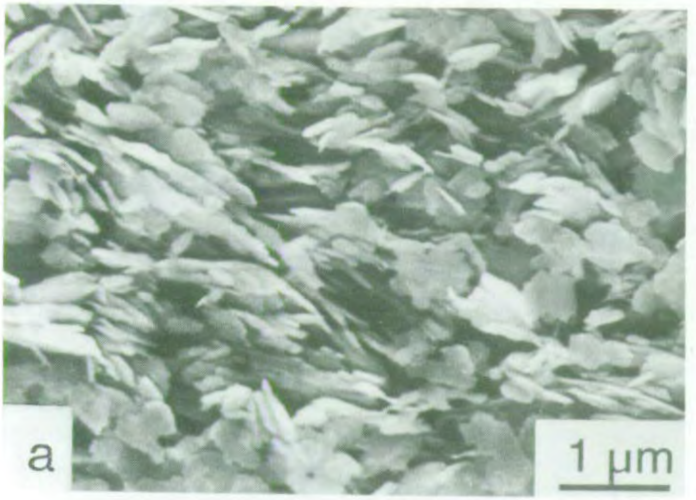

Figure 13. Change in arrangement of St Austell kaolinite (a) 0.010 bar (b) 1 bar.

In this case the value of the void ratio at the shrinkage limit (minimum porosity) is still large, as e = 1.1 *(Tessier [1984])*. Analogous behaviour is seen in illites. In contrast for a smectite, whatever the exchangeable cation, the minimum value of e reaches 0.35. Thus there is a direct relation between the nature of the interlayer space and the shrinkage limit of clays. In effect, for the illites and kaolinites the particles can be considered almost not to be deformed on shrinking. In illites, non-exchangeable K in the hexagonal cavities assures the rigidity of the particles. The drying process only results in *rearrangement at the interparticular level* leading to variations in volume and to a macroscopic structure. In contrast, for the clays with a large number of interlayer spaces with hydrated exchangeable cations, the particles are flexible and the layers can slide on the a b plane and thus adjust themselves *(Suquet [1968]; de la Calle [1977])*. There is complete reorganisation of the clay with variation in water content which can affect all levels of arrangement resulting to cracking and shearing. At the lowest energy levels, there is a considerable change in structure of the system. This change in structure can be provoked by different factors, of which the two main are solution concentration and suction pressure. The former directly affects flocculation.

5. Conclusion

We have shown that clays should be described over a much larger energy range than has been usual and especially for values of $a_w > 0.98$. In this range, potassium clays show hydration behaviour similar to sodium clays. The sodium and potassium smectites at low suctions are much more hydrated than the same Ca and Mg clays which distinguishes the illites *sensu stricto* and kaolinites. The interstratified minerals generally show behaviour intermediate between these two extremes. Thus it is now possible to identify a clay by its hydration behaviour at low suction pressure, but this must be done under perfect control of solution concentration, *i.e.* osmotic pressure.

Once continuity has been established between the structural unit (layer) and the macroscopic arrangement of clays it becomes possible to distingish the main clay types by arrangement of the particles. One can then demonstrate the specific role of physico-chemical factors in the characteristics of the system under study. Results obtained by various techniques (SEM, TEM, SAS) are coherent.

In summary, the results demonstrate that it is not possible to describe the properties of clays, especially when well hydrated, and consequently swelling and structure merely on the basis of classical mineralogy. It is necessary to take into account the geochemical environment and also energetic history *i.e.* climatic or mechanical constraints. On such a basis one can develop an overall strategy for the study of soil calys and thus establish a tie-up with their physical and physico-chemical properties.

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Development of K containing Minerals during Weathering and Suitable Methods for their Determination

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Summary

The development of clay minerals includes the processes of formation, transformation, and decomposition of clay minerals in soils.

The clay formation in soils of temperate climate is mainly a result of mica weathering in the silt and sand fractions. Transformation means alteration of minerals which leads to expansion of K containing clay minerals for which a decrease in layer charge and potassium release are the most important requirements.

Clay decomposition is a consequence of soils becoming increasingly poor in bases and their additional pollution with acidic substances from the environment.

An analysis of individual stages of development is only possible after dividing the clay component into subfractions.

The X-ray methods, the determination of the layer charge by the n-alkylammonium method, and the contraction behaviour after KCl treatment are means of determining the stages of clay mineral development. As long-term K fertilizing proves, K shortgage both decreased yields and accelerates clay mineral transformation. Liming benefits the development of clay minerals because sufficient base saturation prevents clay decomposition. Methodological aspects are described.

1. Introduction

Knowledge of alterations of K containing layer-silicates and of K exchange has been derived mainly from model substances or clays from deposits summarised by *Tributh [1976].*

It is much more difficult to detect transformation processes due to weathering in natural soil clay fractions than it is to carry out an experimental simulation. Exact analysis of the mineralogical composition of the subfractions of clays is possible only by extended fractionation by centrifuges.

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There are already reports existing on the advantages of more detailed determination of mineral constituents and their properties by extended fractionation in clay mineralogical experiments *(Tributh [1967, 1970, 1971])*. My own examinations on clay subfractions with those carried out in close cooperation with *Lehnardt [1974]* and *Hilger-Alexandrou [1976]* indicated that clay mineral development is influenced by the soil environment, *i.e.* according to the degree of base impoverishment differing «end products» are detected.

Among the identification procedures by X-ray diffractometry the contraction behaviour after K treatment has proved to be best suited for the differenciation of transformation stages of soil clays. In cooperation with *Lagaly/Kiel* the close connection between decrease in layer charge and contraction behaviour could be revealed by the alkylammonium exchange *(Tributh [1976])*.

2. Stages of clay mineral development caused by weathering

The extent of clay mineral development is mainly determined by the intensity of weathering and, especially, by the pH shift to the acidic medium. *(Figure 1)*. *Scheffer et al. [1966]* discovered that the coarse particles of the clay fraction are nearly exclusively produced by a cryoclastic clay formation (mechanical weathering), whereas the chemical weathering mainly produces clay fractions < 0.2 µm.

Clay formation in loess soils is fundamentally characterized by weathering of micas in the silt and sand fraction which first leads to reduction in particle size without much change in mineral logical properties. As soon as the mica particles fall below the 2 µm boundary they belong to the clay fraction and are then called illites. According to *Fölster et al. [1963]* approximately 95% of the clay minerals of our soils are produced by wheathering of micas. The (second) possibility of clay mineral genesis often mentioned *(Scheffer/Schachtschabel [1976])*, clay mineral genesis by new formation from silicate degradation products, is certainly of subordinate significance for soils in Central Europe. Since the soil represents an open system, the conditions of environment and concentration required for the new formation of three-layer minerals are not fulfilled, whereas, under certain conditions, formation of halloysites and kaolinites may also occur in our climatic zone.

The *transformation* of mica-type clay minerals begins at a particle size of < 0.2 µm and proceeds from expansion at the edges to a layer distance of 1.8 nm *(Tributh [1976])*. The basic requirement for this alteration is potassium release and reduction in layer charge. The fact that this process runs pararell to the particle size reduction is shown by X-ray diagrams of different clay fractions of a Ukraine chernozem (Figure 2).

The air-dried Ca samples show the smooth transition into fully expandable minerals with decreasing particle size more cxlearly than glycerol treatments.

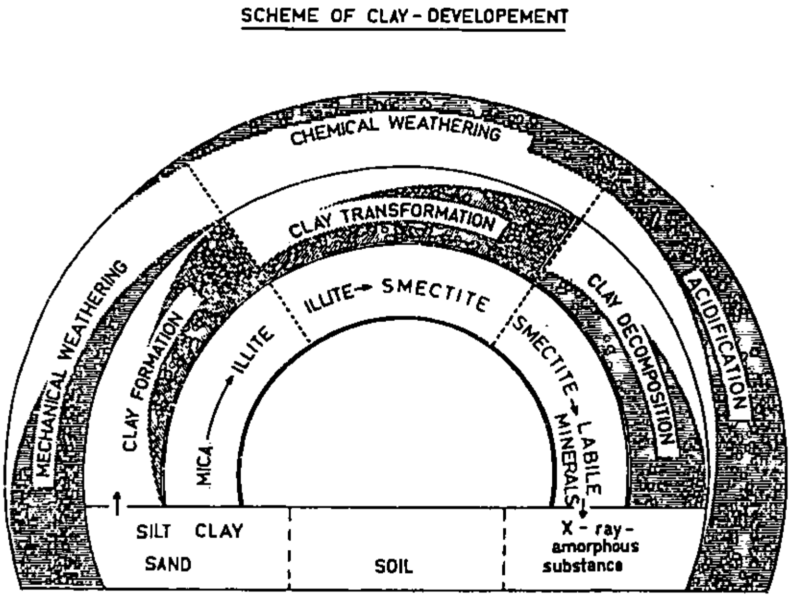
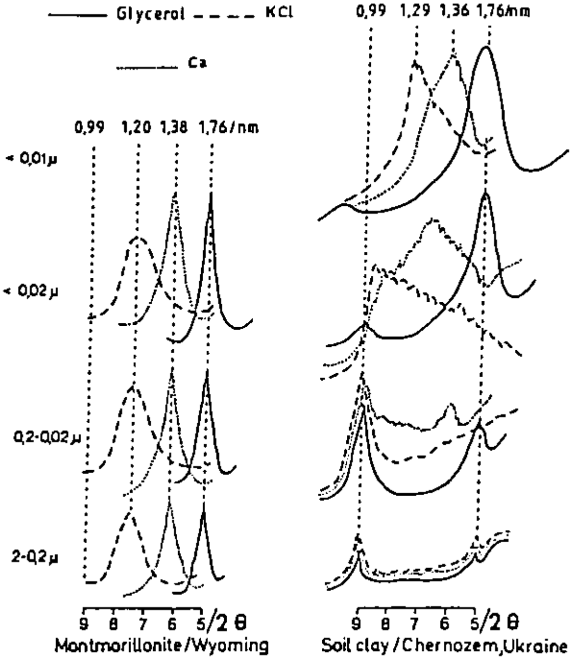


Fig. 1 Dynamics of weathering and clay development



a) *fractionized soil-clays*
(CHERNOZEM/UKRAINE)

particle size µ	*layer-charge*
0,2 – 0,02	– 0,80
< 0,02	– 0,60
< 0,01	– 0,45
< 0,008	< – 0,36

b) *fractionized standard-clays*
(MONTMORILLONITE/WYOMING)

particle size µ	*layer-charge*
complete-fraction	– 0,30
2 – 0,2	– 0,30
0,2 – 0,02	– 0,29
< 0,02	– 0,29

Fig. 2 X-ray diagrams of fractionized standard and soil clays and layer charge data

The qualitative differences are very clearly shown by contraction tests with KCl. While the smectites (1.76 nm) in the fraction 0.2-0.02 μm nearly totally contract to 0.99 nm, only some of the minerals of the fraction < 0.02 μm are able to contract. The minerals of the fraction < 0.01 μm only contract to 1.26 nm, and thus react like the montmorillonites from deposits in Wyoming which reveal approximately the same layer distance in all subfractions. The fact that the tendency to contraction is largely parallel to the layer charge is confirmed by the layer charge data. These data were obtained from the subfractions of the Ukraine chernozem in cooperation with *Lagaly/Kiel.* Only the fraction < 0.008 μm (without figure) of the soil clay almost reaches with < 0.36 the layer charge of the standard Wyoming montmorillonite.

For the development of smectite it is essential that the environment does not change. As long as calcium and magnesium ions are available to replace the released potassium, the transformation of illite leads to smectite which remains stable up to extremely small grain sizes.

The *clay decomposition* of three-layer minerals starts with an extreme expansion beyond 0.2 nm. The coherence of the layers decreases to such an extent that resistence to the expansive power of the glycerol (in the soil: water) is lost, and the interlayer spaces expand to infinity.

The state of «lability» is the first and also the only visible phase of clay decomposition. As soon as the layers are totally independent of each other, the (001) reflex disappears and the diagram exhibits a pronounced continuous increase of intensity to small angles (Figure 3).

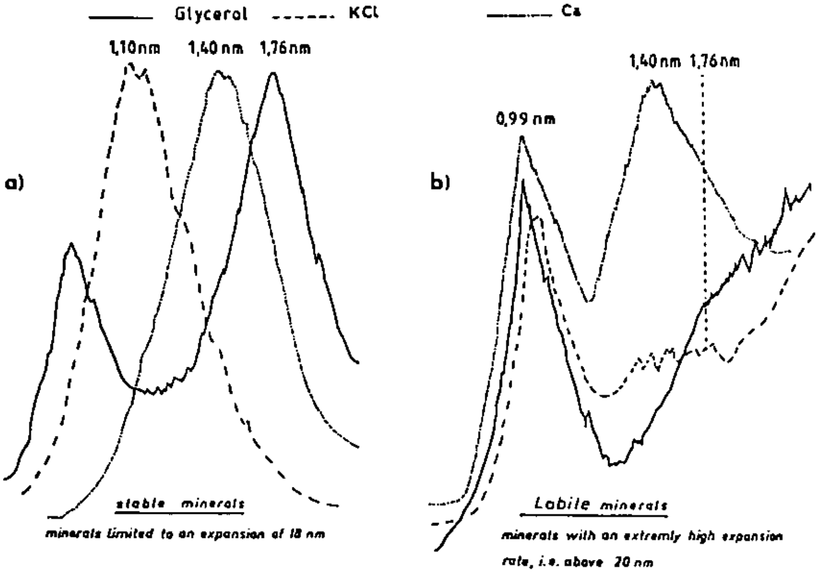


Fig. 3 Examples of stabile and labile minerals of clay fractions < 0.06 μm

The higher concentration of protons must be the cause of clay decomposition because the labile minerals are only found in acidic soils or horizons.

Whereas the protons react like other cations in a slightly acidic environment and replace interlayer potassium ions *(Norrish [1972])*, in higher concentrations they affect the octahedral layer of micas. During this reaction first Mg and especially Fe are removed *(Robert & Pédro [1972])* before the structure is destroyed *(Wells & Norrish [1968]; Mamy [1970])*. Acids of biological origin can produce the same reactions *(Boyle et al. [1967]; Sawhney & Voigt [1969])*. This fact explains why clay decomposition occurs in the upper horizons of grey-brown soils. Clay mineral decomposition related to an increase in soil acidity is characteristic of soil development under neutral conditions. The process can be intensified by supplying additional acid but can also be interrupted or retarded by human activities (see chapter 6).

3. Soil environment determining the «end product» of clay mineral development

As already mentioned in chapter 2, clay mineral development in soils results from alteration of K containing clay minerals by weathering which either leads to formation of other clay minerals or to clay decomposition.

Schwertmann [1964] as well as *Schroeder [1976]* suggested a sequence of transformation products that ends in a tree-layer mineral. According to experiments with fractionized clays of soils at different base saturation *(Lehnhardt [1974]; Hilger-Alexandrou [1976]; Tributh [1976]; Tributh* in *Schönhals et al. [1982])* it can be concluded that no particular transformation scheme is generally valid for all soils. The clay mineral development is dependent on the soil environment. At least three sequences can be distinguished which are determined mainly by the degree of base impoverishment in the soil. They lead to different end products (Figure 4).

CHERNOZEM

MICA ⟶ ILLITE ⟶ TRANSITIONAL MINERALS ⟶ SMECTITE

BROWN LESSIVE

MICA ⟶ ILLITE ⟶ TRANSITIONAL MINERALS ⟶ SMECTITE ⟶ LABILE MINERALS

ACIDIC BROWN SOIL

MICA ⟶ ILLITE ⟶ AL-CHLORITE ⟶ LABILE MINERALS ⟶ X-RAY-AMORPH. SUBST.

Fig. 4 Clay mineral development from mica depending on the milieu of the soil

The following diagram shows the clay mineral development according to our present knowledge (Figure 5).

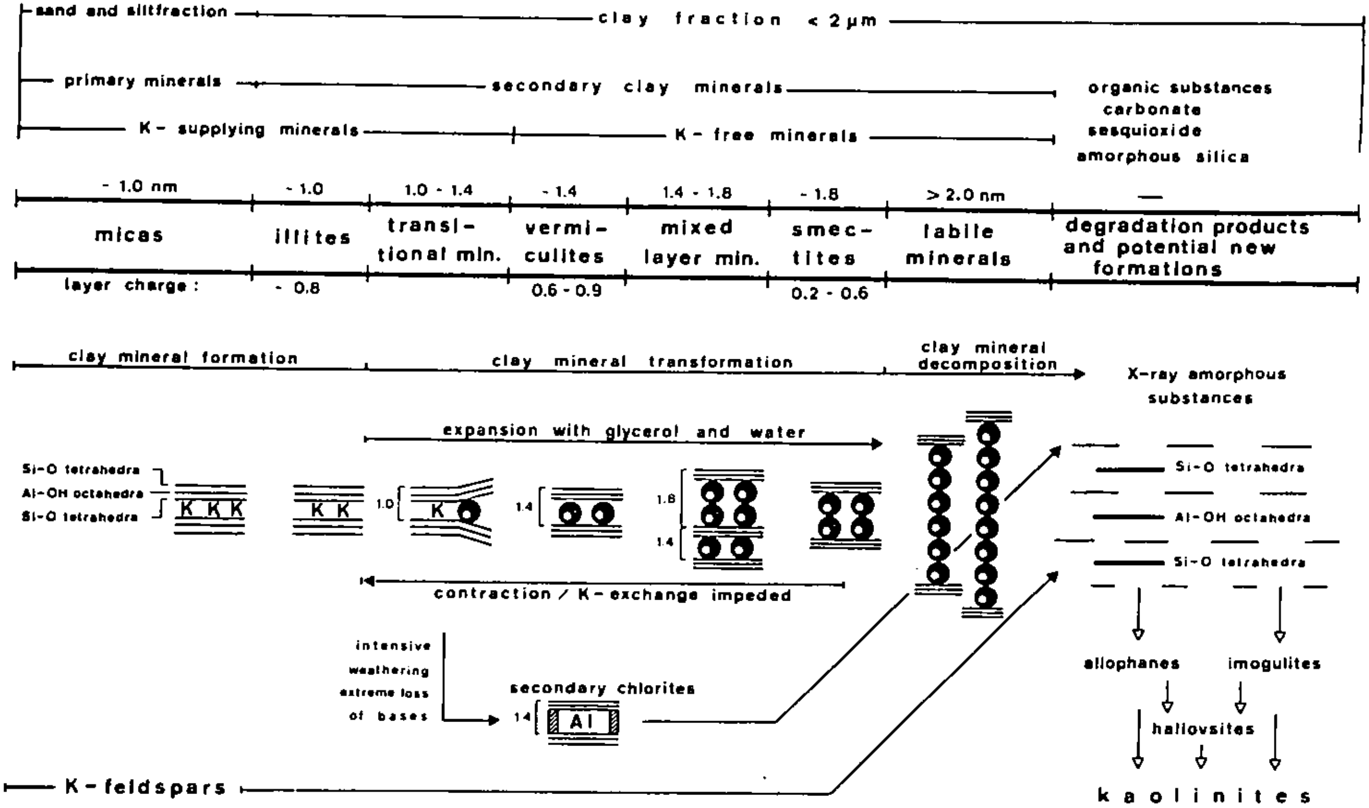


Fig. 5 Summarized presentation of possible stages of clay mineral development

First of all, the boundary of the different grain sizes is marked out by the delimination of the clay fraction < 2 μm from the silt and sand fractions. In the next line primary and secondary clay minerals are distinguished. The clay fraction not only contains silicate clay minerals but also organic substances, sesquioxides, carbonates and amorphous silica.

A further division reveals that minerals act as K suppliers.

According to their significance, mica-type clay minerals are in the centre of the table. The sequence of the minerals was determined by the basal spacings (d values) after glycerol treatment. The initial product of the outline of the development is mica which transforms to illite by passing the < 2 μm boundary. The only difference between illite and mica is that illite has a lower K content which is indicated by leaving out one of the symbolic K letters. *Barshad [1948], Newmann & Brown [1966]* as well as *Robert [1971]* have shown that the first phase of potassium removal can start without any strong lattice alteration. The transition states between illite, vermiculite and smectite comprise transition minerals, mixed layer minerals and labile minerals.

As the schematic outlines illustrate, the «transition minerals» (1.0-1.4 nm) are illites expanded at the edges, as proved by *Graf v. Reichenbach and Rich [1968]* by scanning electron micrographs of pure micas. The layers of the transitional minerals are held together by the potassium in the centre at a layer distance of about 1.0 nm.

The sphere opening the layers at the edge in the schematic outline stands symbolically for glycerol as intercalacting solvent in the laboratory. In the soil the same effect is produced by water molecules. The term «mixed-layer minerals» symbolically represents the existence of various layer distances.

As shown in the outline, layer distances of 1.4 nm and 1.8 nm may occur in packets of layers, but often mica-like layers with d-values of 1.0 nm are included *(Norrish [1972])*.

The term «labile minerals» was proposed on the basis of observations after glycerol treatment. As described in Figure 3, labile minerals represent the first visible phase of clay decomposition.

The degradation products of minerals can be found at the end of the line. In this case they consists of X-ray amorphous substances that are not necessarily without structure. Furthermore, the section contains possible new formations. The spherical allophanes are not exactly delimited as they are considered as degradation, transformation, or formation products by different authors. The arrows pointing down indicate that allophanes as well as imogulites can be formed from silicate degradation products and that they then possibly represent the preliminary stage for the formation of halloysites and kaolinites.

The single minerals or their symbolic equivalents are not connected by arrows to indicate that ordering according to expansibility does not necessarily signify the sequence of clay mineral development. It may serve as an example that vermiculites (≈ 1.4 nm) cannot be detected in most of the loess soils *(Lehnhardt [1974], Tributh [1970], Tributh* in *Schönhals et al. [1982])*.

As emphasized in Figure 4, the soil environment determines the end product of the clay mineral development which can be detected by X-ray diffractometry of subfractions, even at the smallest particle sizes (normally <0.06 µm or <0.02 µm). The long arrow between the mineral name and the outline of layer structures thus only indicates the direction of development.

On top of the outline of layer distances an arrow indicates the area of reaction with glycerol and water. The arrow beneath, pointing in the opposite direction, indicates the tendency to contraction after KCl treatment. K concentration does not occur with labile minerals and, with regard to smectites, it only occurs in coarser fractions (see Figure 2).

In the section ≈ 1.4 nm secondary chlorite is placed outside the line of development. Thus it should be emphasized that fixation of layer distances by Al interlayers only occurs with intensive weathering and extreme base impoverishment.

K-feldspars which are significant as a K resource but do not take part in the formation of 3-layer minerals are placed to the left and at the bottom of figure 5. According to our present knowledge these primary minerals first have to be degraded before kaolinites can be formed.

4. Effects of potassium removal by crops on the transformation speed of illites

In chapter 2 it was inferred that potassium release was fundamental requirement for the transformation of three-layer minerals. It would therefore be expected that severe K depletion through plant uptake would affect the rate of transformation. This was studied on a plot which had received no K fertilizer since 1954 from which 2138 kg/ha K had been lost, and on which corps grew poorly, compared with a loss of 720 kg/ha from the plot receiving K fertilizer *(v. Lieres [1981])*. Furthermore, the crops only grew sparsely.

In other experiments with grasses in Mitscherlich pots, clay mineral investigations also revealed clear differences between the K and K_O (without K) treatments *(Tributh [1981])*.

As can be seen in the X-ray diagrams (Figure 6), the illite content of the K_O sample decreased to a greater extent in the top soil than in the subsoil. This fact particularly emphasizes the influence of the plants which, by K removal, promote the transformation of illite to smectite especially in topsoil. Meanwhile, experiments carried out on other sites (Göttingen, Bonn, Grignon) have confirmed these results *(Tributh et al. 1987)*.

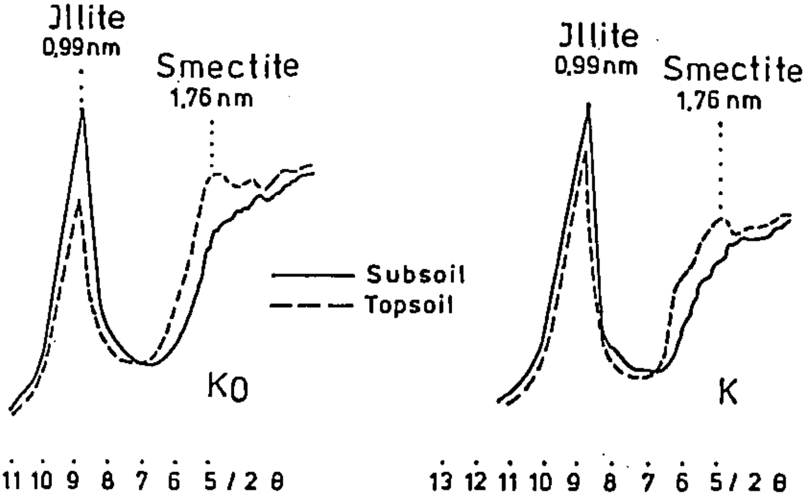


Fig. 6 X-ray diffraction diagrams of the effect of applications of K⁺ fertilizer (fields in Rauischholzhausen near Giessen, Germany)

5. The particular role of ecological systems of forests in clay mineral decomposition

In chapter 2 it is emphasized that clay decomposition is caused by increasing concentration of protons. Soils represent an open system so that during the soil development «base forming» cations can be leached out and cause an increase in acidity.

This process, lasting 15 000 to 20 000 years, is still comparatively short for Central Europe but has already led to the degradation of most of the soils.

On cultivated land natural soil development is interrupted in a positive way by liming and fertilizing and the soils are regraded *(Brümmer [1981])*. In forests, however, acidity has been further increased. In grey-brown soils it even reaches the Bt horizon, and in acidic brown soils it affects the whole profile. Especially in acidic brown earths, in which 97% of all exchangeable cations consits of protons and Al ions, secondary chlorite is formed due to a lack of base forming cations.

Al compounds are intercalated into the interlayers of mica-type clay minerals with relatively high layer charge which had just become expandable by potassium release. Their layer distance is fixed to 1.4 nm so that the interlayer spaces do not take part in cation exchange (see their particular place outside the sequence of development in Figure 5). These three-layer minerals, also called soil chlorites, are not protected from further clay mineral development. They are also subjected to clay decomposition during particle size reduction by weathering. As described in chapter 6, they can also be remobilized by liming. Advanced processes of podsolization, however, have to be assessed differently. Favoured by several generations of coniferous forests, they have even led to a destruction of kaolinite which is normally rather stable in an acidic environment.

Another disadvantageous ecological property beside the formation of organic acids is the special acid supply of coniferous forests. These forests filter SO_2 and its solution products from the air to a higher degree than deciduous forests and deliver them to the soil as sulphurous and sulphuric acid. The amount of acid (in equivalents) can be three times greater than that under a beech forest *(Ulrich [1980a]).* pH values measured in soils under beech forest also indicate that the soil so-called «alkaline fertilization» by leaf fall is not sufficient effectively to stop the increase in acidity *(Runge & Wieners [1984]).*

Unfortunately, the advanced degree of clay decomposition described for the ecological systems of forests also holds for many tropical soils which have experienced long-lasting and intensive weathering.

6. The influence of fertilization on clay mineral development

As shown in the «summarizing representation» in Figure 5, the weathering of primary minerals is the basic requirement for the release of nutrients for plants and the formation of secondary clay minerals. However, the rate of clay mineral transformation and decomposition can be influenced by fertilizing.

In this context it is an interesting fact that, in spite of the increased transformation of illites (Figure 6) in the field without K-fertilizing (chapter 4), the release of K was not sufficient for normal plant growth, and yield decreased. In this relation a change of the experimental procedure can be of interest. A deficiency field that had been tested for ten years was fertilized with farmyard manure for a further twelve years. Not only did the plants at once achieve higher yields, but eight years after the first supply of manure a positive balance was gained and this improved significantly in the following four years. The changes could also be detected by X-ray techniques which revealed a decrease in illite transformation.

The K ions which re-entered the interlayer space following potassium fertilization do increase the stock of soil nutrients because, though with greater difficulty, they can be exchanged. Although contractions occur at certain layer charges (see Figure 2) and the basal spacings are comparable with those of illites (1.0 nm), this process should not be described as «fixation» or «illitization» because the K release produces mica-type minerals by weathering and results in irreversible transformations in the silicate layer which is accompanied by an expansion of the b-axis. Therefore, the original structure of illite cannot be restored when K is again supplied *(Burns & White [1963]; Ellis & Mortland [1959]; Newmann [1970b]; Brown & Newmann [1970]).*

While K shortage merely accelerates the transformation speed of illites, Ca shortage also changes the environmental conditions (decrease of pH) which leads to clay decomposition.

Secondary chlorite (see Figure 5) which is often found under forests can be remobilized by cultivation, in particular by liming *(Niederbudde & Schwertmann [1980])*. In strongly acidic soils it must be taken into account that the soil is not only poor in nutrients but its capacity for nutrient storage is blocked (secondary chlorite), or the layer silicates have been transformed into labile minerals or X-ray amorphous substances with very low storage capacity. Thus, nutrients supplied by fertilizing do not increase the plant available stock but are mainly leached out and also increase water pollution.

In contrast to the interlayer spaces blocked by Al, labile minerals or X-ray amorphous substances as weathering products cannot be transformed into intact three-layer minerals by liming.

Useful fertilizing, however, may positively influence the clay mineral development that is still in process and may prevent further clay decomposition.

7. Methodical aspects

7.1 Winning of clay subfractions

As already mentioned in the introduction, it is difficult to detect transformation processes that are due to weathering by analysing natural clay fractions of soils. An essential requirement for such an analysis is extended clay fractionation *(Tributh [1970])* in which clay subfractions are separated by centrifuge for further analytical investigations (X-ray, CEC).

The pre-treatment and preparation of analytical samples is described in great detail by *Tributh & Lagaly [1986a]*. Therefore, only the significance of dialysis as an important requirement for optimal dispersion should be emphasized. The extended particle size analysis which has been developed as a routine procedure *(Tributh [1972])*, provides diagnostic criteria for the estimation of the quantitative extent of clay mineral development *(Tributh* in *Plass et al [1977]; Tributh* in *Schönhals et al [1982]; Tributh et al [1986])*. It is recommended to use five clay subfractions. Details on the methods can be found in *Tributh & Lagaly [1986b]*.

7.2 X-ray detection of transformation stages in K containing clay minerals

Generally, the expansibility of clay minerals is tested by treatment of the clay samples with glycerol or ethylene-glycol. As indicated by the outline of basal spacings (Figure 5), different stages of expansibility can be distinguished. A disadvantage of the glycerol test, however, is that it does not determine exact layer charges for it functions according to the principle «yes or no». Smectites of different soil clay subfractions expand to the same basal spacing of 1.76 nm, although the layer charges can be very different (see Figure 2).

The qualitative changes of the minerals which take place with decreasing particle size, however, become visible by the contraction behaviour. A comparison of the X-ray diagrams gained after KCl treatment with the layer charges of the clay subfractions shows a clear relationship. No exact layer charge values can be obtained from the contraction test but ranges of layer charges can be distinguished.

1. *Complete concentration* = higher layer charge (0.6-0.8)
   basal spacing ≈ 1.0 nm

2. *Incomplete contraction* = medium layer charge (0.4-0.6)
   basal spacing ≈ 1.0 nm but
   slightly asymmetric
   up to 1.6 nm

3. *Slight contraction* = low layer charge (< 0.4)
   basal spacing lies between
   1.2 nm and 1.3 nm as in
   montmorillonites of deposits

A rough classification like the above may be significant both for the estimation of K fixation and for useful fertilization. Therefore, the KCl contraction test will be described in some detail:
First, 100 ml clay suspension samples are taken from a clay suspension obtained by pretreatment of the soil (removal of carbonates, iron oxides and humus materials) *(Tributh & Lagaly [1986a])* and precipitated with $CaCl_2$. The sample is centrifuged and the solution decanted. The Ca treatment is repeated three times with 1 *N* $CaCl_2$. Then the sample is washed once with distilled H_2O. About a third of the sample is transferred into another centrifuge tube for the KCl treatment. The remaining two thirds of the Ca sample are used for X-ray determination, with or without glycerol treatment.

The sample in the centrifuge tube is dispersed in 50 ml 0.1 *N* KCl solution and again centrifuged. After decanting the clear (!) solution, the KCl treatment is repeated three times. Then the sample is washed once with distilled H_2O and decanted only when the solution is clear after prolonged centrifuging. Finally, the sample is X-rayed after three to four days of air drying.

Robert [1972] described the concentration test with KCl as a method which makes it possible to differentiate between «real» montmorillonites and smectites formed by transformation in the soil. However, the contraction test was carried out by him in a slightly different way (drying of the K-clay up to 110 °C and subsequent glycerol treatment) than by *Schwertmann & Politz [1961]*.

7.3 The alkylammonium method for layer-charge determination of smectites and vermiculites

Determination of the exact layer charges in soil smectites and vermiculites gives risk to serious problems because the clay minerals can be separated in a quantitative way only in very rare cases. Thus, chemical analysis and calculation of the layer charge from chemical data are generally insignificant and misleading. Estimation of layer charges by X-ray powder diffraction methods has the advantage that quantitative separation of smectites and vermiculites is not required.

The soil samples are reacted with alkylammonium ions

$$C_{n_C}H_{2_{n_{C+1}}}NH_3^+ \ (n_C = 6, \ldots\ldots\ldots 18)$$

which exchange quantitatively the inorganic interlayer cations (Figure 7).

Short chain alkylammonium ions arrange themselves in monolayers between the silicate layers. As the chain lenght n_C increases, a point is reached where the monolayer becomes close-packed. Longer alkylammonium ions form bilayers (Figure 8).

At the point of close-packing, the area of the alkylammonium ion A_C is identical or very near the equivalent area A_e. Thus, from n_C at which the monolayer transforms into the bilayer, the layer charge is easily calculated. The calculations are effortless as described by *Lagaly [1981].*

The layer charge determination is complicated by the fact that the charges are not distributed uniformly (left part of Figure 9).

In particular, soil smectites may possess a broad distribution of the charges from layer to layer and also within the individual layers. It is the particular advantage of the alkylammonium method that the distribution is directly measured.

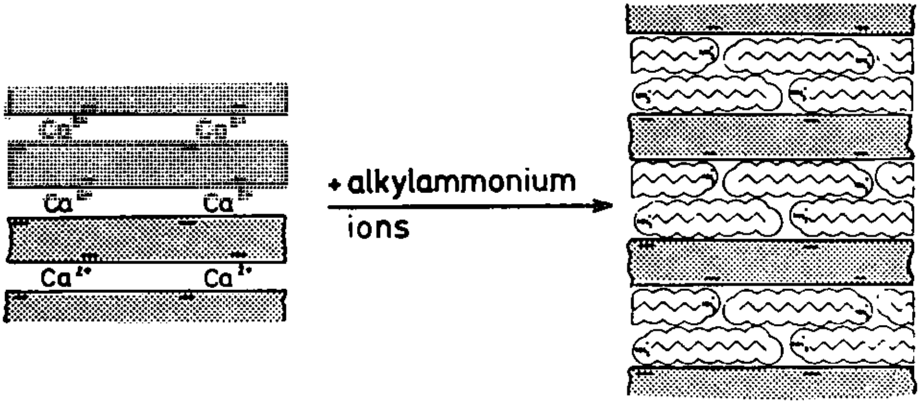


Fig. 7 Exchange of calcium ions of smectites by alkylammonium ions

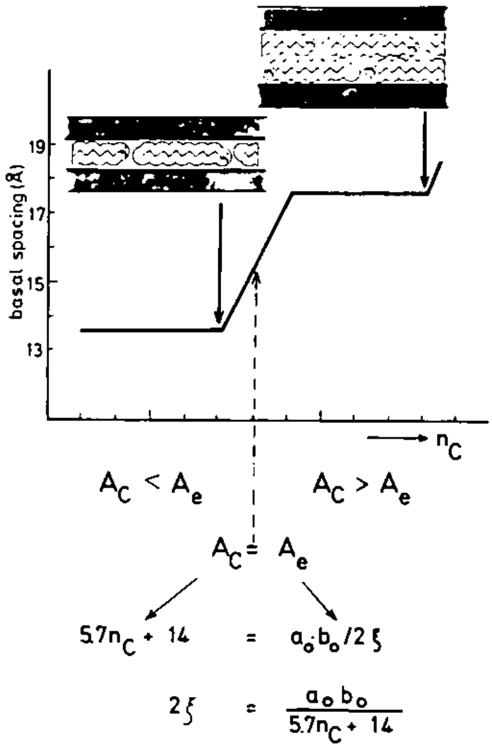


Fig. 8 Alkylammonium monolayers and bilayers in smectites

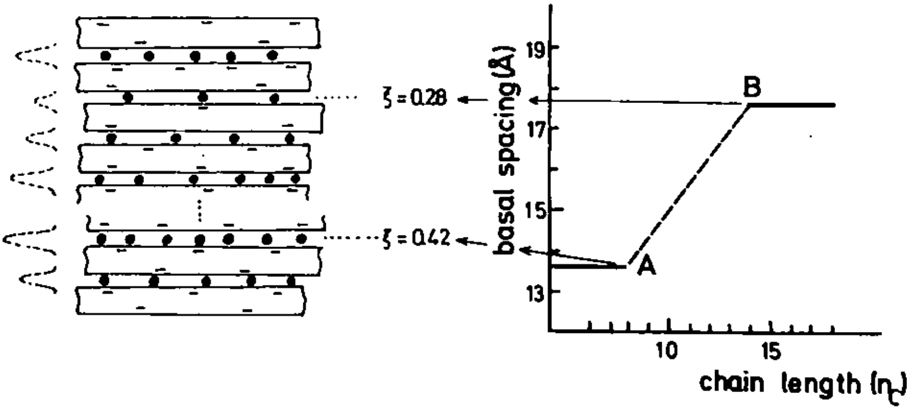


Fig. 9 Smectites with non-uniform charge distribution and calculation of the upper and lower limit of the interlayer cation density

Non-uniform charge distribution (charge heterogeneity) causes broadening of the monolayer/bilayer transition (Figure 9, right).

What is the practical procedure? First, select the range of chain lenghts that is anticipated to comprise the monolayer/bilayer transition; for smectites it is often sufficient to use the alkylammonium ions with $n_C = 10, 12, 14, 16$. Uneven values of n_C (9, 11, 13, 15, 17) may or may not be included depending on the precision desired. Second, react the samples with aqueous solutions of the alkylammonium chlorides (or formiates) to exchange the inorganic interlayer cations.

Intercalation of alkylammonium ions (C_6-C_{18}): 100 mg clay are suspended in 10 ml (concentration 1-0.02 M depending on the alkyl chain lenght) alkylammonium formiate solution and kept in a closed centrifuge tube at 60 °C over night. This process is repeated. Then, after centrifuging and repeated washing with alcohol and drying, the layer distance can be determined by X-ray powder technique.

A simplified procedure has been described by *Ruelicke & Kohler [1981]*. The charge distribution data are calculated from the variation of basal spacings with n_C (Figures 8, 9). Recently, a method has been developed to improve the calculation of the basal spacings from the profiles of the basal reflections *(Stanjek & Friedrich [1986])*. This method includes corrections (by computer) for the Lorentz and polarization factors.

Generally, the determinations are made on samples without any pretreatment. In soil samples, however, pretreatments (removal of iron oxides and organic materials, fractionation) are inevitable. The reduction/oxidation processes during the pretreatment somewhat change the layer charge and charge distribution. The alkylammonium method can detect these changes. They are, even if modest, clearly expressed in the charge distribution but often cause only a minor deviation (± 0.01-0.02 eq/$(SiAl)_4O_{10}$ of the layer charge (as the average of the interlayer charge densities).

The procedure for vermiculites is the same, the reaction period during cation exchange (generally two periods of 24 h) should be somewhat prolonged. Basal spacings of the alkylammonium derivatives of vermiculites may change stepwise as for smectites or can increase linearly. In both cases the evaluation of the layer charge data differs from that for montmorillonites *(Lagaly [1981, 1982])*.

In conclusion, alkylammonium ion exchange is actually the most precise method for determining the true layer charge. Even small differences, for instance between different fractions, are recognized by the charge distribution curves.

Finally, two further applications should be mentioned. The strong increase in intensity of the (001) reflection after alkylammonium ion exchange (Figure 10) enables the detection of very small amounts of smectites (considerably below 5%!).

In bentonites and soils (in soils only after removing organic material) the smectite content can be reliably estimated from the content of carbon which can easily be determined by combustion *(Lagaly [1981])*.

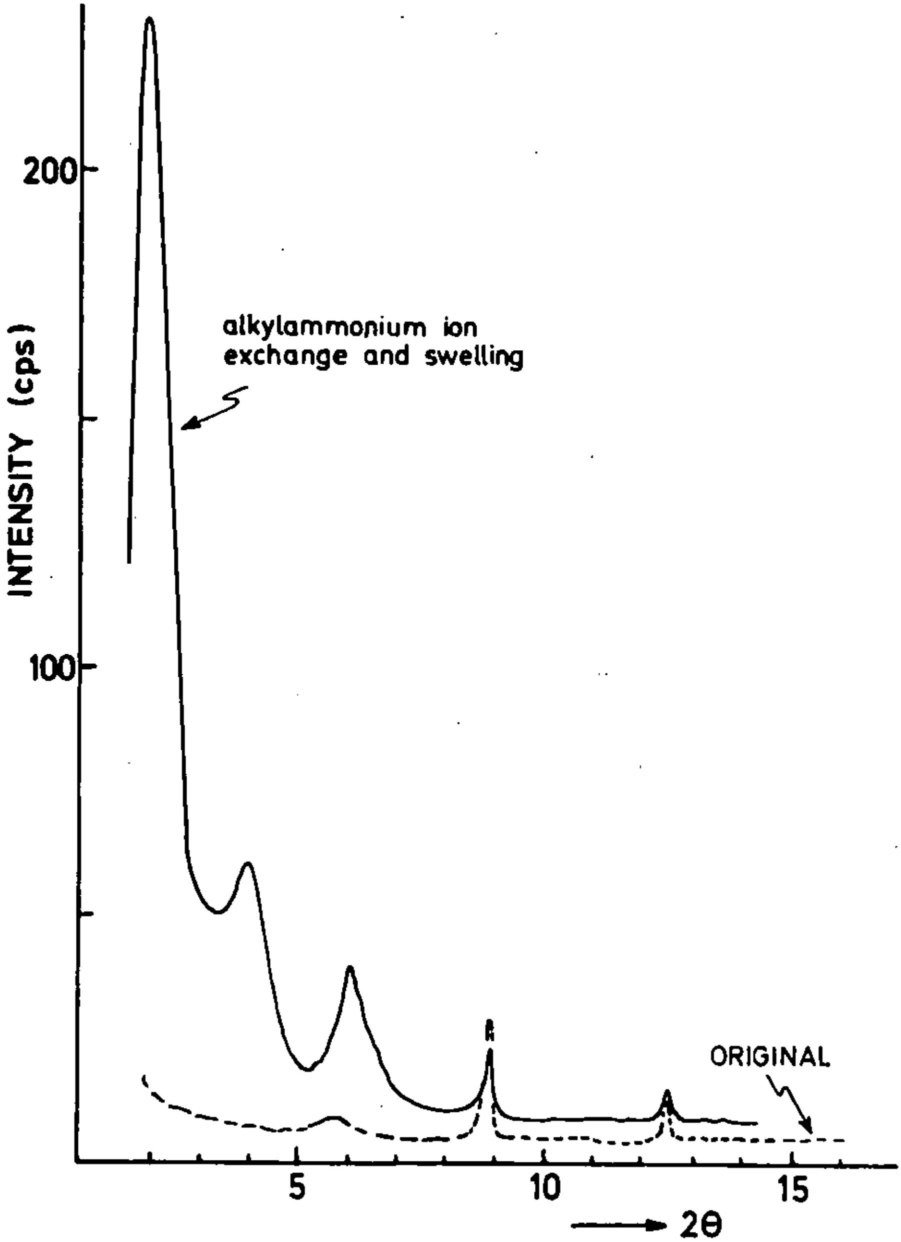


Fig. 10 Increase in intensity of the (001) reflection after alkylammonium exchange

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Scanning Electron Microscopy and Microprobe Techniques for Soil-K Characterization

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Summary

Scanning Electron Microscopy (SEM) and *Energy Dispersive Spectrometry (EDS)* provide, as a system, a powerfull tool for direct investigation of soil structure and composition.

Soil characteristic fabrics were obtained, reflecting correlations between soil composition, exchangeable complex and the electrolyte content in pore water. SEM micrographs of soils after rain simulation experiments, present at the very surface of fractured samples, a clean silt grain layer due to the clay dispersion and to the downward movement into a clay accumulating «washed in» zone. The thickness of the silt and of the «washed in» layers are reflecting the size fraction content and soil sodicity.

Due to the fact that lack of homogeneity and surface roughness are strong disturbing parameters in X-ray microanalysis, specific methodology for potassium evaluation was recommended: *(i)* characterizing the active part of the soil matrix using oriented films of intermediate thickness on carbon support, *(ii)* using standards having mass absorption coeficients for potassium K α line close to the analysed sample, *(iii)* optimizing working parameters *e.g.* electron energies at low values and take off angles related to the topographic effect.

1. Introduction

Both *Scanning Electron Microscopy (SEM)* and *Energy Dispersive Spectrometry (EDS)* were applied in soil analysis as independent techniques from the very beginning of their development. *Blaske [1969], Gillot [1969], Bohor & Hughes [1971]*, presented scanning electron micrographs and emphasized the possibility of the SEM technique to bring direct information on soil fabric by continuously varying the examined specimen area from the optical microscopic range of magnification up to a few sq. µm. In his work on clay minerals *Tovey [1971]* emphasized

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the oriented character of a clay structure, and presented an optical technique for quantifying the topographic information obtained from scanning electron micrographs. Particle size and shape were correlated to the diffusion path of exchangeable cations and structural imperfections were attributed to an increase in interlayer penetration of the exchangeable cations *(Wells & Norrish [1968], von Reichenbach [1976])*. More recently, *Tovey & Socolov [1981]* published a review of quantitative SEM methods for soil fabric analysis.

The electron microprobe X-ray analyzer was used in its early stages as an independent tool in soil investigation. One of the first works using this instrument was reported by *Rausell-Collom et al. [1965]*, in which point-by-point analysis of calcium and potassium illustrated the replacement of potassium by calcium at the edge of a mica flake in an artificial weathering experiment.

Recent works use the *Analytical Electron Microscope (AEM)* as a tool for elemental and structural characterization of clay minerals by applying thin film techniques. *Anand et al. [1985]* in experiments on the influence of microenvironment on K feldspar found a consistent correlation between the composition and the structure.

The capacity of a soil to supply potassium to plants is dependent upon the K content and the rate of its release by the primary minerals as well as upon the quantity and the type of clay minerals. SEM/EDS use appropriate preparation techniques (freeze drying, critical point drying) to minimize artifacts due to the drying process. In processes, such as ion diffusion in soil, where effects of pore size and their distribution are important factors, these techniques could bring support to conventional experiments, thus supplying simultaneous and rapid information on texture and composition at the microscopic level.

It is well accepted that rough surfaces introduce errors in elemental quantification by EDS analysis *(Small et al. [1979])*. On the other hand every step in sample preparation introduces some artifacts, making it impossible to look for the mobile potassium content in its original location.

The aims of this paper are: *(i)* to analyze the potassium detectability by EDS in soil systems, *(ii)* to present basic SEM/EDS abilities to investigate films of fine fractions for semiquantitative evaluation and *(iii)* to characterize soil matrix structure *e.g.* relationships between the adsorption complex and the morphological pattern.

2. Soil structure analysis

2.1 Preparation methods

In preparing representative soil samples for SEM observations, the main difficulty arises from the necessity of removing the water from the soil sample (the analysis is performed in vacuum) without destroying the original texture. For soils with low moisture content, the procedure is quite straitforward. *Tovey & Wong [1973]* reviewed six techniques used for fluid removal from soil samples: oven drying, air drying, controlled humidity drying, substitution drying, freeze drying, and critical-point drying. For sensitive soils, with high moisture content, the last two techniques are needed; it is well-accepted that artifacts are generated by dehydration, regardless of the way the drying is performed.

For textural studies in our laboratory, an alternate solution has been adopted to minimize these artifacts. For loess soils with low moisture content, the first step is to cover a trimmed sample of 1 sq. cm and 2-3 mm thick – with a carbon layer in order to secure mechanically the surface particles. After fracturing and attaching the exposed surface to the SEM stub, the less bonded particles are removed by a peeling procedure. The samples are double-coated with carbon and gold before observation in the microscope. For soils with high moisture content,the sample is freeze dried and in order to assure fast cooling, its size must be limited to a few cubic millimeters.

For qualitative EDS analysis, the fractured surfaces are observed after applying carbon masks to limit the exposed area and to minimize the charging and topographic effect. Semiquantitative analyses are carried out on oriented films on a fraction of soil less than 2 µm, using standards of similar roughness.

2.2 SEM – Structural analysis capabilities

The large depth of focus, the resolution down to 100 Å and the capability to obtain stereo pictures, made the scanning electron microscope from the very begining of its existence a suitable technique for soil fabric studies.

Lohnes & Demirel [1978], made a thorough review of the research on clay and clay soil fabric using SEM and pointed out a good correlation between the structure and the tests that characterize their mechanical behaviour.

Two problems, sample preparation, as already mentioned, and quantitative assessment of soil fabric remain the main limitations of this technique. *Tovey & Socolov [1981]*, while acknowledging difficulties, succeeded in quantifying SEM methods for the evaluation of soil fabric, for oriented samples.

In an effort to explain weathering processes, both techniques – SEM-EDS and AEM – facilitate the observation on diagenetic transformation in minerals. Experimental extraction of interlayer K in biotite was directly visualized in SEM. *Von Reichenbach [1976]* presented SEM evidence that potassium dissolve in mica minerals at the exchange fronts, penetrating into the particle as the weathering proceeds. The biotite unit, after releasing K ions, presents wavy areas around the contour; as a consequence of diminishing strength between the layers, expansion takes place, promoting further physical weathering; finally the unit is fractured in small particles.

The active role of the different components of soil concerning K availability to the plant is well known *(Bray [1954], van Diest [1978])*. K diffuses through the soil by way of both, water-filled soil pores and water films surrounding soil particles.

Two important influences on K mobility in a soil-water system, amongst other factors, are the adsorbed phase and the free electrolytes in pore water. These two factors, usually measured by independent methods, may be simultaneously approached by SEM/EDS as they reflect relationships, between the chemical and the mineralogical components in the soil-water system.

Ali & Turner [1982] presented SEM micrographs showing the stages in the development of authigenic K-feldspar, in which intrastratal dissolution was responsible for providing the interstitial environment with the necessary potassium, aluminium, and silicon ions. Using EDS, for preliminary and semiquantitive analysis, in conjunction with electron probe for mineral identification and chemical analysis they presented the diagenetic sequence: illite – quartz – K feldspar – illite – kaolinite.

Bryan & Williams [1982] comparing the X-ray diffraction data with EDS analysis, found that bulk chemistry using X-ray spectra indicates large variations in oxide evaluation of up to 15% standard deviation for K_2O, due to the uneven distribution of the analyzed particles. When size-fractioned samples were analyzed, higher accuracy was obtained making this technique a valuable complement to the structural information provided by X-ray diffractometry.

Lanier & Jones [1979] using SEM under laboratory consolidation conditions found a series of correlations between the development of grain aggregates and water salinity in kaolinite clay. Kaolinite particles flocculating in the fresh water present large aggregates in which individual grains link face-to-face. Increasing salinity enhances the development of multiple kaolinite grain aggregates.

Chen et al. [1976] studied freeze-dried specimens, and presented SEM micrographs showing different fabrics for montmorillonite with calcium and sodium in the adsorption complex. When calcium was present in the complex, large irregular aggregates characterized these structures. When calcium was exchanged by sodium, an arrangement with large thin units with small distances between them and small pores was obtained.

The character of adsorbed water around the clay particles has been extensively investigated *(e.g. Martin [1960])* and the correlation with the cation mobility in soil water systems has been established. For potassium mobility in soil, the possibility of observing structural modification as a response to changes in adsorption phase, presents practical significance. Natural soil with low as a well as high water content, in undisturbed structure, analysed by SEM/EDS, provides experimental data correlating mobility with the presence of specific components and their structure.

2.3 Structural factors as influenced by exchangeable cations.

The important role of exchangeable cations/electrolyte concentration in K mobility is well accepted. Estimating the transformation in soil fabric by SEM analysis, when the soil water system changes as a result of variation in cation exchange complex, may offer very usefull qualitative information.

In our laboratory *(Gal et al [1984])* significant structural modifications were found in two types of soil with different exchangeable cation ratios, when low electrolytes in pore water were supplied.

Fractured samples of Netanya sandy loam soil, with 26% montmorillonite in the 11% clay fraction, shows, after rain simulation with distilled water, different structures for two levels of exchangeable sodium percentages (ESP)-1.0, and 11.6. In Figure 1a a sample with low ESP shows, at low magnification, large aggregates randomly oriented. Sand grains covered with a thin film of clay are seen throughout the profile. Figure 1b (magnification of the center of Figure 1a), shows randomly oriented clay aggregates. At higher magnification (Figure 1c), stereo pictures present a strong orientation of the clay particles. For the same soil, with higher sodium concentration in the exchangeable complex ESP 11.6, the top first layer contains many cleaned grains (Figure 2), suggesting some dispersion process of the clay particles, stripping of the thin film of clay from the coarser sand grains, and a downward movement of the small clay particles during the rain simulation.

In the same experimental conditions, but with a Golan clay with a 65% fraction less than 2 μm (mainly montmorillonite and kaolinite) the effect caused by the presence of different exchangeable cations was even more definite. In Figures 3 and 4, the characteristic structures of the clay soil (with ESP 1.6 and 10.3) present a naked-silt-grains layer on the top of the «washed-in» layer after rain simulation with distilled water. The thickness of the silt layer (50μm at low sodicity and about 250μm at high sodicity) and the density of the «washed-in» layer increase with an increase in soil sodicity, creating a well-developed crust. Characteristic to the «washed-in» layer with high ESP are macrovoids lined with compact clay (Figure 5).

These structural observations are in good agreement with the infiltration rate data of *Agassi [1981]* and *Kazman [1983]* obtained on the same soils. In their experiments, using a rain simulator and distilled water, they found that the infiltration rate (mm/h) factor was more sensitive to a certain exchangeable cations-electrolyte concentration in soil-water system, than to the permeability of the underlying soil.

In an effort to obtain a correlation between the structures and the EDS analysis in clay minerals, oriented films on carbon supports were analyzed after being air-dried. Figure 6 shows less than a 2 μm fraction of clay soil for two different ESP's. In Figure 6a, on a soil sample micrograph with ESP 1.0 one may distinguish at low magnification large aggregates with pores between them, randomly disposed. When calcium is present in the exchangeable complex, a thin and strong oriented water film keeps the particles tight in a compact arrangement. The compact character of the aggregates is seen at a higher magnification in Figure 6b. In Figure 6c at ESP 11, the clay particles are organized in a more isotropic structure with face-edge contacts between them. At higher magnification in Figure 6d, microporosity of this clay can be observed, suggesting the presence of sodium in the exchangeable complex. In this case, a thicker, less oriented water layer around the clay particles is responsible for the face-edge arrangement.

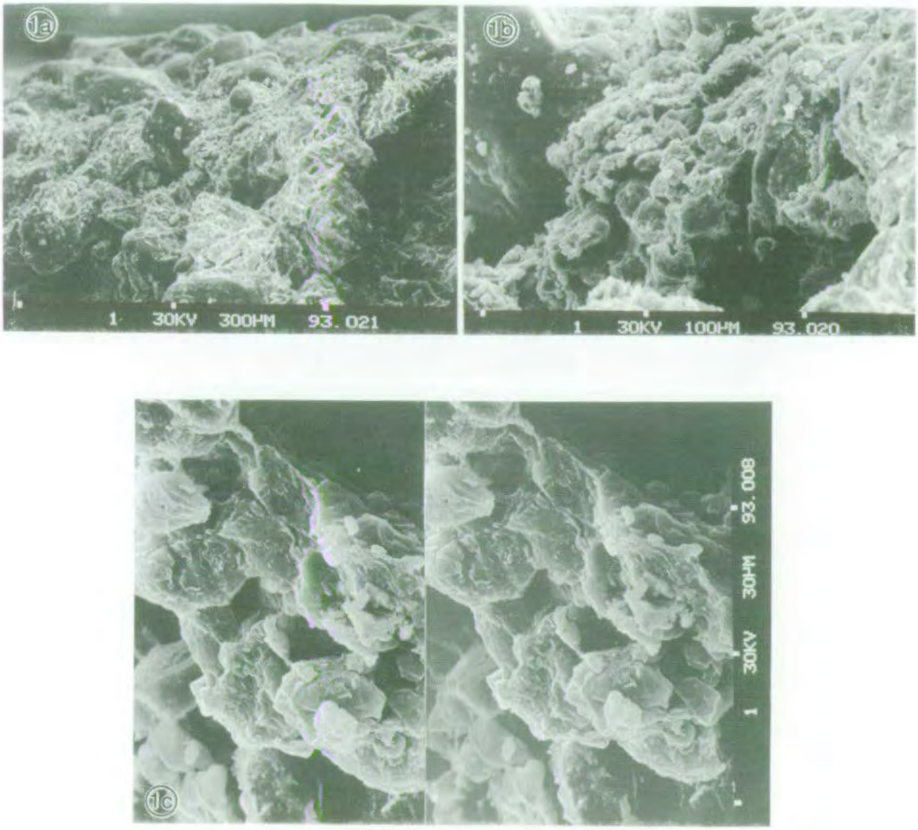


Fig. 1. SEM micrographs of a Netanya sandy loam soil with low sodicity ESP 1.0: (a) low magnification of fractured area showing clean grains at upper layer; (b) detail of previous picture with random oriented clay aggregates; (c) stereo pair of above clay aggregates.

Fig. 2. Stereo pair of compacted area of naked grains on soil surface after being submitted to rain simulation with distilled water (bar 100 μm).

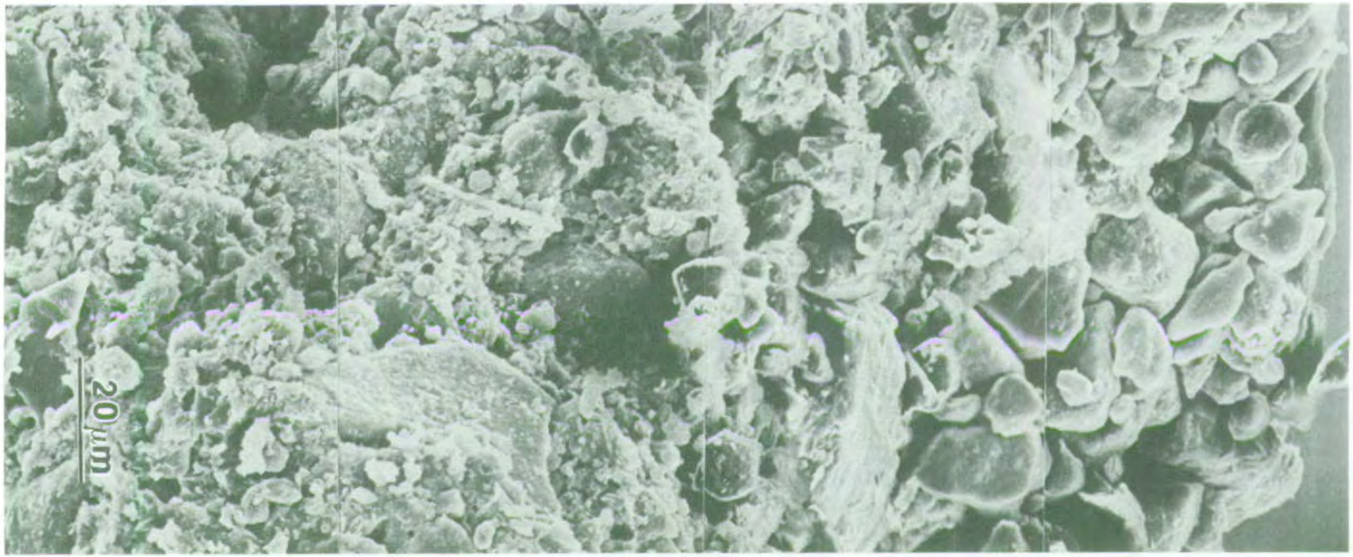
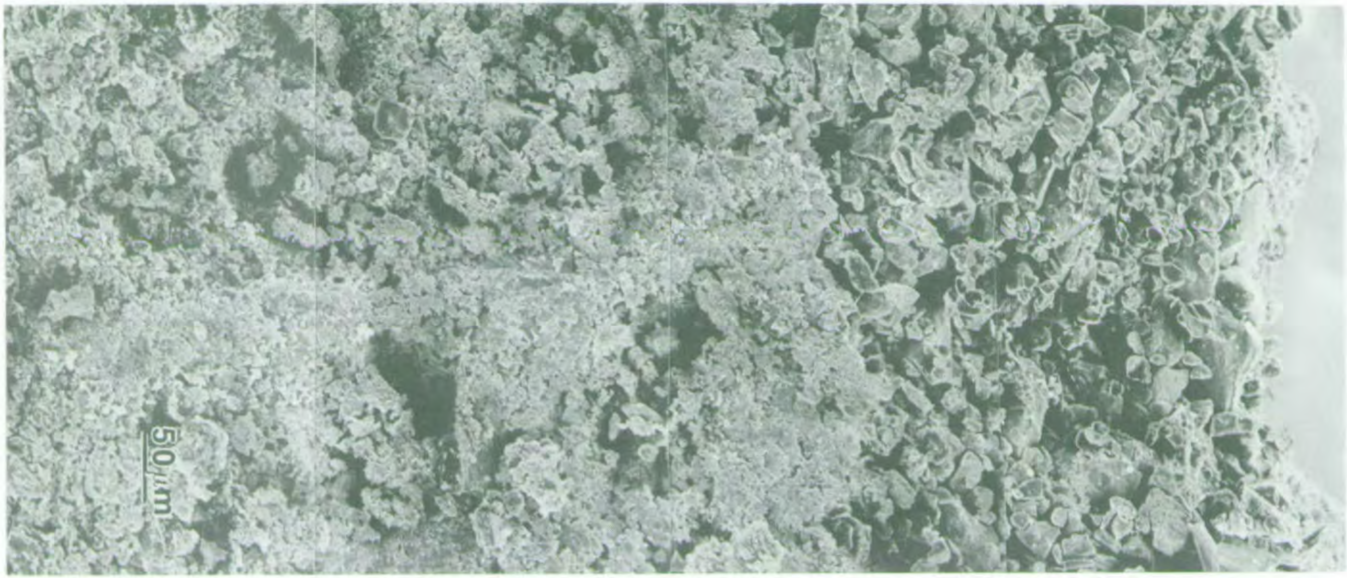


Fig. 3. SEM micrograph of a fractured sample in Golan clay soil with ESP 1 showing the displacement of small clay particles.

Fig. 4. SEM micrograph of fractured area in Golan clay soil sample with ESP 10.3 showing a well developed crust.



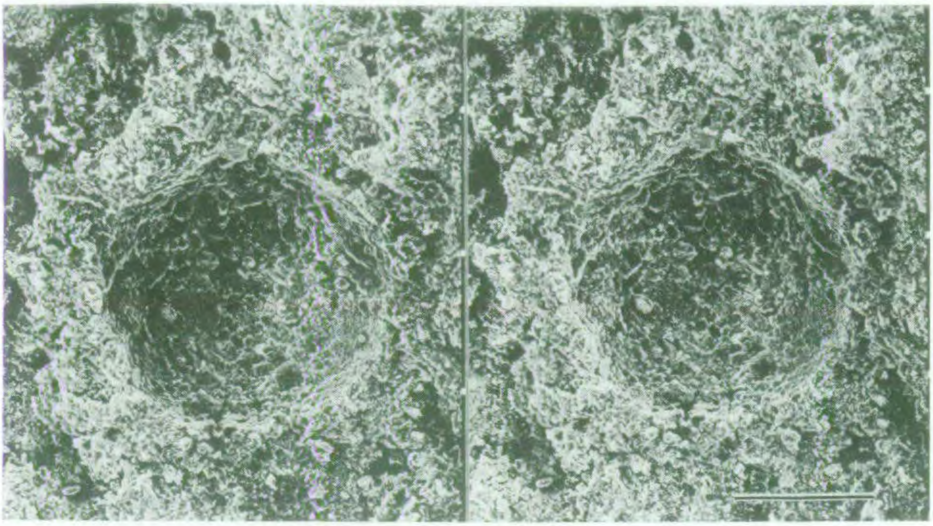


Fig. 5. Stereo pair of void, with clay lining wall, in well-developed crust (Golan clay with ESP 10.3, bar 100 μm).

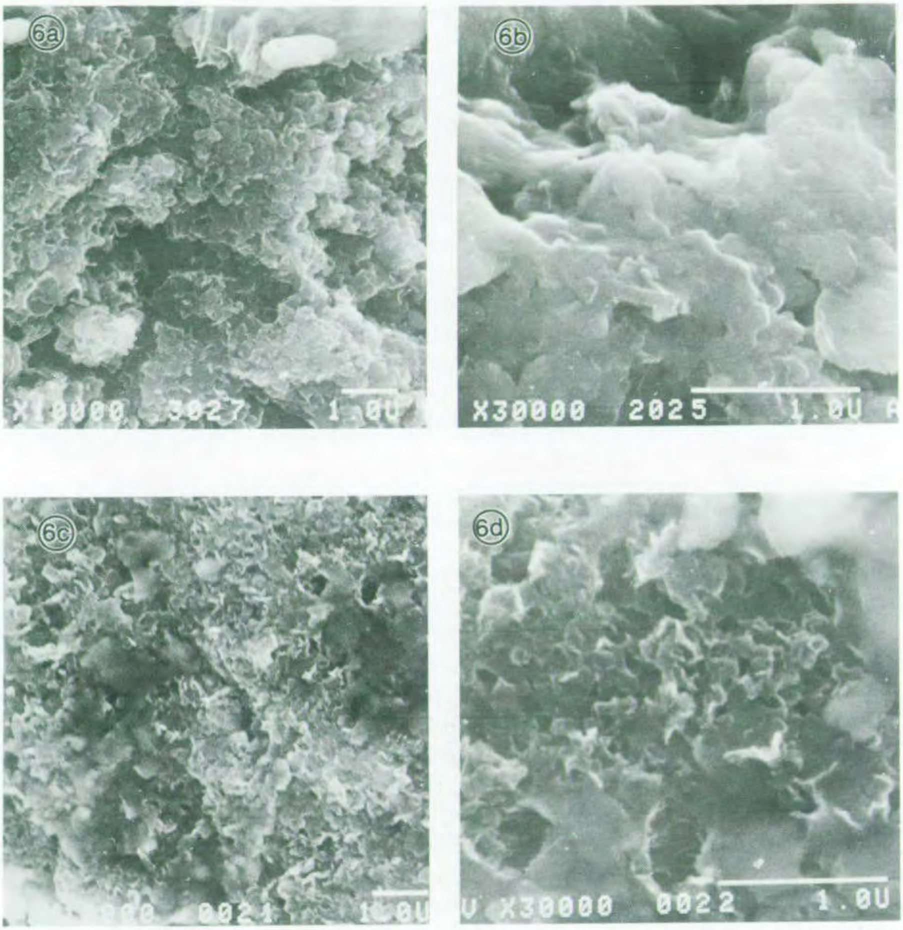


Fig. 6. Fine fraction (< 2 μm) in Golan clay: (a) and (b), ESP 1.6, magnification × 10 000 and × 30 000; (c) and (d), ESP 10.3, magnification × 10 000 and × 30 000.

3. Strategies for potassium quantification

3.1 Qualitative analysis of soils

Although different alternatives are available *(Newbury et al [1986])*, a qualitative analysis of cohesive soils may be performed on thin films of intermediate thickness using SEM/EDS instrumentation. The system (see Appendix, Figure A1) has the ability to measure characteristic X-ray line energies, and relate those energies to the presence of specific elements. Elemental analysis is performed by measuring the energy and intensity distribution of the X-ray signal generated by a focussed electron beam in a sampled volume. Such an analysis for components with an atomic number greater than 11 can be accomplished in a few minutes. Simultaneous data on morphological characteristic and chemical composition could be obtained in a SEM/EDS system, if instrumental limitation and sample preparation are carefully considered.

In a qualitative analysis of potassium in soil, and as a first step towards a quantitative analysis, the soil matrix characteristics have to be evaluated. As can be seen in the SEM micrograph (Figure 1), the soil specimen when fractured presents large aggregates randomly oriented with a pore network between them. In ideal conditions, accurate optimization of the instrument and statistically significant peaks given by accumulation of an adequate number of counts in the spectrum, strong artifacts due to the surface roughness and lack of homogeneity in the sampled microvolume, are the principal limitations to be considered.

In our laboratory, the characteristics of the clay size fraction of the soil are investigated, and the detection of potassium in such a matrix is accounted for. Thin films from a clay suspension are deposited on carbon supports, air dried and their topographic effect checked. If the topographic feature hides the detector's view, the specimen is rotated (see Appendix, Figure A1) in order to provide to the emerging X-ray a free path to the detector. An even dispersion is obtained in the thin film which makes the qualitative X-ray microanalysis (XM) aceptable. In Figure 7a, b and c, the SEM micrographs of a clay fraction of Golan soil (mainly montmorillonite) are shown. At low magnification (×1000 Figure 7a) a rather homogeneous pattern is found, and the sample is considered proper to XM without further correction for flatness. At a higher magnification (×10 000 and 0° tilt angle, [Figure 7b]) homogeneity was maintained. At 30° tilt (Figure 7c), which is necessary for instrumental optimization, corrections have to be considered. We found very reproductive spectra covering all the thin film when volumes of 10^{-5} mm^3 were sampled. Figure 8 shows X-ray spectra taken for common clay minerals on oriented films: (a) illite, (b) kaolinite, (c) Ca montmorillonite. The operational conditions were: electron acceleration 10 and 15kV; take-off angle 30°; accumulation time 50 sec, with a rate of 3000 cps on the entire range.

Potassium has its Kα and Kβ X-ray line energies at 3.313 keV and 3.589 keV respectively; as seen in Figure 8 in this region of the spectrum, with above working conditions, the background radiation is relatively low, making possible to detect a low concentration of this element (see ∯ 4).

For statistical reasons, the minimum size of a peak should be three times the standard deviation of the background at the peak position, in order to be identifiable. If the peak intensity of the potassium Kα line at 3.313keV is I and the standard deviation for the same position in the continuum spectrum is $(\overline{N})^{1/2}$, then, in order to be accepted as a peak

$$I > 3(\overline{N})^{1/2}$$

where the standard deviation is reflected and measured by the thickness of the background due to statistical fluctuations.

Common interferences in analyzing K in clay minerals occur when Ca and/or Fe are present (Figure 8c). Unless the sample contains a high concentration of calcium, potassium can be detected by its Kα peak at 3.313 keV, but no evaluation can be made due to the difficulties encountered in background computation. As shown in the next section (3.2), a correction strategy is needed in order to improve the analysis.

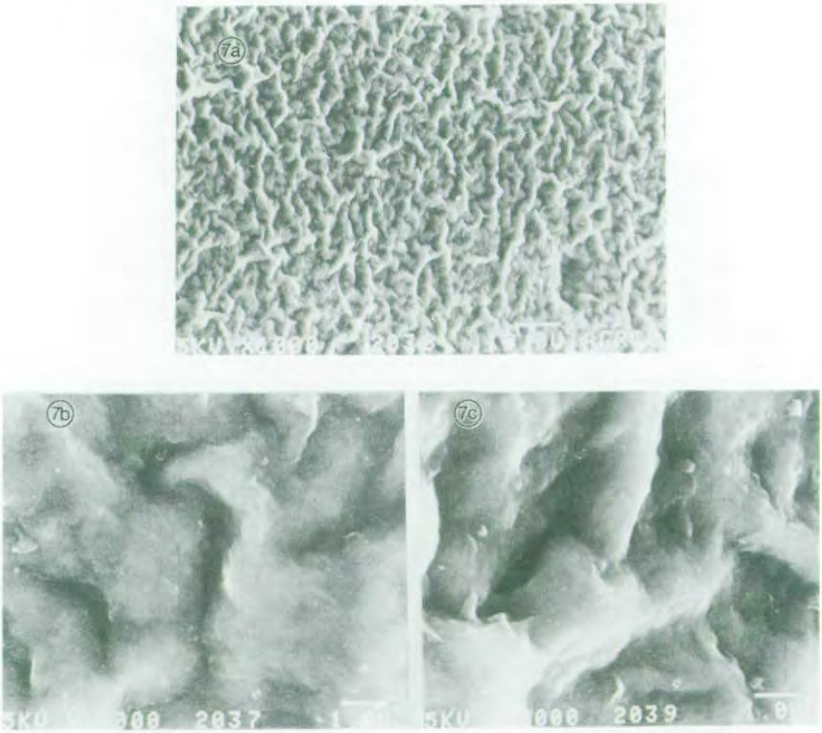


Fig. 7. Thin film from clay fraction (< 0.2 μm) from Golan clay soil: (a) at low magnification (× 10 000) homogeneous pattern, characteristic for well-oriented structure of Na montmorillonite; (b) at higher magnification (× 10 000) and perpendicular to electron beam, flat appearence of surface; (c) 30° tilt, rough pattern.

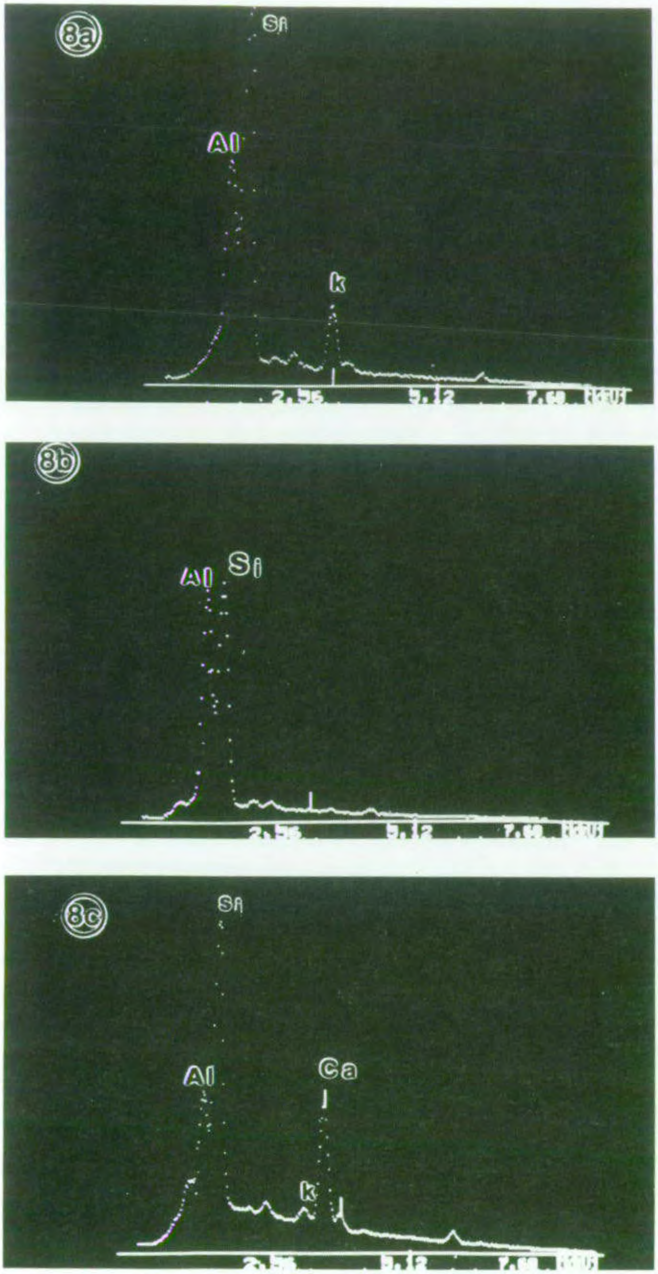


Fig. 8. X-ray spectra of common clay mineral in fine fraction of soil, for qualitative estimation: (a) illite; (b) kaolinite; (c) Ca montmorillonite.

3.2 Towards a quantitative analysis

Weight fraction of an element in a compound sample can be estimated by measuring the relative intensity (unknown specimen *versus* standard) of its characteristic peak in the X-ray spectrum. The correlation is not a straightforward one; it depends on both material and the instrumental conditions.

For soil specimens when potassium has to be evaluated by X-ray microanalysis, the main difficulties are related to the sample homogeneity and to its similarity to the standard.

Ziebold & Ogilvie [1964] developed an empirical approach, using calibration curves (mass fraction *versus* corrected relative intensity) for specimens of a known composition. A set of equations for all the components is needed, and the constants must be determined experimentally. The empirical approach technique is time-consuming, and sometimes impossible for certain multi-component specimens.

In our laboratory, for X-ray microanalysis of potassium in the clay fraction of soil, an alternative technique is used. If a well-oriented film can be obtained, the mass fraction may be expressed in a first approximation by the ratio:

$$C_i/C_{st} \approx I_i/I_{st} \quad (1)$$

where C_i and C_{st} are mass fractions of the sample, and of the standard, respectively; and I_i and I_{st} are the measured intensities of the X-ray line of the element in the sample and in the standard, respectively.

According to *Castaing [1951]*, the above approximation is valid if the sample and the standard interact similarly with the electron beam and can be used for an initial estimation of composition. In Table 1, estimation of the potassium content given by Eq. (1) is carried out for the three principal components present in the clay fraction of the soil. The second column presents the measured intensities I_i of the Kα line for potassium at 3.313 keV, after background subtraction. In columns 3 to 6, C_i is presented as being calculated from Eq. (1) using standards KI, KCl, KNO_3, and biotite. Values C_i very close to the actual concentrations were obtained when the mass absorption coefficient $(\mu/\varrho)_i$ and the flatness of the sample (Figure 9a) and of the standard (Figure 9b) were close enough.

For an accurate X-ray microanalysis, ZAF corrections (see *Appendix*) are recommended to compensate the different behaviour in electron matrix interaction; they are reflected in peak intensities in the sample and in the standard. The correction equation has a general form *(Goldstein et al [1981]):*

$$C_i = (ZAF)_i\, k_i \quad (2)$$

where the weight fraction C_i of the analyzed element i is correlated to k_i (the relative intensity ratio measured experimentally), using three correction factors, Z_i, A_i and F_i, in the computation model.

Table 1 Potassium mass fraction in clay samples as determined by X-ray analysis and affected by standard used.

Sample	X-ray Intens. (I)	KI	KCl	KBr	KNO_3	Biotite
Illite*	2319	0.072	0.115	0.087	0.048	0.077
Kaolinite	96"	0.003	0.005	0.004	0.002	0.003
Montmorillonite	1187	0.037	0.059	0.045	0.025	0.039

"Peak not acceptable for XM

*K fraction in that clay : 0.074 *(Feigenbaum et al. [1975])*

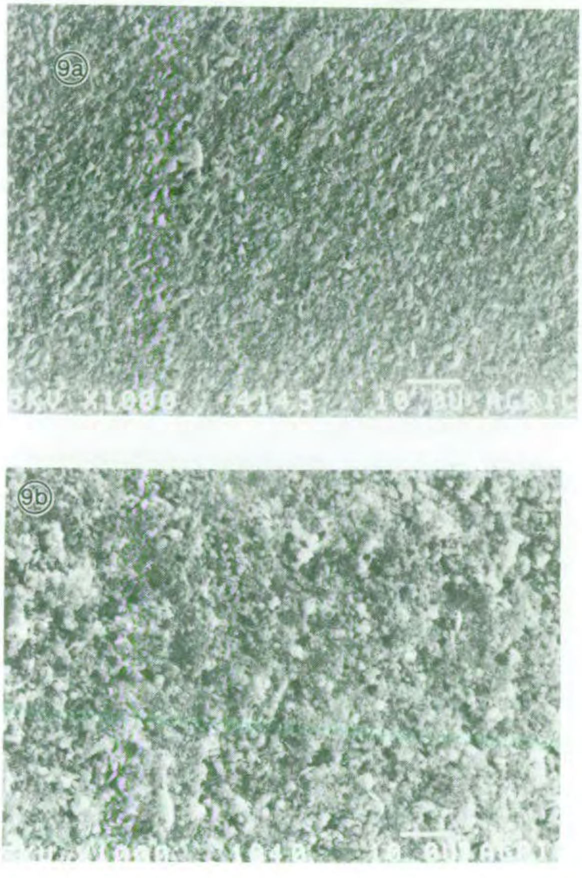


Fig. 9. Oriented thin film of 2 µm, fraction on carbon support at × 1000: (a) illite clay; (b) biotite sample used as standard.

From these three factors, A_i the absorption correction factor, provides an important contribution by compensating the different responses of the sample and the standard, so that the electron beam action is corrected to:

$$A_i = f(x)_{st}/f(x) \tag{3}$$

The absorption function $f(x)_{st}$ for the standard, and $f(x)$ for the sample express the attenuation of the generated X-ray photons, due to absorption, emerging from the sample surface to the detector. The X-ray attenuation depends on the instrumental conditions (operating and geometric) and on the material properties (absorption coeffients μ/ϱ, mean atomic number $\overline{Z}$, and mean atomic weight $\overline{A}$). If the sample and the standard have similar characteristics, the two absorption functions are almost equal and the A value is close to the unit.

Calculation of the absorption correction using *Philibert's [1963]* expression for the absorption function $f(x)$, gives:

$$1/f(x)_i = (1+x_i/\sigma_i)[1+(h_i/(1+h_i))x_i/\sigma_i] \tag{4}$$

where, for

$$h_i = 1.2A_i/Z_i^2 \text{ for the element i,} \tag{4a}$$

$$x_i = (\mu/\varrho)_i \csc \psi \tag{4b}$$

$$\sigma_i = (4.5\times10^5)/(Eo^{1.6}-Ec^{1.6}) \tag{4c}$$

$$h = \sum_j C_j h_j \text{ and } (\mu/\varrho) = \sum_j C_j(\mu/\varrho)_{ij} \tag{4d}$$

where $(\mu/\varrho)_{ij}$ — mass absorption coefficients for the X-ray line of element i in the element j, in the sample or the standard.

ψ — X-ray emergence angle

E_o — operating voltage

E_c — critical excitation voltage

Z_j — atomic number of element j

A_j — atomic weight of element j

In the Eqs. (4) to (4d) the index i refers to potassium and j to all the components including i in the sample or standard.

Figure 10 shows the effect of the electron energy (accelerating voltage E_o) and of the take-off angle (the angle between emergencing X-ray path and the detector direction) on the absorption coefficient factor computed from Eqs. (3) and (4), for an illite matrix. The absorption correction increases (in absolute values) with the increase in acceleration voltage and the decrease in take-off angle. The efficiency for the X-ray generation by electron interaction with the specimen, has a maximum value E/E_c that ranges between 3 and 5, where E is the electron energy, and E_c is the energy of the appropriate ionization level of the atom. From this statement, as well as from our experiments, a maximum efficiency is obtained for the potassium excitation condition at $E_0 = 10$ kv. The take-off angle is harder to optimize in a standard SEM/EDS system due to instrumental limitations, but stage improvements and manipulations could be helpful. The resulting low correction factor for potassium in soil components (Figure 10), (1% at 30° take-off angle) makes the approximation contained in (1) a valid semiquantitative analysis, if a proper standard is considered.

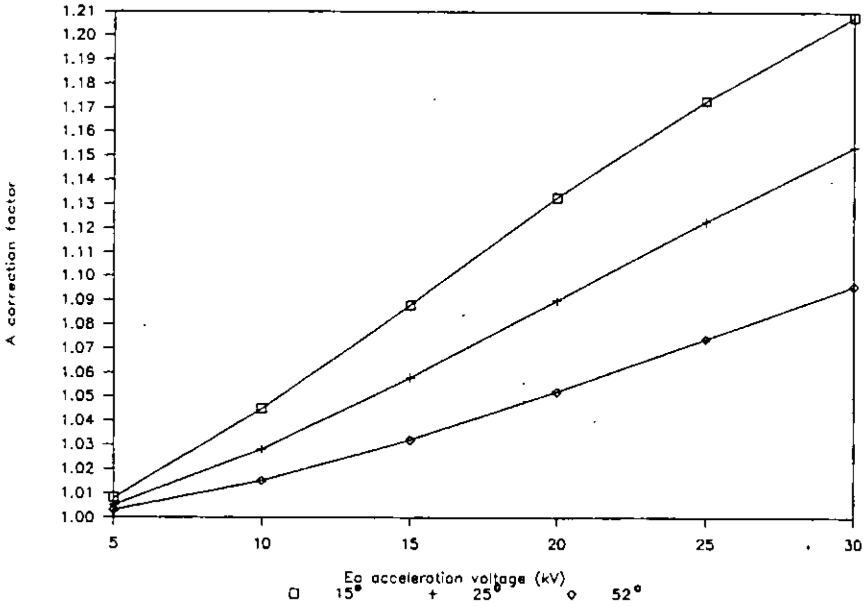


Fig. 10. Absorption correction factor for potassium Kα X-ray line in illite clay.

Figure 11 presents the absorption correction factor computed for the potassium Kα X-ray line in soil components (take-off angle 25°), as a function of acceleration voltages. Relatively low correction values are needed (between 2 and 4%) at a working voltage of 10 kV for the major components in soil. For this reason, semiquantitative evaluation of potassium in such matrices could be carried out without absorption corrections.

The low energy needed when operating the EDS for potassium XM, makes it possible to use inorganic salts as standards; they present the advantages of having their absorption function f(x) close to those of the soil sample, and the corresponding $A_i = f(x)_{st}/f(x)$ ratio close to the unit. In Figure 12, a comparison between different standards shows values close to the unit for absorption correction factors in clay matrix, when standards with similar absorption mass coefficients are considered. These results are in good agreement with the results obtained by X-ray measurements (Table 1 and 2). The biotite standard has $\mu/\varrho = 363$ very close to $\mu/\varrho = 364.38$ for illite.

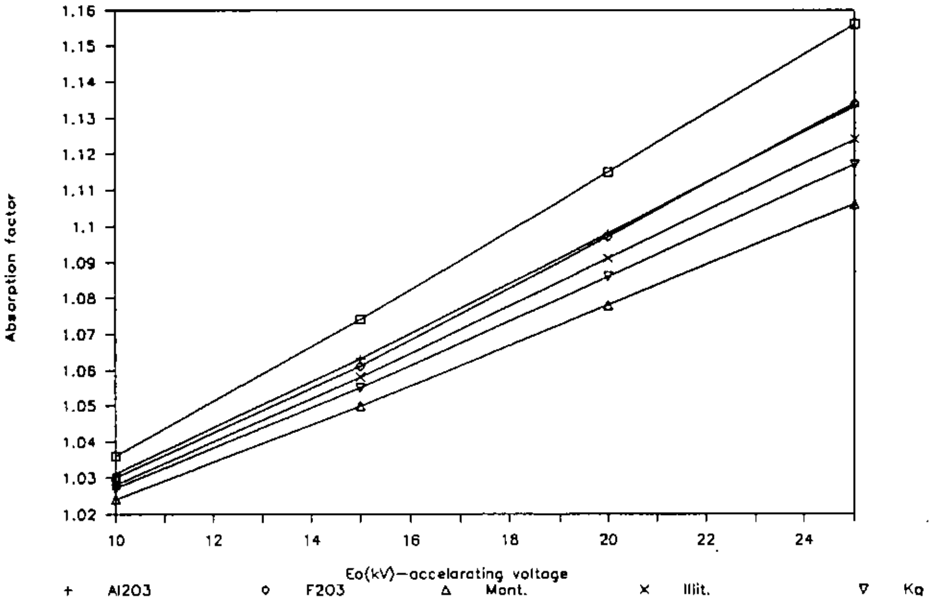


Fig. 11. Absorption correction factor for potassium Kα X-ray line in soil matrix components.

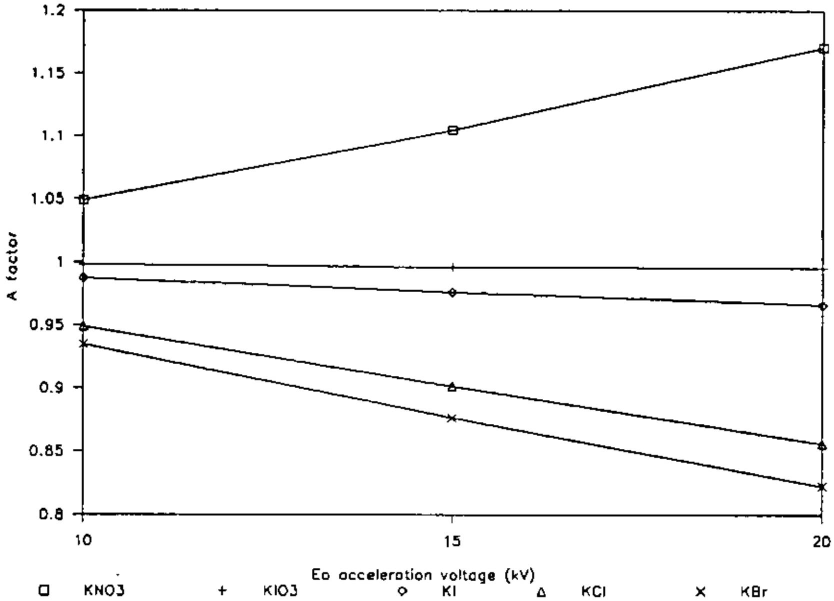


Fig. 12. Comparison between different standards.

Relative low corrections for Zi factor (see Table 3) were computed for soil components if biotite was considered as standard. Due to the difference in mean atomic number between Fe_2O_3 and biotite, the correction factor Zi was found higher in this case.

The other coefficient of ZAF, F- the fluorescence correction is considered a less influencing factor.

Table 2 Absorption correction factor for potassium Kα in soil fraction matrix.

Sample	$(\mu/\varrho)i$	hi	A-KI (481.9)	A-KCl (658.3)	A-KNO_3 (148.5)	Biotite (363.0)*
Illite	364.38	0.246	0.989	0.956	1.041	1.001
Beidellite	370.45	0.254	0.990	0.957	1.043	1.001
Kaolinite	363.99	0.260	0.989	0.956	1.042	1.002
SiO_2	418.13	0.240	0.998	0.965	1.051	1.011
Al_2O_3	382.33	0.243	0.992	0.959	1.045	1.004
Fe_2O_3	348.71	0.160	0.983	0.950	1.035	0.995

*the values in parenthesis are the μ/ϱ mass absorption coefficients of the standards for K∝ line of potassium

Table 3 Atomic number correction factor for potassium Kα in soil matrix.

Sample	$\overline{Z}$	Si	Ri	Zi(KI)	Zi(KCl)	Zi(Biotite)
Illite	11.54	0.144	0.949	1.333	1.088	1.013
Kaolinite	10.55	0.145	0.948	1.344	1.097	1.022
SiO_2	10.79	0.148	0.961	1.353	1.104	1.029
Al_2O_3	10.64	0.145	0.962	1.325	1.081	1.007
Fe_2O_3	20.59	0.126	0.913	1.213	0.990	0.922
Biotite*	9.69	0.108	0.722	1.316	1.074	
KI*	44.99	0.093	0.818			
KCl*	18.05	0.129	0.924			

$\overline{Z}$ — mean atomic number; Si and Ri correction coefficients

Zi — atomic number correction factor $Zi = (Si/Si'^*)(Ri'^*/Ri)$

* — standards

4. Discussion

When using SEM/EDS for measuring local K concentration in the soil, one has to be aware about the difficulties and limitations characteristic to that method. The lack of homogeneity of the sampled volume and the roughness of the surface are strong disturbing parameters which impose special conditions for SEM/EDS evaluation:

- optimize working parameters *e.g.* electron energies at low values and high take-off angles related to the topographic effect.
- restrict this techniques to well defined systems like oriented films of intermediate thickness on low electron absorbing media (*e.g.* carbon support)
- use of standards having values of mass absorption coefficients for potassium Kα line, very close to the analysed sample.

For an illite sample, results show good reproductibility and acceptable concordance with the actual concentration in potassium, when biotite is considered as standard. In fact, in this ideal case, the conventional ZAF correction is not necessary. Using the actual concentration of the sample and the standard to calculate the correction factors, the values for A (absorption correction factor) were close to unity in the actual working conditions. In this case a higher level of sophistication in quantitative analysis is not even needed.

An important concern of the analyst is to ascertain the MDM (minimum detectable mass fraction), when using a SEM/EDS system. The intricacy of the problem lies in the fact that MDM is a function of several parameters concerning both, the specimen characteristics and the instrumental conditions. *Wittry [1980]* expresses the detection limit as a function of Ip/Ib the ratio of X-ray intensities measured at the peak intensity Ip and the corresponding background Ib position. In this context the background is assumed to be the same in the sample and in the standard. A very strong dependence of the concentration limit on Ip/Ib ratio results. Diagrams of the typical dectability limits in EDS analyses *(Levin [1986])*, place potassium, when in a matrix with low absorption coefficients, in a convenient position: under favorable working conditions, detectable concentration limits could reach 0.1-0.3%.

No matter how important all the above limitations and working conditions appear when SEM or EDS are separatly applied in soil analysis, their simultaneous use, offers very significant advantages: the system is able to relate detector orientation to topography, to evaluate surface structural similarities of specimen and standard in the specific EDS sampled microvolume and mainly to provide many correlating data between structure and specific components.

Appendix: Definitions and Notations

Energy-dispersive X-ray spectrometer. In a scanning electron microscope a specimen is irradiated by a finely focused electron beam, which may be static or swept in a raster across the surface of the specimen. When the electron beam impinge on a specimen surface the incident electrons lose their energy in electron-specimen interactions and sygnals containing information abouth the specimen could be capture by various detectors. If the X-ray signal from the sample passes through a beryllium window into a cooled lithium-drifted silicon detector and is processed in order to provide characteristic material photon energy, the system is called energy-dispersive spectroscopy EDS (see Figure A1)

ZAF technique uses a theoretical approach in order to introduce three matrix effect corrections.

Zi – atomic number correction factor compensates for the amount of incident electrons which are not involved in X-ray generation, due to backscattering and retardation processes. From fundamental consideration *(Heinrich [1981])* this factor adjust the differences between the mean atomic number in the spectrum and in the standard.

Ai – absorption correction factor compensate the absorption of X-ray of the measured element by the other elements in the matrix.

Fi – the fluorescence correction is required when parasitic fluorescence appears due to the fact that the characteristic X-ray energies of the elements j are sufficient to excite X-ray secondarily from element i.

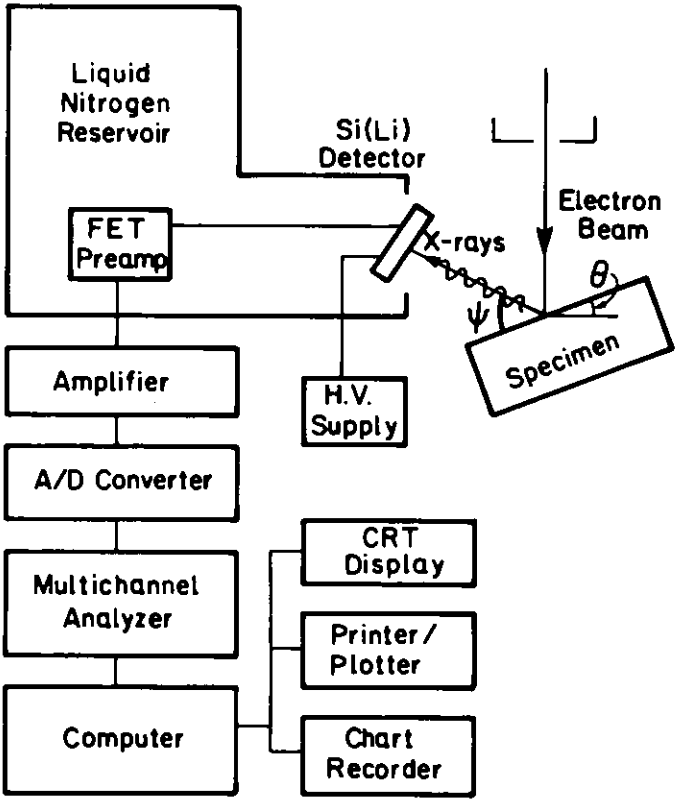


Fig. A1 (Appendix). Bloc diagram of EDS system (adapted after *Levin [1986]*); Θ-specimen tilt, ψ-take-off angle.

Symbols

K – potassium

Kα, Kβ, – X-ray line energies

ESP – Exchangeable sodium percentage

$Z = \sum_j C_j Z_j$ – average atomic number

$\overline{A} = \sum_j C_j A_j$ – average atomic weight

χ – absorption parameter = $(\mu/\varrho)\csc\psi$

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X-ray and Neutron Diffraction

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Summary

X-ray and neutron diffraction are important methods for the identification, quantitative analysis and study of the potassium-bearing layer silicate clay minerals found in soil. The basic principles of the structural chemistry of these compounds are described and recent advances in experimental facilities reviewed. Methods for examining both micaceous and interstratified minerals are discussed, with particular emphasis on the fundamental principles of the diffraction process. Diffraction patterns from these materials can be extremely complex and great care must be taken in their interpretation if meaningful results are to be obtained.

1. Introduction

In this paper I shall review briefly the structures of some of the potassium bearing minerals found in soil and the techniques currently available for their investigation by X-ray and neutron diffraction. Potassium occurs in the micaceous 2:1 layer silicate clay minerals and also in one of the components often present in «mixed-layer» or «interstratified» clay minerals. It is on these layer silicates that I shall concentrate in this paper. Other important potassium-bearing minerals include the alkali feldspars (sanidine, orthoclase, microcline, etc) and the zeolites (phillipsite, heulandite-clinoptilolite, etc). These are the subjects of comprehensive reviews by *Smith [1974]* and *Sand & Mumpton [1978]*. Feldspars, which are often found as accessory minerals in soil (especially in the coarser size fractions), are geologically very important minerals and have an extensive literature. Zeolites are materials of great industrial importance, to the extent that there is a journal, «Zeolites», solely devoted to their study.

Research in soil mineralogy must be directed towards two objectives. Firstly, we need to obtain a better understanding of the structures and chemical and physical properties of the minerals present. For example, it is apparent that the methods of formation and indeed even the structures of the so-called interstratified minerals are not at present well understood. This type of material is common in soil clays and may also have considerable importance in petroleum exploration (see *e. g. Jeans*

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[1982]; Eberl [1984]; Stoessell and Ferrell [1986]). Such fundamental work often requires investigation of rather idealised, «museum», samples. However, study of these well-characterised materials is essential if meaningful results are to be obtained. Secondly, we must learn how to apply knowledge gained from these well defined systems to the more disordered materials found in soils. Here our ability to describe the system is usually severely limited by its ill-defined nature. A wide range of structurally similar «minerals» which may, however, have very different physical properties, can be produced by chemical substitution. In these circumstances merely identifying the different phases can be difficult and, as will be shown below, with the techniques currently available analysis on even a semi-quantitative basis may be almost impossible.

The remaining sections of this paper are intended as a guide, for non-specialists, to the basic principles of the interpretation of diffraction patterns from disordered materials and to the advanced experimental facilities which are likely to become widely available in the next few years. Small-angle scattering methods, which can be of great value in studies of the structural arrangements (texture) of hydrated clays on a larger scale (up to ~ 5000 Å) will not be discussed as they are described in some detail in other papers in this volume *(Pédro [1987]; Tessier [1987]).*

2. Structures of micaceous and interstratified minerals

A short review of the structures of the phyllosilicate clay minerals is given by *Brown [1984].* More extensive treatments of this topic may be found in the monographs edited by *Greenland and Hayes [1978], Brindley and Brown [1980] and Newman [1987]. Bailey [1984]* has also recently edited a major review devoted entirely to micas.

The structures of the phyllosilicate layer minerals are in essence quite simple. They consist of stacks of aluminosilicate layers, either superimposed directly on each other or separated by interlayer material. The layers may be of two types, either 1:1 (containing 1 tetrahedral and 1 octahedral sheet) or 2:1 (containing 2 tetrahedral and 1 octahedral sheet). The tetrahedral sheets are formed by corner-linking $(Si/Al)O_4$ tetrahedra into an infinite network of hexagonal rings. The octahedral sheets are formed by placing cations (*e. g.* Al, Mg, Fe, etc) in the 6-fold coordinate sites found between two close-packed layers of anions. In the 1:1 minerals one of these close-packed anion layers is formed from the apical oxygen atoms of the tetrahedral sheet, together with additional anions (usually OH or F) placed at the centre of the hexagonal rings to complete the close packing. In the 2:1 minerals both close packed layers of anions are of this type. Further divisions may be made, on the basis of the site occupancies of the cations in the octahedral sheet, into dioctahedral and trioctahedral subgroups. Different polytypes (or polytypoids) are formed by different layer stacking arrangements and further divisions into mineral species may be made on the basis of chemical composition.

In detail the structures are more complex than this simple scheme suggests. The tetrahedral sheets, for example, are usually distorted by rotation of the tetrahedra so as to be dimensionally compatible with the octahedral sheet. By means of these, and other, distortions 1:1 and 2:1 layers with a wide range of chemical composition can be formed, and this allows the layers to have a range of net electrical charge. For example, replacement of Si by Al in the tetrahedral sheet and of trivalent by divalent cations in the octahedral sheet leads to an increasingly negative layer charge. The true (as distinct from brittle) micas have a net layer charge of 1 per $O_{10}(OH)_2$ formula unit. This charge is balanced by large monovalent cations, usually potassium, which lie in the hexagonal cavities at the base of the tetradrahedral sheets and serve to key one 2:1 layer to the next. Their large size results in the increased basal spacing (~ 10Å) from that found in minerals without interlayer cations such as pyrophyllite and talc (9.2-9.4Å; *Rayner and Brown [1964]; Rayner and Brown [1973]*). In the idealised structure the potassium ion is coordinated by 12 anions, but usually structural distortions result in 6 near and 6 more distant neighbours. The primary coordination of the potassium is therefore either octahedral or ditrigonal-pyramidal, depending on the polytype. Structures with octahedral coordination appear to be more common and would seem to be energetically more favourable. Structural formulae of some mica group minerals are given in Table 1 (after *Brown [1984]*).

Table 1 Structural formulae of some mica group minerals including clay micas

		cations		anions
interlayer		octahedral	tetrahedral	
		trioctahedral		
phlogopite	K	Mg_3	(Si_3Al)	$O_{10}(OH)_2$
biotite	K	$(MgFe^{2+})_3$	(Si_3Al)	$O_{10}(OH)_2$
		dioctahedral		
muscovite	K	Al_2	(Si_3Al)	$O_{10}(OH)_2$
paragonite	K	Al_2	(Si_2Al)	$O_{10}(OH)_2$
phengite	K	$(Al_{1.5}Mg_{0.5})$	$(Si_{3.5}Al_{0.5})$	$O_{10}(OH)_2$
celadonite	K	$(Al\ Fe^{3+})_1\ (Mg\ Fe^{2+})_1$	Si_4	$O_{10}(OH)_2$
glauconite	$K_{0.85}$	$(R^{3+}_{1.4}R^{2+}_{0.6})$	$(Si_{3.75}Al_{0.25})$	$O_{10}(OH)_2$
illite	$K_{0.8}$	$(R^{3+}_{1.65}R^{2+}_{0.35})$	$(Si_{3.55}Al_{0.45})$	$O_{10}(OH)_2$

The micaceous material found in soil clays is often referred to as «illite». *Środoń and Eberl [1984]* consider that a more specific nomenclature is now needed. They define «illitic material» as «a general petrological term for the approximately 10Å component of the clay-size fraction synonymous with the term «illite» as used by *Grim et al. [1937]*». «Illite» itself is defined to be «non-expanding, dioctahedral, aluminous, potassium mica-like material which occurs in the clay size (<4 μm) fraction». It should be noted that features such as the potassium content and polytype, which may be very difficult to determine, are not specified in this definition. The composition of illite and in particular its potassium content appears to be variable. This point is discussed in the reviews by *Brindley [1980]* and *Eberl and Środoń [1984]*. A potassium content in the range 0.7-0.8 per $O_{10}(OH)_2$ has been often reported, though *Środoń et al. [1985]* have suggested that two kinds of material may occur having potassium contents of 1.0 and 0.55K per $O_{10}(OH)_2$ unit respectively. Reduction of the K-content leads to problems of charge balance. *Brown and Norrish [1952]* suggested that the lack of K might be accommodated by the introduction of H_3O^+ (hydroxonium) ions, a suggestion which seems to have been neither proved nor disproved by more recent experiments.

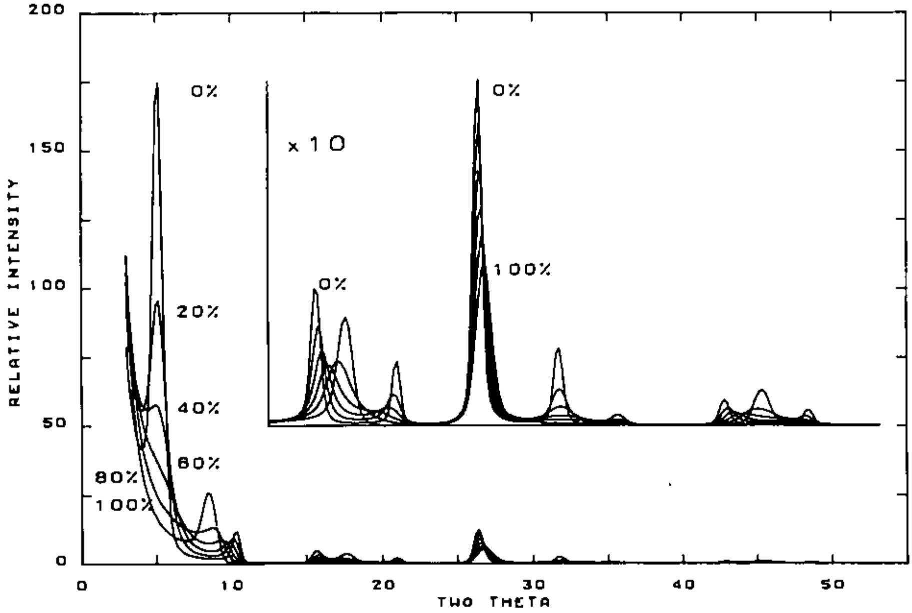


Fig. 1. Calculated 00l diffraction patterns (CuKα) from randomly interstratified illite – (ethylene glycol) montmorillonite. The numbers indicate the percentage of illitic interlayers.

Interstratified minerals are complex materials when considered both structurally and also in terms of their diffraction patterns. Here different interlayer species (and sometimes different layer types) occur within the same crystallite. The sequence of layers and interlayers may show long-range order, as for example in rectorite and corrensite *(Bailey [1982])*, short-range order or complete disorder (see *e.g. Reynolds [1980]* for a review of these materials). As will be discussed later, the term «crystallite», in this context, is ill defined. In this paper it is assumed to refer to a coherently diffracting unit. Interstratified materials are unusual in that they give diffraction patterns whose «Bragg reflections» are not rational orders of an interplanar spacing. Figure 1 shows an example of this, giving the calculated patterns from randomly interstratified illite-smectite of different compositions. Illite-smectite is probably the most common and important of the interstratified materials, at least among soil clays. It consists of 2:1 alumino-silicate layers with interlayers that may be either illitic (*i. e.* non-expandable and containing potassium ions) or smectitic (*i. e.* expandable interlayers containing solvated cations). Further details of the structure of this material will be discussed below.

3. Advances in experimental facilities

The facilities for X-ray and neutron diffraction available to soil mineralogists have improved greatly over the last few years, with new radiation sources and detectors and increased automation and computing power. Many of these advances, which are reviewed briefly below, are too recent to have had much impact to date, but it seems certain that the next 10 years will see dramatic changes in the way which diffraction patterns are measured and interpreted.

3.1 New radiation sources

A number of dedicated *Synchrotron Radiation Sources* now exist (*e. g.* Synchrotron Radiation Source (SRS), Daresbury U.K.; National Synchrotron Light Source (NSLS), Brookhaven, U.S.A.) as well as institutes allowing «parasitic» use of high-energy physics facilities. Synchrotron sources provide very intense, parallel, plane-polarised beams of X-rays with a continuous spread of wavelengths from about 0.2Å upwards. They are thus effectively «white» sources which are suitable both for diffraction experiments and also for other techniques giving structural information such as *EXAFS* (*E*xtended *X*-ray *A*bsorption *F*ine *S*tructure). A general review of synchrotron radiation has been published by *The Royal Society of Chemistry [1986]*. Although it appears to have found little or no application in clay mineralogy so far, there are a number of groups working on applications of synchrotron radiation to powder diffraction. Its main advantages in this field would seem to be:

1. low-resolution patterns can be obtained in energy-dispersive mode very rapidly (less than 1 second per pattern) – see *e.g. Buras, Gerward, Glazer, Hidaka and Staun Olsen [1979]*.
2. very high resolution angle-dispersive patterns can be obtained *(Hastings, Thomlinson and Cox [1984])*.
3. short wavelength X-rays are available ($\lambda \leqslant 0.2$ Å) which can penetrate large samples
4. novel experiments utilising X-ray anomalous scattering are possible over a complete range of wavelength *(Georgopoulos and Cohen [1985])*.

It is possibly the last that is of most interest to soil mineralogists *(Wood, Nicholls and Brown [1986])*.

Neutron sources have shown similar advances. As well as conventional steady-state reactors *(e.g.* Institut von Laue-Langevin (ILL). Grenoble), very intense pulsed sources are now available *(e.g.* ISIS, Rutherford-Appleton Laboratory, U.K.). These are particularly suitable for time-of-flight (energy-dispersive) powder diffraction. For example, the high resolution powder diffractometer (HRPD) at ISIS will, when operating at full power, allow patterns to be collected with a resolution approximately four times better than that of most conventional diffractometers *(e.g.* D1A at ILL, Grenoble) in about 60 minutes.

3.2 New detectors

Recently, several novel X-ray powder diffractometers have been developed using position-sensitive detectors *(Wölfel [1983]; Shishiguchi, Minato and Hashizume [1986])*. These detectors are essentially elongated proportional counters coupled with a delay line so as to enable a reading of position as well as X-ray intensity to be obtained. One example of such an instrument, which is commercially available, is decribed by *Wölfel [1983]*. This detector measures simultaneously over an angular range of 45° in 2θ and allows diffraction patterns to be measured in typically 3-5 mins. Although the resolution of such instruments is, at present, not as good as that of a conventional parafocussing powder diffractometer it is more than adequate for most applications in soil mineralogy.

3.3 Automation

Recent advances in electronics have produced major changes in X-ray diffractometer control systems. All modern powder diffractometers, even if of conventional *(e.g.* Bragg-Brentano parafocussing) design, are now driven by stepping-motors and have digital output. Older instruments can usually be upgraded at modest cost. The ready availability of step-scanned digital output, rather than analogue output to a chart, allows much more advanced methods of data analysis, such as least-squares profile refinement (see *e.g. Brown and Wood [1985]* for an application of this method in soil mineralogy) to be used routinely.

3.4 Computing

Advances in computing have been even more dramatic than those in instrumentation. The last five years has seen an enormous increase in the speed and power of microcomputers. For example, a workstation rated at > 1 Mips (million instructions per second), with 4 Mbyte memory and high-resolution graphics currently costs less than £10 000 in the U.K. A machine of this power can perform complex analyses of diffraction patterns very rapidly. It seems likely that the next few years will see the development of interactive «expert systems» for use in clay mineralogy (a crude example of such a system is provided by the search/match programs currently used to identify materials from powder diffraction patterns using the *JCPDS (Joint Commission on Powder Diffraction Standards)* data-base; see *e.g. Schreiner, Surdukowski and Jenkins [1982])*. «Real-time» methods, in which the future course of an experiment can be influenced by on-line analysis of the data already collected are also likely to become of increasing importance.

4. Qualitative and quantitative estimation of micaceous materials

X-ray diffraction is one of the most widely used techniques for identification and quantitative analysis of clay minerals. It has advantages over electron microscopy for this purpose in that, as a greater volume of material is examined, an analysis more representative of the bulk sample may be obtained. It should be remembered, however, that in conventional laboratory powder diffractometry the X-rays will penetrate into the sample by only a few tens of microns and thus surface effects may be important. Neutron diffraction (and possibly also synchrotron radiation) can examine much larger volumes of material because of the lower beam attenuation, but the limited availability and high cost of neutron diffraction facilities at present preclude their use for routine analyses. In this section I shall concentrate mainly on the difficulties involved in X-ray analysis of soil clays with particular reference to the analysis of micaceous phases. Many of the problems outlined below have no immediately obvious solution. This discussion, therefore, presents a rather cautious view of the subject but one which it may be salutary to consider.

4.1 Experimental arrangements

At present almost all X-ray diffraction studies of clays are made using diffractometers based on Bragg-Brentano parafocussing reflection geometry. These instruments are mechanically robust and produce high count-rates but it should be remembered that in other respects reflection geometry is not the most suitable arrangement when accurate measurements at small values of 2θ are required. Detailed aspects of experimental technique are discussed by, for example, *Klug and Alexander [1974]* and *Brown and Brindley [1980]* and will not be considered further here. One comment which should be made, however, concerns the instrumental resolution employed. Generally the receiving slits provided with these instruments are finer than is necessary for soil mineralogical studies. For example, in the Rothamsted X-ray laboratory, using Philips PW1050 «vertical» powder goniometers, it has been found that a 0.6 mm (~ 0.2° 2θ) receiving slit can be used to advantage and that the diffracted beam Soller slits can often also be removed, giving a considerable increase in count-rate without significant loss of detail in the diffraction patterns (for further discussion see *Brown and Brindley [1980]*).

4.2 Qualitative analysis

In principle, the micaceous minerals are readily identified by a strong 10Å basal spacing visible on diffraction patterns from samples which are air-dried or solvated with ethylene glycol. Small amounts of interstratified swelling interlayers can be detected by irrationality and asymmetry of the basal reflections, the division between dioctahedral and trioctahedral minerals can be made on the basis of the 001 relative intensities and from the spacing of non-basal reflections and the polytype determined by comparison of the diffraction pattern with those from known standards. Further details of this methodology are given by *Brown and Brindley [1980]* and *Środoń and Eberl [1984]*. In practice, with soil clays much of this information is likely to be unobtainable. If the micaceous minerals are present in small amounts even the 10Å reflection may appear only as a shoulder, and observation of higher orders is usually hampered by the overlap of peaks from other minerals *(e.g.* mica 003/quartz 101). Computer analysis of the data (smoothing, differentation, profile-fitting etc.) can provide additional information but the variability of the minerals leads to a system which seems to be mathematically too ill-defined to enable many of these techniques to be used to their full potential. Further experimental work such as separation of the clay fraction into several size divisions may be of assistance but is tedious when many samples have to be examined and requires a large amount of the material. Complementary techniques such as optical and electron microscopy should not be overlooked. The former, applied to the coarser size fraction, can often give much useful information very rapidly.

4.3 Quantitative analysis

The intensity diffracted by an infinitely thick specimen of a mixture of «fine powders» may for, the purposes of this discussion, be written in the form

$$I \alpha \frac{I_o\,(Lp)\,P_{ij}\,|F_{ij}|^2\,g_j}{\overline{\mu^*}\;V_j^2\;P_j} \qquad (1)$$

(see *International Tables for X-ray Crystallography, 1968* for further details) where

I_o = incident beam intensity
Lp = Lorentz and polarisation correction
$\overline{\mu^*}$ = average mass attenuation coefficient of the mixture
P_{ij} = multiplicity of the ith reflection from the jth component
F_{ij} = structure factor of the ith reflection from the jth component
V_j = unit-cell volume of the jth component
g_j = mass fraction of the jth component
P_j = density of the jth component

Equation (1) provides the basis for several methods of quantitative analysis (*Brindley [1980b], Klug and Alexander [1974]* give useful summaries). In principle the problem is straightforward, involving comparison of the diffracted intensity from the mixture with that from pure standards or with that calculated from the known crystal structures of the compounds. If exact standards are available then the analysis is indeed simple, even if the patterns contain overlapping reflections as «profile-refinement» methods (see *e.g. Brown and Wood [1985]*) may be used. Figure 2 shows an example of this method. Here the diffraction patterns of kaolinite and hematite are added and fitted by least-squares to the diffraction pattern obtained from a mixture of these two materials containing nominally equal parts by weight. The relative amounts and relative zero shifts of the two patterns were determined automatically by the program. Using calculated mass operation coefficients, the percentage of hematite was found to be 48.4%, in good agreement with the nominal composition. It should be mentioned that this illustrative example probably represents a lower limit on the accuracy of such work as no great care was taken with the preparation of the mixture or in the X-ray diffractometry, the patterns being collected for purposes other than tests of the analysis method.

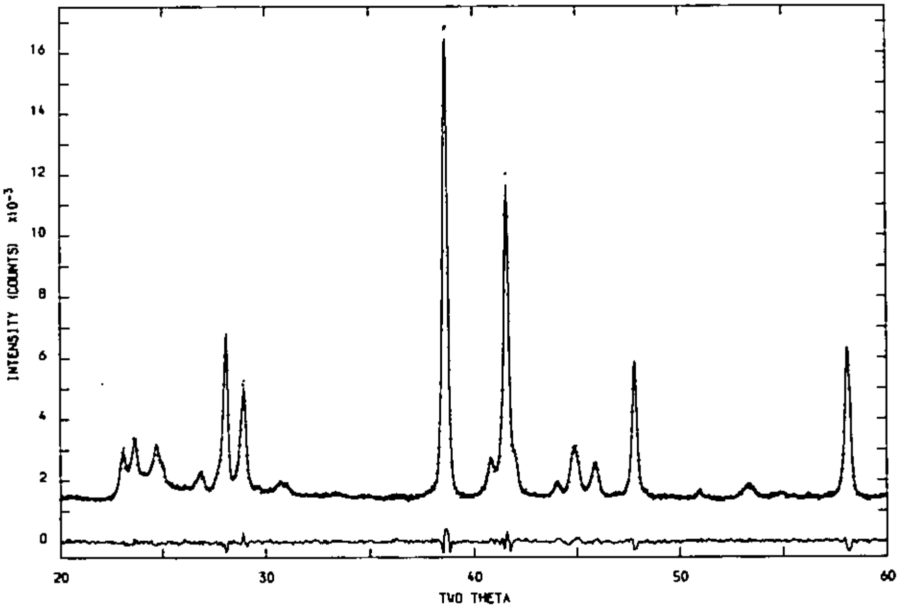


Fig. 2. Quantitative analysis by least-squares profile refinement. The points give the measured diffraction pattern from a kaolinite-hematite mixture. The full lines are the calculated pattern, formed by the addition of patterns from the pure materials, and the difference pattern.

Unfortunately, in real soil clay analyses the process is much less straightforward. Methods such as that described above depend on the availability of either observed or calculated «standard patterns» which are representative of the minerals in that particular soil. It is not clear at present how these might be obtained. One possibility is to use patterns from a restricted range of standards which are then modified by computer to match more closely those in the material being examined, and some success with this type of method has been achieved recently for the admittedly rather more simple case of the estimation of iron oxides *(Brown and Wood [1985])*. It is generally considered, however, that, at present, only semi-quantitative analysis of soil clays is possible. The methods usually adopted (see *e.g. Bullock and Loveland [1974])* involve putting equation (1) into the form

$$I \alpha w_j g_j \qquad (2)$$

where w_j is a weighting factor valid for a particular reflection (usually of index 00 l) from a particular mineral. Integrated areas of peaks from the different minerals are obtained from the diffraction pattern and converted to relative mass fractions via (2). These are then normalised to 100% to give the composition of the clay. Even this simplified scheme suffers from a number of theoretical and practical drawbacks such as:

1. What structural model should be used to calculate w_j?
2. What Lorentz-polarisation factor should be applied?
3. What background correction should be used?
4. What percentage of the clay fraction may be assumed to be crystalline?

The importance of points (1) and (2) can be seen by reference to Table 2, where a hypothetical binary mixture of a 1:1 kaolinitic and a 2:1 micaceous mineral is considered. It can be seen that the relative weighting factor varies by a factor of 7.4 depending on the assumptions made. In compiling Table 2 no attempt was made to use structures which gave extreme values and other sources of variation such as the choice of atomic scattering factors could also have been included. Thus we may conclude, for example, that a diffraction pattern containing 10Å and 7.2Å peaks of equal intensity could be interpreted to indicate compositions ranging from 35% mica: 65% kaolin to 80% mica: 20% kaolin, a situation which is clearly unsatisfactory. In general it appears that, for analyses based on the 10Å mica reflection, failure to recognise the trioctahedral nature of a mica such as biotite can result in its concentration in the soil clay being over-estimated by a factor which can be as large as 5.

A final comment concerns the occurrence of «amorphous» material. Soil clays frequently show much low angle scattering. It is tempting to attribute this to instrumental «background», but it is more likely to be a real effect since it is not found when specimens of pure minerals are examined. The most probable explanation is that it arises from «amorphous» material, possibly single alumino-silicate layers. It thus seems likely that procedures such as that described above for the estimation of soil-clay compositions will overestimate the amounts of «crystalline» clay minerals relative to the total amount of matter in the sample.

Table 2 Semi-quantitative analysis of clays from basal reflections

	$2M_1$ Muscovite[1] (002)	1M Biotite[2] (001)	Dickite[3] (002)
$\lvert F \rvert$	63	80	102
V_c (Å^3)	932.6	492.8	659.5
P (g cm^{-3})	2.84	3.05	2.60
$\frac{\lvert F \rvert^2}{V_c^2 P} \times 10^3$	1.61	8.64	9.20
2θ CoKα°	10.30	10.26	14.36
Lp (Random Powder)[4]	61.3	61.81	31.3
Lp (Single Crystal)[5]	5.50	5.53	3.91
w_{rel} (Random Powder)	0.34	1.85	1.0
w_{rel} (Single Crystal)	0.25	1.32	1.0

1. *Güven [1971]*
2. *Takeda and Ross [1975]*
3. *Newnham [1961]*
4. $=(1 + \cos^2 2\theta)/2 \sin 2\theta \sin\theta$
5. $=(1 + \cos^2 2\theta/2 \sin 2\theta$

5. Analysis of interstratified minerals

5.1 Fundamental principles of diffraction by disordered systems

Interstratified minerals are among the most difficult materials to analyse by X-ray diffraction. Their «crystals» – it is even doubtful whether such a word is truly applicable – are usually very small, perhaps less than 100 Å thick, and can potentially exhibit almost all other known forms of disorder (stacking faults, strain, chemical substitution etc.). In these circumstances many of the assumptions normally used in X-ray crystal structure analysis fail and it is therefore essential that mineralogists working in this field have a clear understanding of the concepts involved and of their limitations. The purpose of this section is to illustrate some of these concepts using a set of calculated 1-dimensional diffraction patterns. This is analogous, in the case of interstratified minerals, to analysis of the basal (00l) reflections to determine the interlayer stacking sequence. There are a number of excellent monographs on diffraction from disordered materials. *Woolfson [1970]* gives a good account of basic diffraction theory, which is also covered in more detail by, for example, *James [1962]* and *Warren [1969]*. The small monograph by *Wilson*

[1962] provides an excellent introduction to disorder which again is covered in more detail by *Guinier [1963]* and *Cowley [1975]*. Recently, *Welberry [1985]* has also published a most useful review of this topic.

Figure 3a shows the diffraction pattern from a set of 10 perfectly regularly spaced point scatterers with coordinates $\mathbf{r}_n = n\mathbf{c}$, where n is an integer and $\mathbf{c}$ a lattice vector (the lattice repeat was arbitrarily chosen to be 4 × the wavelength, *i. e.* $\mathbf{c} = 4\lambda$). The pattern is calculated by forming the diffracted amplitude

$$A(s) = \sum_n \exp 2\pi i \mathbf{r}_n \cdot \mathbf{s}$$

where the summation is taken over the scattering centres and $s = 2\sin\theta/\lambda$. Multiplying this quantity by its complex conjugate produces the diffracted intensity. The side-bands visible between the main diffraction maxima become more prominent as the number of scattering centres (≃ the «crystallite size») is reduced. In principle these bands should be visible on diffraction patterns from fine clays and indeed they have occasionally been observed *(K. Norrish*, private communication). Normally, however, the sample will contain a range of crystallite sizes, the effect of which is to smear out the side-bands into a smooth «tail» surrounding the Bragg reflections. Figure 3b shows the pattern from a larger (50 points) but otherwise identical crystal. Note the decrease in width of the Bragg reflections and relative decrease in the side-bands. Figure 3c corresponds to a «randomly perturbed regular structure» with 50 scattering points at coordinates $n\mathbf{c} + \delta_n$, where δ_n was chosen to be randomly distributed in the range $(- c/16) < \delta_n < (+ c/16)$. The pattern shown is the average of those from 20 such crystals. Note that the widths of the Bragg reflections are unaltered by the disorder but that their intensity decreases at larger angles (the «temperature factor» effect). The loss in intensity from the Bragg reflections appears, since the displacements are uncorrelated, as an additional background (the «von Laue monatonic diffuse scattering»). This ideally should be a smooth function of 2θ. The fluctuations shown in the figure occur because of the small number of realisations of the crystal used in the computation of the average pattern. The three patterns discussed so far all originate from systems which are «long-range ordered», i.e. systems in which our knowledge of the atomic coordinates does not depend on their distance from the origin. Figure 3d shows the pattern from a rather different type of material, akin to a paracrystal (Hosemann and Bagchi, 1962). Again a set of 50 point scatterers was used, this time with positions given by $\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{c} + \delta_n$, where, as before, $c = 4\lambda$ and δ_n is randomly distributed in the range $(-c/16) < \delta_n < (+ c/16)$. This system, which is arguably a closer approximation to the structure of material in soil clays than the small regular crystals of the previous examples, is fundamentally different in that it is not long-range ordered. The variance of the position of the nth point relative to the chosen origin increases without bound as n increases. It can be seen that this type of disorder has two effects. The intensities of the diffraction maxima decrease with increasing Bragg angle while their widths increase. The effects on the diffraction pattern of crystallite size and of distortions are thus fundamentally different. The former gives diffraction maxima whose half widths (expressed in terms of s) do not alter for the different orders (when expressed in terms of 2θ an apparent increase with angle is seen due to the change of variable). The latter gives maxima which broaden with increasing scattering angle. Often in papers on soil mineralogy the «crystallite size» is estimated via the Scherrer formula (see *e.g. Wilson [1962]):*

$$\varepsilon \simeq \lambda/\beta \cos \theta$$

where β is the width at half-height of the diffraction maximum. Applying this formula to the reflection at 60° from Figure 3c gives a size of approximately 200λ, very close to the true value of 196λ. The same procedure applied to Figure 3d, however, gives a value of about 40λ. Moreover, the result obtained in this case will depend on which reflection is measured, the particle size apparently becoming smaller as the d-spacing decreases. Both Figure 3c and Figure 3d, however, correspond to systems which have 50 diffracting units and which are of very similar physical extent. It can be seen that naive measurements of «particle size» can be very misleading and should be treated with great caution. The «coherence length» of the material in Figure 3d is smaller than the physical length of the «particle» and has a value that changes with d-spacing, becoming smaller as the d-spacing decreases. Thus, the finer the detail in which the material is examined, the more disordered it appears to be (note, however, that a true measure of the «particle size» can in principle be obtained from the small-angle scattering *i.e.* by measurement of the instrumentally accessible region of the zero-order reflection at $2\theta = 0°$, see *e.g. Guinier [1963]; Pédro [1987]; Tessier [1987]).*

Figure 4 shows some examples of an interstratified system. The patterns are calculated from 50 point assemblies with the points separated from each other by either 3.5λ or 4.5λ. In Figure 4a these two separations alternate forming a long-range-ordered superlattice. The true periodicity is now 8λ and the number of Bragg reflections is therefore doubled (*c.f.* Figure 3b). Note that the 8th order ($2\theta = 60°$) is absent because for this reflection the points scatter exactly out of phase. In Figure 4b the two separations occur at random. Sharp maxima are produced where orders of the two allowed separations have similar or identical spacings (*e.g.* $3.5/7 = 4.5/9 = 0.5$) as this corresponds to a periodicity not disrupted by the interstratification. Figure 4c corresponds to an intermediate, short-range ordered, system in which the probability of unlike spacings following each other is 85%. This is an example of a Markov chain with nearest-neighbour interactions. It can be seen that the diffraction pattern is intermediate between the ordered and random cases and has maxima whose widths vary with angle in a non-systematic manner. This object has short-range order: our ability to predict its properties (in this case the position of the points) diminishes as we move away from the chosen origin. The nearest-neighbour model is the simplest example of short-range ordering. Other schemes, which may involve more than next nearest neighbour interactions, have been observed in clay minerals and are reviewed by *Reynolds [1980].*

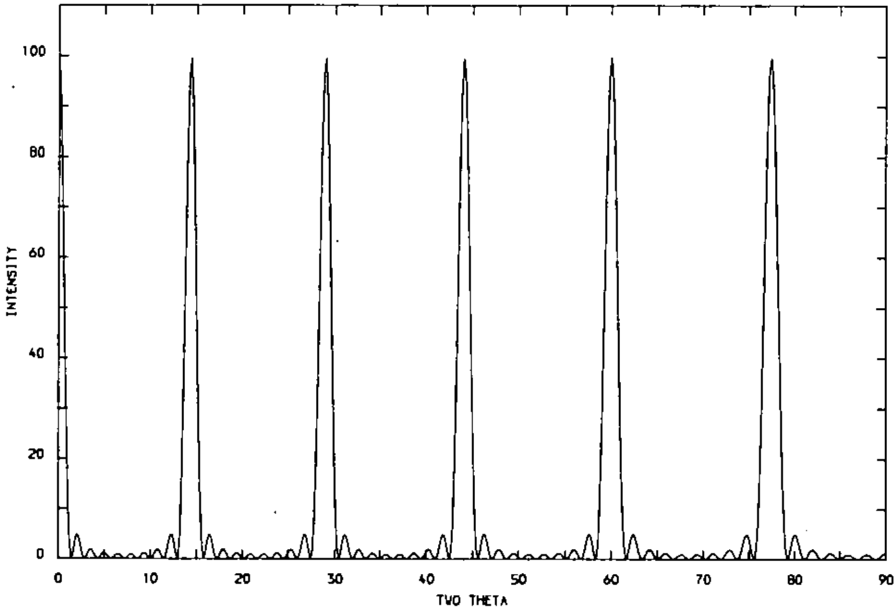
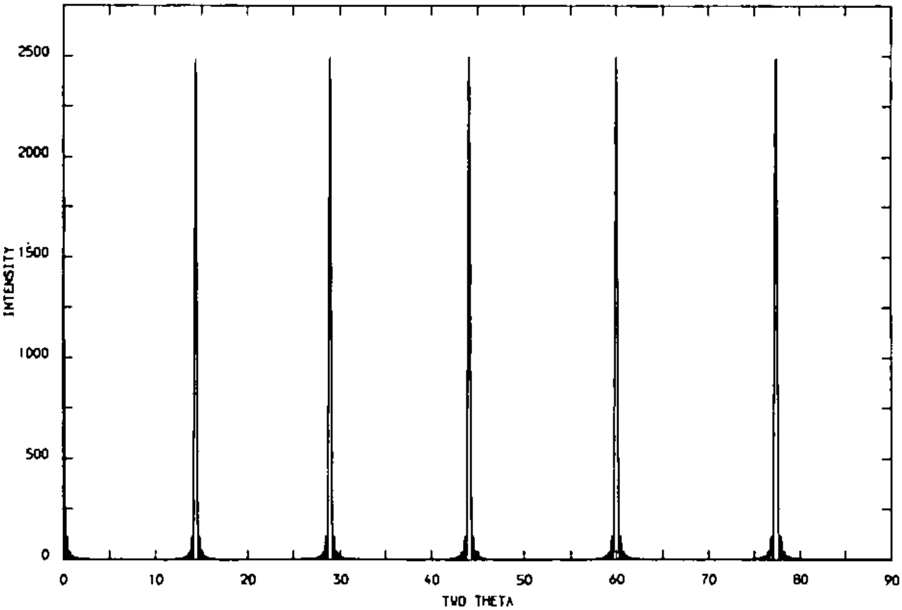
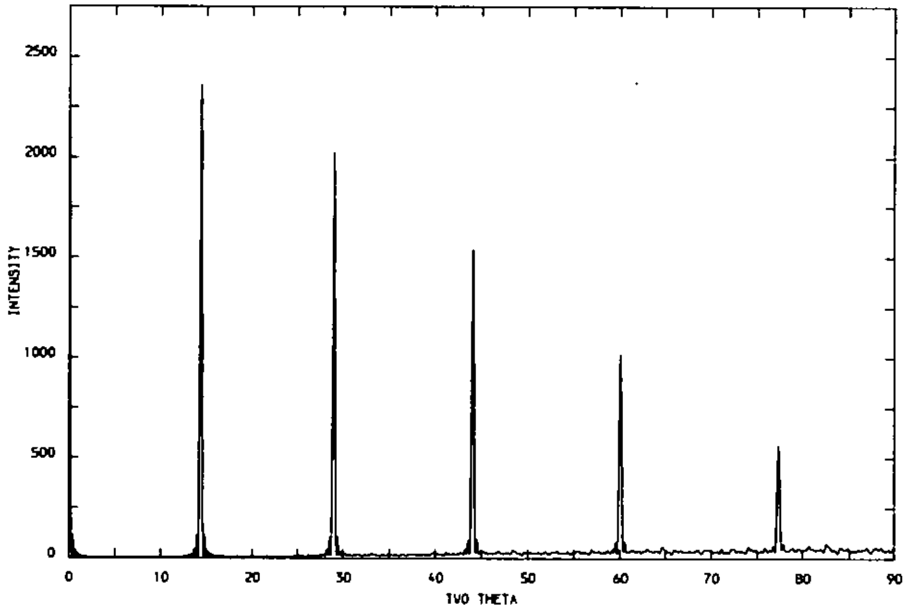


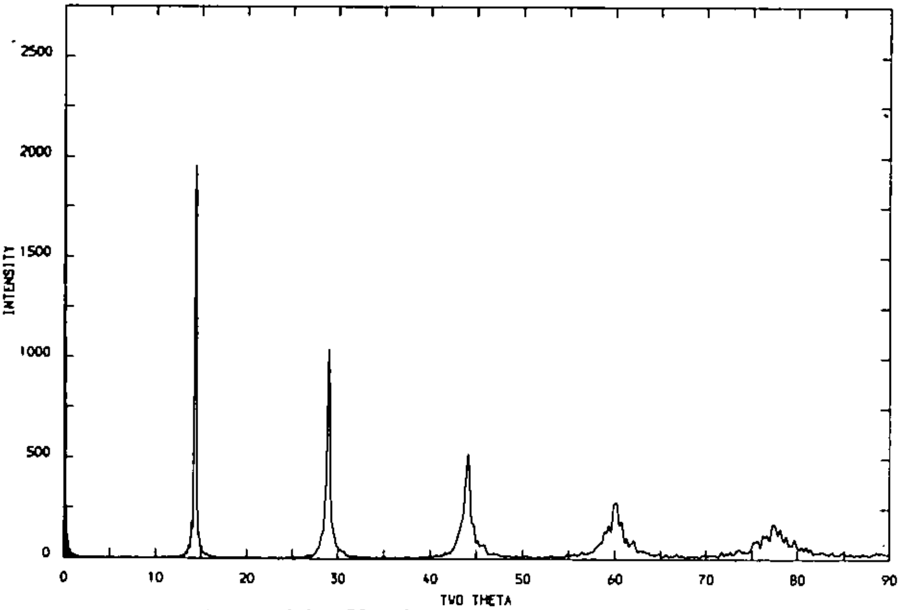
Fig. 3. Calculated one-dimensional diffraction patterns from arrays of point scatters
a) Perfect crystal containing 10 points



b) Perfect crystal containing 50 points



c) Randomly perturbed crystal containing 50 points



d) «Paracrystal» containing 50 points
The patterns shown in c) and d) are the average of several realisations of the model.
For further details see text.

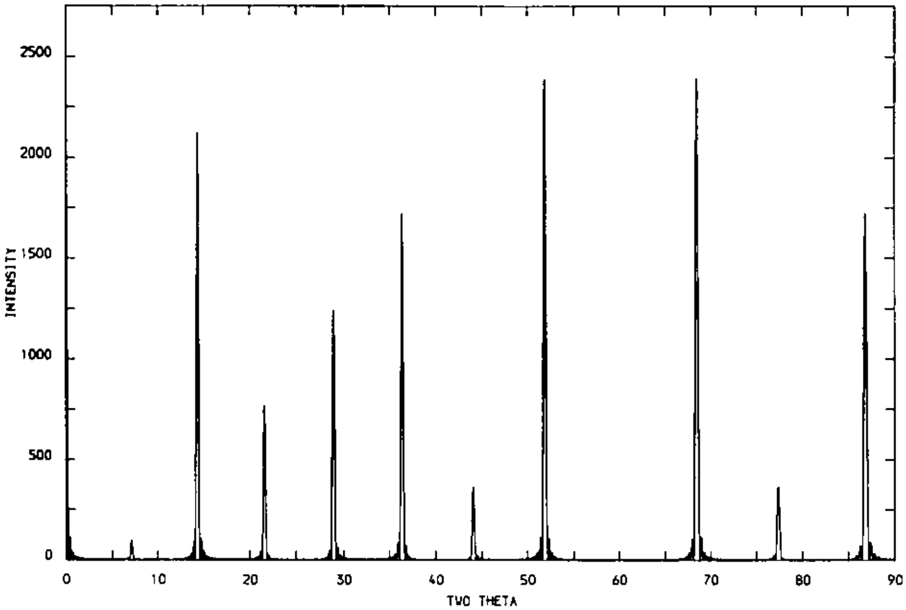
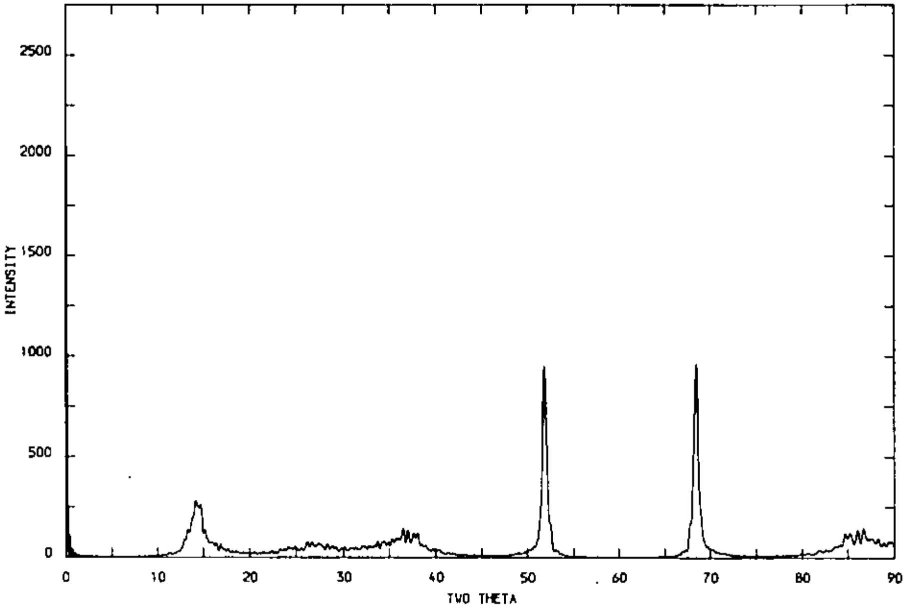
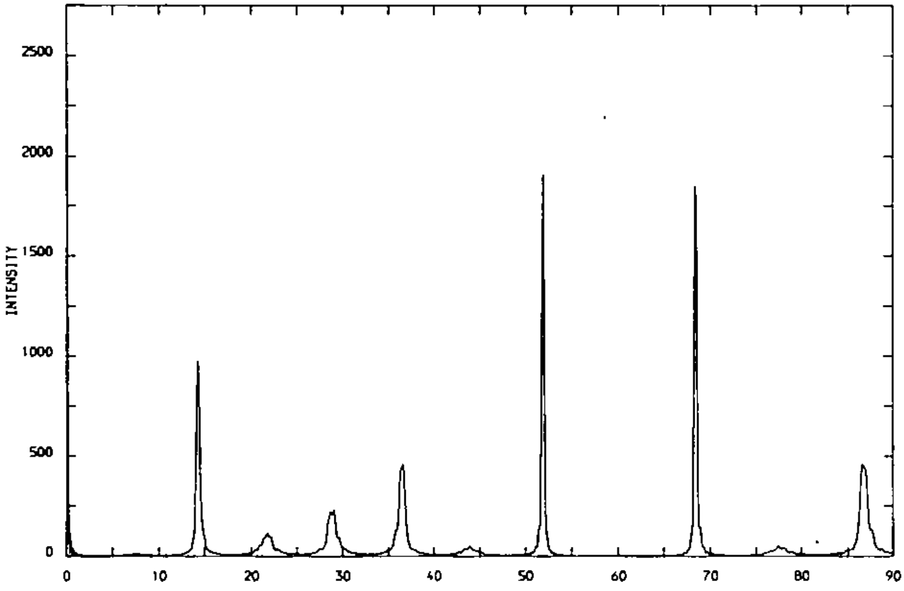


Fig. 4. «Interstratified» diffraction patterns from arrays of point scatters.
a) Superlattice



b) Randomly disordered



c) Short-range ordered
In each case an array of 50 points was used and for b) and c) an average was taken over several realisations of the model. For further details see text.

Finally in Figure 5 we examine the concept of «interparticle diffraction» recently introduced by Nadeau and co-workers (see below). Here two perfect crystallities each with lattice vector $c = 4\lambda$ and containing 5 points are separated by $c \pm \delta$ where δ is a random displacement within a specified range. The patterns shown in the figure are the average of those from 50 such objects. If $\delta = 0$ (Figure 5a), the pattern from a perfect 10 point crystal results. For $-0.05\lambda \leqslant \delta \leqslant 0.05\lambda$ the effect over the 2θ range shown in Figure 5 is almost negligible and even for $-0.125\lambda \leqslant \delta \leqslant 0.125\lambda$ it is very small. Figure 5b shows the pattern for $-0.25\lambda \leqslant \delta \leqslant 0.25\lambda$. It can be seen that even for this large displacement the pattern is not greatly altered. In particular the half widths of the peaks are little changed, even for the fifth order ($2\theta \simeq 77°$) increasing by only about 20%. Figure 5c shows the effect of a still larger displacement $-0.5\lambda \leqslant \delta \leqslant 0.5\lambda$. Now the pattern changes from that from a «10-point crystal» to that from a «5-point crystal» as 2θ increases. For comparison Figure 5d shows the pattern from a perfect 5-point crystal. Simultations involving larger displacements (*e.g.* $-1.0\lambda \leqslant \delta \leqslant 1.0\lambda$) give patterns which are subjectively similar to Figure 5c.

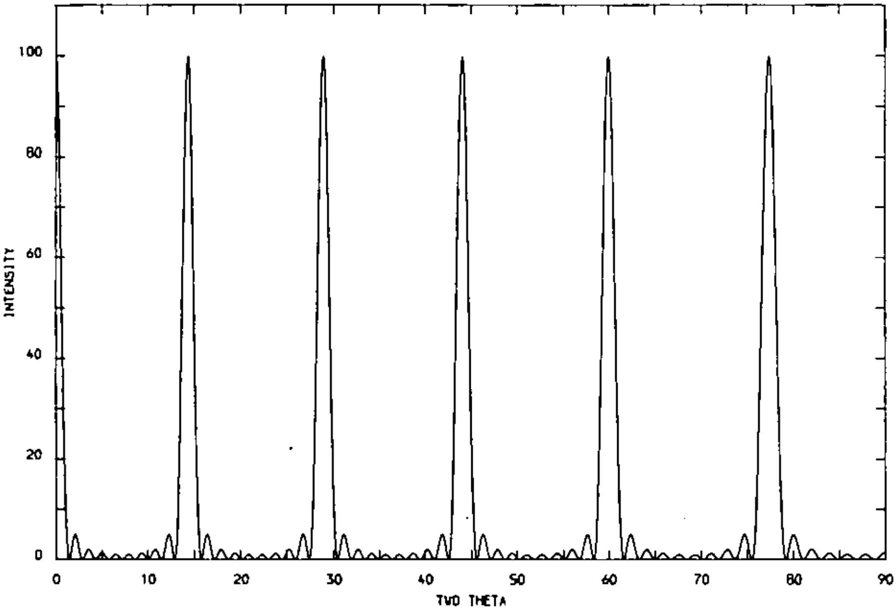
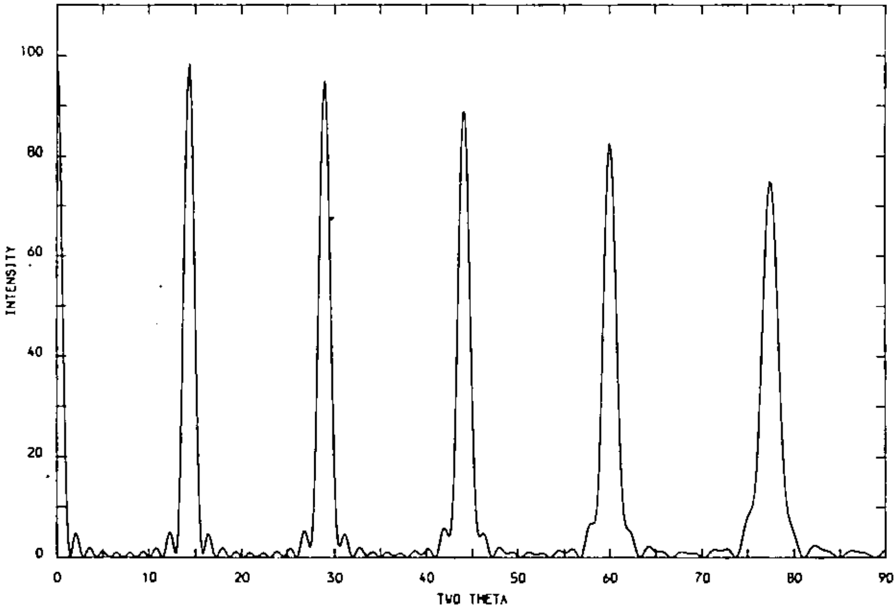
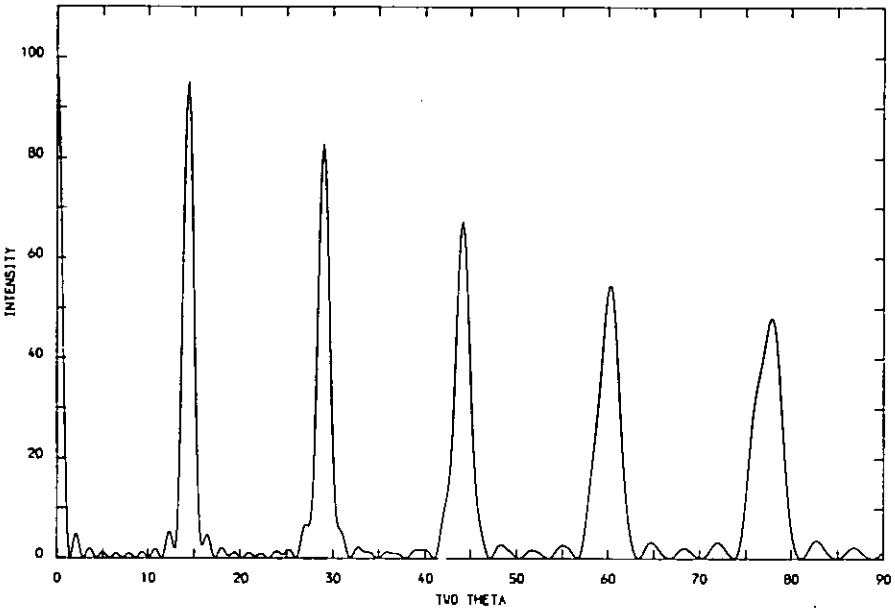


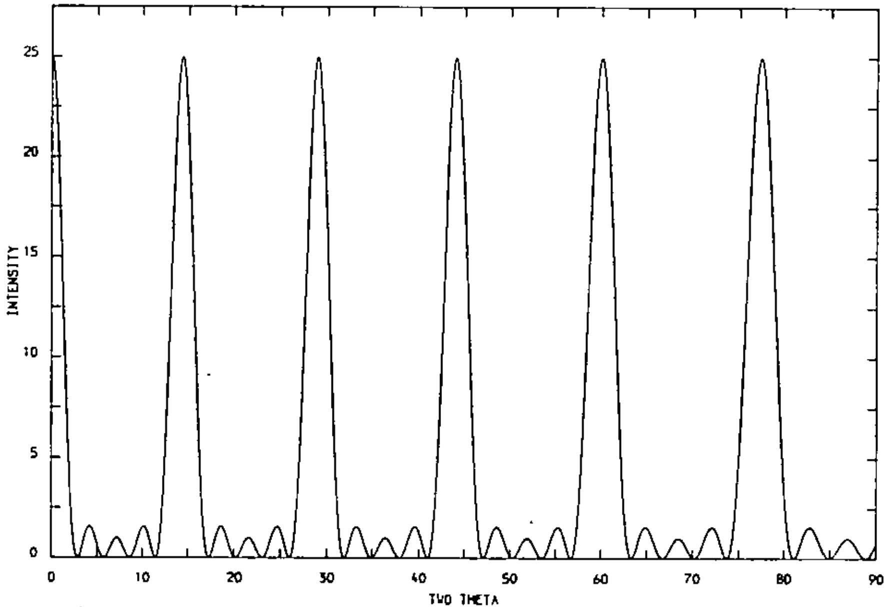
Fig. 5. «Interparticle diffraction»
a) Two 5-point crystals in perfect register



b) Displaced by up to ±0.25λ



c) Displaced by up to ±0.5λ



d) 5-point perfect crystal

For b) and c) an average was taken over several realisations of the model. For further details see text.

The examples described above are greatly simplified but serve to illustrate many of the effects observed in interstratified systems. One point which should be stressed is that diffraction patterns of the type produced by interstratified minerals can result from very poorly ordered materials. In many cases it is questionable wheter the term «crystal» is even applicable and any view which considers the system in terms of small well-defined discrete crystallites is very naive. Especially in the case of swelling materials, a more useful analogy might be to consider the case of a smectitic liquid crystal (see *e.g. Chandrasekhar [1977]*), a material that has structural coherence over a finite length without necessarily being divided into discrete domains of this size.

5.2 Methods of analysis and interpretation of results

The methods used to interpret diffraction patterns from interstratified clays are reviewed in detail by *Reynolds [1980]*. Usually only the 001 (basal) reflections are considered as this greatly simplifies the calculations whilst allowing the major features of the structure, *i.e.* the layer-interlayer stacking sequence to be determined. The requisite data can be obtained by using oriented samples. Generally an indirect method of interpretation is employed in which the observed diffraction pattern is compared with a set of patterns calculated for different values of the adjustable parameters in the model (see *e.g. Reynolds and Hower [1970]; Weir and Rayner [1974]*). The model most often used *(Reynolds [1967])* is based on a Markovian approach involving junction probabilities to determine the sequence of interlayers. For randomly interstratified systems the algorithms devised by *Wright [1975]* should also be mentioned. These are mathematically elegant and allow a number of additional features such as strain broadening to be introduced.

Possibly the most precise work in X-ray diffraction from clay minerals is that by *Tchoubar and co-workers* (reviewed by *Tchoubar [1984, 1985]*), where the complete 3-dimensional diffraction pattern is modelled rather than just the basal reflections. To date most of this work has concerned kaolinites and smectites, but there appears to be no reason why interstratified materials cannot be studied in this way. Another recent development is the use of least-squares profile refinement *(Wood and Brown [1984, 1987])*. Here *Wright*'s *[1975]* algorithms are used to calculate the 001 diffraction pattern which is then fitted by least-squares to data collected from oriented samples. This approach allows the «best» values of the adjustable parameters in the model to be determined on a formal basis. Application the method to a (much studied) interstratified illite-smectite from a Denchworth series soil clay gave results in better agreement with its chemical composition than those obtained previously by more conventional methods. This analysis also enabled the correlation coefficients between the different refineable parameters to be obtained, some of which were found to be very high. In particular, the average particle size was found to be 98% correlated with the scale factor for the pattern, suggesting that estimates of particle size for such systems are likely to be inaccurate (see above). In these circumstances it may be very advantageous to place the data experimentally on an absolute scale *(Pons et al. [1980])*.

Both of the methods reviewed in the previous paragraph require «pure» specimens. Techniques more easily applicable to samples containing a mixture of minerals have been described by *Środoń [1980, 1981, 1984]*, who has produced a set of nomograms for the estimation of mineral composition from measurements of a few key reflections. These essentially provide an alternative, rapid, means of applying Reynold's model, since they are based on calculations made using the method of *Reynolds and Hower [1970]*. Even this approach, however, may not always be applicable to soil clays as it requires accurate determination of the positions of some of the higher-order peaks which may well be too weak and diffuse to allow this. Other, more approximate, methods are also not without pitfalls. If random interstratification is assumed it might be thought that the percentage of swelling interlayers could be determined by comparison of the strong first-order reflection with the traces shown in Figure 1. Unfortunately, there are serious difficulties in this. For example, considering the smectitic rich end of the composition range, it is found that the position of this reflection does not shift greatly as the amount of illitic interlayers increases but instead decreases in intensity. Thus even if this peak position could be determined accurately (which is itself a non-trivial process) it is unlikely to provide a reliable estimate of composition. An analysis on the basis of intensity would require a diffraction pattern from which the background intensity had been subtracted. Failure to consider this will result in an overestimate of the percentage of illitic interlayers.

Finally, it is pertinent to make a few further comments on the interpretation of the results from diffraction experiments on interstratified systems. In the preceding section it was shown that the diffraction patterns observed from clay minerals could be produced by very poorly ordered systems, to the extent that it is questionable whether terms such as «crystal» are really applicable. The different types of disorder can, in principle, be distinguished from each other by, for example, the behaviour of the halfwidths of the peaks with 2θ, but in a real case it may be difficult to separate the effects of size, strain, stacking faults etc. Much of the previous work on interstratified minerals has neglected strain broadening in favour of size broadening, probably solely for resons of convenience in computer programming. More precise studies of both micas and swelling materials have indicated that both these terms are important *(Kodama, Gatineau and Méring [1971]; Ben Brahim et al. [1983]; Wood and Brown [1987])*. When examining the results obtained from X-ray diffraction it must always be remembered that the values of the parameters, and indeed even the parameters themselves, will reflect the model used to interpret the data. The model most often used in work on interstratified minerals is the Markov chain, junction probability, approach of *e.g. Reynolds and Hower [1970]*. Although this seems to explain successfully many of the features found in diffraction patterns it is only an approximation (a point well appreciated by its original authors) and it should not be inferred that the formation of the mineral therefore necessarily proceeds via a similar stepwise process. Other types of simulation, Monte-Carlo methods, Ising models etc., are also applicable and may attract more attention in the future (see *e.g. Ziman [1979]; Welberry [1985]; Plançon et el. [1983]; Bethke and Altaner [1986])*.

Even within the confines of a single model the results may be viewed in different ways. For example, *Reynolds [1980]* considers the case of a binary system (A, B) containing less than 50% of species A and in which the probability of A succeeding A is zero. *Reynolds* refers to this as the «perfectly ordered case involving nearest neighbours». However, since A must always be followed by B, it is possible to define a new «species» C = (AB) and this system then becomes a *random* mixture of C and B. Both of these models give identical diffraction patterns and cannot be distinguished experimentally. The problem (if indeed it is a problem) can be resolved only if some preference is expressed for the «fundamental units». Recently, *Nadeau and co-workers (Nadeau et al. [1984a, b, c, 1985])* have proposed that interstratified minerals have as their «fundamental particles» thin illitic crystals. This work has done much to stimulate discussion, especially with regard to diagenetic transformations but its true significance has yet to be demonstrated *(Ahn and Peacor [1986]; Sawhey and Reynolds [1985]; Mackinnon [1987])*.

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Coordinator's report on the 1st working session

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The general feeling might have been that the subjects treated during the first session were far removed from the day-to-day preoccupations of the average agronomist. This impression was dispelled by the lecture delivered by Dr. *Pedro* (Versailles). He described the changes in the approach of the soil scientist to the study of clay mineralogy from the early colloid chemistry of clays considered as amorphous substances through what may be termed the classical approach consisting in X-ray or I. R. studies of highly purified mineralogical clay samples. The present day approach is characterized by the use of more and more sophisticated physical techniques on the one hand and, on the other hand, by the study of natural soil samples in undisturbed field conditions. This implies that mineralogical clay studies are now carried out at «their natural water content» and no longer on perfectly dessicated soil samples with one or two layers of water. The advantages of this approach are obvious: first of all direct measurement of important properties relating to the surface chemistry of clay minerals becomes possible; secondly the architecture of the natural pore systems becomes directly visible. The concepts of «domains» and «quasi-crystallinity» which had been used rather loosely in the past, are now firmly established.

Classical methods such as the well known soil water retention curve may be combined with modern observation techniques as demonstrated by *Tessier.* The interest of this communication lies in the fact that the fabric of the porous material is examined at «biological water contents» *i. e.* at water contents which are normally found in the soil. At these water contents the interlayer spacings become much larger than 2 layers of water and important processes such as electrolyte exclusion or surface diffusion of ions are considerably modified.

The conclusion presented by *Tessier* that understanding the properties of clays requires that their geochemical environment and their energetic history be taken into account is illustrated in more detail by the presentation of *Tributh* on the formation, transformation and decomposition of clay minerals. It should be emphasized that a process which he describes and which has been referred to recently as «cationic denudation» has assumed tremendous importance over the last few years. The reason for this interest is twofold: the impact of acid precipitation on soil and vegetation in industrial countries is well known. On the other hand, in many countries of the humid tropics, especially at high elevation, this terminal stage of cationic denudation has reached a point where the productivity of the soil has sunk to a very low level due to aluminium toxicity. In many countries, no economic correction of this situation is possible. It must be recognized that the easy correction of soil acidity in industrial countries by the use of marl, lime, basic slag, etc. has led to neglect the study of the correction of soil acidity by way of a minimum input technology. To what extent complexation by organic substances, magnesium and potassium fertilization can alleviate this situation remains a pressing object of study.

The use of highly sophisticated techniques was described by *Arcan and Wood.* Rather than go into a summary of their presentations, which were much condensed anyway, I think that it would be fitting to emphasize two incidental comments made by the two speakers. As mentioned by *Arcan,* sophisticated hardware will only do what it is told to do and not what we expect it to do. It is also noteworthy that for the first time in a potash colloquium, the phrase «expert systems» was mentioned. It was mentioned here in the rather restricted context of data acquisition and treatment. It seems obvious that in the not too distant future, accumulated knowledge will be organized in expert systems from which the practical agronomist, making full use of his own expertise and of the possibility of the machine, will arrive at an optimalised prediction of the economic return from potash manuring.

Chairman of the 2nd Session

Prof. Dr. *A. van Diest,* Dept. of Soil Science and Plant Nutrition, Agricultural University of Wageningen/The Netherlands; member of the Scientific Board of the International Potash Institute

2nd Session

K Release and K Fixation

Potassium Fixation and Release

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Summary

The fixation and release of potassium in soil are part of a dynamic, reversible process controlled primarily by the type and particle size of the primary and secondary minerals present. The process is also affected by soil structure, soil pH and liming, manuring, temperature, wetting and drying and freezing and thawing, and the action of plant roots. Potassium exchangeable to a solution of an ammonium salt is the most widely used estimate of plant available K. Non-exchangeable K is usually determined, if at all, by the historical methods of exhaustive cropping in pots or by extraction with acids. Electroultrafiltration is used by some organizations to produce a multi-element extract. There has been some success in modelling K availability and uptake to field crops. Potassium fixation is generally measured against K exchangeable to ammonium, magnesium or rubidium salts, but acids and ion exchange resins have been shown to extract fixed K.

At present, the routine determination of K fixation and release seems likely to continue to be made by simple and inexpensive procedures involving extractions with ammonium salts or acids. More sophisticated methods, which provide data on all categories of soil K, appear destined to remain the favoured tool of some scientists, and to be used only for research purposes. Progress is most likely to come from the application of models which take into account the amount and especially the rate of release of exchangeable and non-exchangeable K, soil structure and heterogeneity, the movement of nutrients through the soil, root distribution, morphology and uptake, and climate.

1. Introduction

Potassium release from soils is often viewed as ‹good› because it replenishes exchangeable K used by crops, but potassium fixation ‹bad› because it makes added K unavailable to the plant: *Kittrick [1966]* stated that K fixation in vermiculite involved irreversible interlayer contraction; *Acquaye et al. [1967]* found that 91% of K added to soil containing vermiculite and interstratified vermiculite/mica was fixed; *Doll & Lucas [1973]* reported that 92% of the K applied to a sandy clay loam soil in Michigan was fixed, and that tomato production was increased by applications of up to 1600 kg K/ha. While K fixation is certainly a problem in the short term, I believe that in the long term it should be viewed as a benefit to agricul-

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ture. Only very few soils lose K to drainage by leaching; instead the K is held by the soil, but not in a way that makes it completely unavailable; it can be released slowly *(Johnston [1986])*. This can be very important in meeting crop needs and, in most cases, cannot be compensated for by fresh K.

The subject of potassium fixation and the availability of residual K was reviewed by *Beckett [1970]*. More recent considerations of both K fixation and release have been made by *Mengel & Kirkby [1982]* and *Martin & Sparks [1985]*, and *Quémener [1986]* gave an extremely useful review of all aspects of soil K.

Whilst this paper reviews mainly current methodology it also considers briefly the processes involved in K release and fixation because without this it is difficult to properly assess the methods discussed.

2. Processes of K release and fixation

2.1 Minerals involved in K release and fixation

Potassium release and fixation in soils is chiefly a function of the amounts and types of primary and secondary minerals present and their particle size, particularly in the clay fraction, and of the activity of K in solution around these minerals *(Feigenbaum [1986])*. Those minerals which determine whether K is released or fixed have been reviewed by *Rich [1972]*.

Those which release K are:

(i) primary minerals – biotite and muscovite mica, and the feldspars orthoclase and microcline;

(ii) secondary minerals – hydrous mica (illite), and interstratified minerals containing these, and the zeolites phillipsite and clinoptilolite.

Potassium fixation was first noted by *Dyer [1894]*. It occurs in those secondary minerals which have expanded, or partially expanded interlayers: vermiculite, hydrous mica (illite), and smectite, and has also been reported in glauconite, beidellite, nontronite and amorphous materials. *Sparks & Huang [1985]* suggested that hydrous micas fix K under wet or dry conditions, but montmorillonites only after drying.

Some have found evidence for K fixation by allophanes *(Schuffelen & van der Marel [1955]; Barber [1979]; Yamada & Shoji [1982])* but this cannot be by interlayer contraction. *Martini & Suarez [1977]* attributed it to changes in crystallinity and hydration, especially when the clay was subject to wetting and drying (see below).

A further possible method of ‹fixation› is the formation of insoluble K compounds especially aluminosilicates. This was found to be relatively unimportant compared with fixation in 2:1 layer silicates in some recent work by *Shaviv et al. [1985]*.

2.2 The dynamic process of K release and fixation

While certain minerals will only release K (micas, feldspars) and some can only fix K (true montmorillonites which contain no unexpanded residual mica layers), some minerals will both release and fix K (illites). In soils, which usually contain a range of minerals, fixation and release are part of a dynamic reversible process, the main reactions of which are summarized in Figure 1. Some authors present this equation rather differently. *Bertsch & Thomas [1985]* permit K to be released from non-exchangeable sources directly to the solution phase; they also show only the release of K from the mineral phase and imply that the reverse process, the fixation of K into a mineral phase, is not possible. However, there is sufficient evidence to prove that K can move all the way out from the mineral matrix and all the way back into it, under suitable conditions.

Potassium in layer silicates is held at negatively charged sites at the surface of 2:1 layers (Figure 2.). The primary process involved in K release and fixation in layer silicates is the exchange of potassium and other, notably larger, hydrated cations, with a consequent change of the interlayer space. Release is accompanied by a decrease in layer charge and some chemical changes. A full description was given by *Rich [1972]* and more recently by *Sparks & Huang [1985]*, and will not be discussed further here.

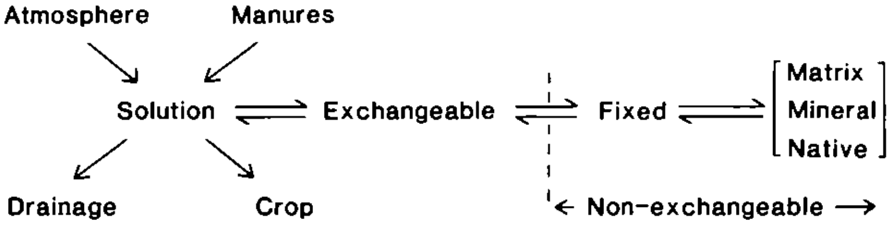

Fig. 1. The dynamic equilibrium of soil potassium.

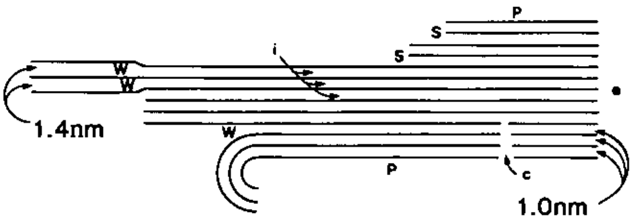

Fig. 2. A schematic drawing of a 2:1 layer-silicate clay showing 1.0 and 1.4 nm layers and planar (p), edge (e), interlayer (i), wedge (w), crack (c), and step (s) exchange sites.

There have been some attempts to show that dissolution of layer silicate minerals is an important factor in K release *(Feigenbaum & Shainberg [1975]; Feigenbaum et al. [1981])*. However this only appears to be true for acid conditions (pH ≤ 3). At neutral or near neutral pHs the primary process is ion exchange *(Feigenbaum et al., [1981])*. Once ions are close enough (*i.e.* once their oscillating volumes overlap) exchange is virtually intantaneous, taking only 10^{-12} seconds. Thus it is not the exchange process *per se* which controls the rate of release and fixation of K in soils and clays, but the movement of K and other ions to and from adsorption sites *(Nye & Tinker [1977])*.

Potassium in feldspars is part of the crystal structure. Its release is therefore a surface-controlled dissolution process *(Sparks [1986])*, although the dissolution may not proceed congruently, i.e. the surface may not all be dissolved at the same rate but pits and cracks may form at crystal defects. Dissolution of feldspars will make a significant contribution to K supply in temperate climates only under conditions of podzolization, but may be very important in humid tropical climates *(Quémener, 1986)*.

2.3 Factors affecting K release and fixation

Mineralogy determines K release and fixation, but many other factors influence it; these were listed by *Rich [1972]* and by *Sparks & Huang [1985]*. *Martin & Sparks [1985]* also presented a useful discussion on the various factors, including the role of H_3O^+.

Fixation and release in soils are affected by *(i)* the size of the mineral particles involved, *(ii)* soil pH, *(iii)* rainfall and temperature, *(iv)* manuring, *(v)* soil structure, *(vi)* wetting and drying and freezing and thawing, and *(vii)* plant roots. Only the last three will be discussed here.

The rate of fixation and release of potassium in soils in the field is controlled by the rate of diffusion of ions to and from exchange sites. Soil structure thus greatly affects fixation and release because it determines the size and shape of pores *(Heming & Rowell [1985])*. In unsaturated soils in the field exchanging ions may often be able to move only along the charged surfaces of particles. Such surface-mobility has been investigated by *Staunton & Nye [1983]* and *Staunton [1986]* and is discussed by *Staunton & Nye* (this volume).

Wetting and drying and freezing and thawing are said to affect both K release and fixation. *Beckett [1970]* and *Sparks & Huang [1985]* list many references which are said to support this. However, only that of *Fine et al. [1940]* suggests that freezing and thawing affect both release and fixation, and most of their soils released K on freezing and thawing; only a very few fixed K and then only in small amounts. *Eberl (private comm.)* has found no effect of freezing and thawing on K fixation in smectites. Wetting and drying can affect the adsorbtion/desorption equilibrium chemically by changing the activity of ions in the soil solution, and also can exert a simple physical effect and increase fixation by assisting layer realignment and collapse, or K release by stressing clay layers and causing particles to break. Freezing changes the structure of liquid water, increasing its volume. It can thus increase interlayer space and make the movement of K and other ions easier, facilitating K release, but any contraction on thawing is only to the former spacing. It thus seems unlikely that thawing would increase the ability of soils to fix K.

It was thought that plant roots excreted H^+ and thus always increased K release. *Nye [1986]* and others have now shown that roots excrete both H^+ and HCO_3^- depending on the balance of anions and cations taken up *(Römheld [1986])*, but either way plant roots have a profound effect on the availability of K. *Steffens [1986]* emphasized that K uptake depends on root distribution and characteristics. *Barber [1985]* quotes *Kuchenbuch* as finding that roots acquired K from only 14% of the soil volume, and *Beringer [1985]* says that as little as 3% of the soil may be available to plant roots. If the K used by the plant comes from such a small soil volume then much non-exchangeable K must become available to the plant from the soil around roots. However, recent studies *(Barraclough [1987a])* suggest that the diffusive flow of K may often be sufficient to meet the needs of a winter wheat crop yielding 10 t/ha of grain.

3. Methods used to study K release

The equilibrium shown in Figure 1 separates soil potassium into exchangeable and non-exchangeable fractions. This clear separation owes more to what has been measured in the laboratory than to the true situation in the field. However, because methods of analysing soil K are most conveniently split into those for exchangeable and non-exchangeable K, this tradition will be followed here. A list of methods used to measure these fractions is in Table 1, compiled from *Grimme & Németh [1979], McLean & Watson [1985]* and *Sparks & Huang [1985]*.

Table 1. Methods for measuring soil K (after *Martin & Sparks [1985]; McLean & Watson [1985]; Németh & Grimme [1979]*)

K Fraction	*Method*
Solution	Batch equilibration or column leaching with water Extraction by pressure membrane or centrifugation (which extract K in the soil solution) Activity ratios
Exchangeable	Batch equilibration or leaching with dilute solutions of salts (especially NH_4^+) and acids (citric, nitric) Electroultrafiltration Silver thiourea Mehlich 1 ($HCl + H_2SO_4$) and 2 (acetic acid, ammonium fluoride, ammonium chloride, HCl) Ammonium bicarbonate + DTPA Bray 1

Table 1 *contd.*

K Fraction	*Method*
Exchangeable (contd.)	Exchange isotherms and other equilibrium data Potassium potentials Calcium acetate lactate (CAL-K) Double lactate (DL-K)
Non-exchangeable	Exhaustive cropping Leaching with dilute acids and salts Boiling with dilute acids Boiling with concentrated acids Repeated extractions with NaTPB Repeated extractions with oxalic acid Repeated extractions with Ca or H resins Sodium cobaltinitrite Hot $MgCl_2$ Electroultrafiltration Electrodialysis
Mineral	Selective dissolution with Na-pyrosulphate fusion
Total	HF digestion
Multi-fraction	Q/I curves EUF Sequential extraction by resins Boiling HNO_3

3.1 Exchangeable K

Methods used to measure exchangeable or plant available K have usually involved simple extractant techniques. Perhaps the earliest was that of *von Liebig [1872]*, followed by *Dyer [1894]* who used 1% citric acid believing that roots exuded an extract with approximately this acidity; many subsequent methods have also tried to mimic the action of plant roots. Solutions of ammonium salts are probably the most widely used extractants now, followed by calcium and barium salts, but the list is almost endless. Those values obtained with different ammonium salts are very closely related, and correlate well with all salt extracts *(Johnston [1986])*, and it does seem that a simple extraction with an ammonium salt, most commonly ammonium acetate, gives a very useful indication of that K which is immediately available to a crop. The use of ammonium acetate may diminish, however, with the wider availability of instrumental techniques in which the acetate ion interferes with detection.

Because plants take up K from the soil solution, many of the methods used measure the concentration or activity of K in solution, either alone or in combination with other ions present. Exchange isotherms and all the associated parameters have proved useful in assisting our fundamental understanding of exchange processes in the soil but they have been of little use in practical predictions of K availability. *Woodruff [1955]* and then *Arnold [1962]* were perhaps the first to suggest the use of a free energy parameter to assess K availability, but many others followed (see *Goulding [1983]*). The most recent work along these lines at Rothamsted has been the calculation of critical potassium potentials by *Page & Talibudeen [1982a,b]*. There seems little likelihood of any such method being put into practice for advisory purposes. One of the main hindrances to applying ion exchange data to predicting K availability has been the concentration of exchange studies on binary (two-ion) systems. This was necessitated by the complexity of the calculations for exchanges involving more than two ions. However, studies of ternary (3 ion) systems have recently been made and data used to construct models of more realistic soil systems (*Nir et al. [1986]; Shaviv & Jury [1986]; Sposito [1986]*). Such models offer a real step forward in K advisory work.

Q/I curves have enjoyed a little more success than exchange isotherms and are still applied today to assess K availability (*Nair & Grimme [1979]; Sparks & Liebhardt [1981]; Evangelou et al. [1986]*). As well as providing a measure of available K they show how this fraction is buffered by the soil. However, opinions are divided on their usefulness for practical purposes. *Sparks & Huang [1985]* reported the effectiveness of the various Q/I parameters for determining K availability, and showed how they changed with cropping, liming, etc. By contrast, *Bertsch & Thomas [1985]* thought that Q/I curves were not truly representative of K relations in a given soil *because* they changed with cropping, and anyway were too expensive for everyday soil testing.

3.2 Non-exchangeable potassium

There is no agreed standard method for assesssing K reserves, and very few methods are available to farmers for routine determination of reserve K. In the U.K., *Fisons* (now *Norsk Hydro*) began offering a service in 1977 (see *Sutton & Blake [1977]*) but the method has never been published.

Martin & Sparks [1985] give a comprehensive list and discussion of 16 methods used to measure non-exchangeable K. Similar, but slightly less comprehensive reviews were made by *Doll & Lucas [1973]* and *McLean & Watson [1985]*. It is not possible in this paper to mention every method used, let alone every variant of each method. Instead the most widely used and/or useful methods, will be discussed briefly in relation to their advantages and disadvantages.

3.2.1. Historical

Of the early methods, those which are still used today are exhaustive cropping in pot experiments and strong acid extractants.

Pot experiments. Any experiment which involves taking samples of field soils, growing a crop on the soil to exhaustion (sometimes with one or more resowings) and measuring the K taken up by the crop with time gives information on K availability, with steps or breaks in the release curve being related to changes in source. One of the most important requirements of laboratory analyses of any nutrient, however, is a standard technique. The standard methods of pot culture (Chaminade, Stanford de Ment and Neubauer) were reviewed by *Quémener [1979]*. Pot techniques are immediately attractive because one might expect a direct simple relationship between K uptake by plants in pots and in the field. Unfortunately there are very large differences between plants growing in the field and in pots, whether in growth chambers, glasshouses, or even in open air. The main factors which contribute to the difference are: *(i)* weather and the very large effect climate has on all aspects of plant growth; *(ii)* plant root distribution and morphology – plants in pots explore most of the soil, but plants in fields explore only a small part of the soil volume; *Beringer [1985]* suggested that as little as 3% of the soil in the field may be used by a crop, *Johnston & Mitchell [1974]* that one years' cropping in the glasshouse was equivalent to 12 in the field, and *Moberg & Nelson [1983]* found that several years exhaustive cropping in pots was the equivalent of 60 years cropping in the field; *(iii)* soil heterogeneity – the soil used in a pot experiment will have been thoroughly mixed to ensure that it is homogeneous; soil in the field is far from being homogeneous, as *Beckett* (this volume) explained. In spite of this, many still use pot experiments to calibrate laboratory methods without attempting to properly relate what they measure to what happens in the field *(Binet et al. [1984]; Graley [1981]; Ghorayshi & Lotse [1986])*.

Strong acids and other extractants cannot be said to mimic plant uptake, but they are much quicker and more convenient than pot experiments. Because of this they are widely used to measure non-exchangeable K. The boiling nitric acid methods of *Haylock [1956]* and *McLean [1961]* which measure Available, Step, and Constant rate K are the most widely used *(e.g. Jia Xian & Jackson [1985]; Al-Kanani et al. [1984]; Sailakshmiswari et al. [1985]). Hsu et al. [1979]* found boiling nitric acid to be a good predictor of K availability to plants in pots in the latter stages of growth when, presumably, non-exchangeable K was being taken up. However, *Singh et al. [1983]* found little correlation between any of the parameters measured by strong acids and winter wheat grown in the field, and *Doll & Lucas [1973]*, reviewing methods recommended for soil K analysis, describe strong acids as useful for research purposes but not for practical advisory work.

3.2.2. More recent methods

Electroultrafiltration (EUF) was developed by *Németh [1982]*. Water is percolated through a soil while the soil is subjected to an electric field which is increased stepwise; the temperature is also varied. The K collected in several solution extracts is analysed and plotted against time. Certain fractions have been shown to correlate with K availability as measured in the field and laboratory. Opinions on its usefulness differ. Many have reported very good correlations of EUF parameters with crop data *(Plant & Soil, 1985, 83)*, others *(e.g. Sinclair [1982])* have found little advantage over conventional methods. The reluctance to accept it seems to be because: *(i)* EUF rarely removes as much K as simple extractants such as ammonium accetate, so how can it truly predict the release of K reserves? and *(ii)* EUF equipment is complex and relatively expensive compared to that normally used for estimating soil K. However, EUF has been suggested to predict not just K availability, but also that of other macro and micro nutrients (see *Németh [1985]*). It has therefore been adopted by certain organizations which require a multi-element analysis, and in this context may well have its place. In these situations it may be less expensive than a traditional soil test laboratory.

Sodium tetraphenylboron, NaTPB, is a precipitant which has been extensively used in work with clays and soils *(Quémener [1979,1986])*. The amounts extracted correlate well with K released in pot experiments, but they are sometimes rather less. *Quémener [1979]* remarks on the high cost of the salt and suggests that this is perhaps the main reason for its lack of application in advisory work. A method for its use in the routine determination of K reserves has recently been proposed by *Jackson [1985]* and is in use in New Zealand, but like so many other methods it seems destined to remain the favoured tool of some scientists, used primarily for research purposes.

Ion exchange resins have been used for many years to extract soil K and other ions (see *Quémener [1979]*). Early work used only single extractions and results were found to be little better than those with simple salts *(Arnold [1958]; Haagsma & Miller [1963])*. More recently multiple extractions of the same soil sample with resins have been used to build up K release curves *(Talibudeen et al. [1978]; Havlin & Westfall [1985])*. Such curves seperate the three main categories of soil K – exchangeable, fixed, and mineral matrix or native – and reflect soil clay content and mineralogy, and manuring and cropping history. They are the same in form and magnitude to those of cumulative uptake curves obtained by growing ryegrass in pots in the glasshouse, and quantities calculated from them have been found to correlate well with the uptake of K by a range of field-grown crops *(Goulding [1984])*. Used with strong acid extractions, a complete picture of soil K content and release can be obtained which includes all fractions of soil K. Recently *Goulding and Loveland [1986]* suggested that such data could be used to provide background data and perhaps map soil K preserves. However, because of the complexity and long duration of extractions needed to prepare release curves, ion exchange resins are likely to remain a research tool. Several research groups have also been modelling K release curves obtained from resin exchange studies *(Talibudeen et al. [1978]; Havlin et al. [1985]; Sparks & Huang [1985])*. These may provide a means of predicting K availability.

3.3 Modelling K release

Recently there have been an increasing number of attempts to use models to predict K availability and uptake. Early models examined nutrient movement to, and uptake by single roots or plants (see *Nye & Tinker [1977]*), but models have recently been applied to predicting K (and P) uptake by plants in pots and in the field. The model of *Jungk & Claasen [1986]* includes nutrient uptake characteristics, root and root hair length, exchangeable and non-exchangeable K, diffusion coefficients, and concentration gradients. It fitted data on K depletion from soil and uptake by maize in pots very well. The authors suggested that it could be used to understand and quantify processes and interactions in the soil-root system.

Silberbush & Barber's *[1984]* model predicted well the K uptake of five cultivars of field-grown soybeans (which exhibited a range of uptake characteristics) on two rather similar silty loam soils. The model accommodates nutrient concentration and buffer power, diffusion rates, root length and root growth rates, and nutrient influx rates. More recent tests *(Barraclough, 1987b)* with field-grown winter wheat were very unsatisfactory, however, with the model overpredicting K uptake by 4 times and underpredicting P uptake by 20 times.

4. Methods used to study K fixation

Rather less work has been done on K fixation than on K release. This is not really surprising as the area of soils subject to serious K fixation problems is fairly small, especially in the developed countries. *Addiscott & Talibudeen [1969]* listed the more important methods used to measure K fixation; that most widely used was to measure K fixed relative to ammonium exchange in both clays and soils, either kept moist or after drying:

Fixed K = (Initial Exchangeable K + Added K) − Exchangeable K after fixation

Van Diest [1979] thought that NH_4^+ might not be the best exchanging cation because, being the same size as K^+, it might be fixed, thus trapping some K and erroneously increasing the measured fixation capacity.

Other methods involved extracting fixed K from the soil with acids or exchanging it with various ions (e.g. *Beauchamp [1982])*, and some also used x-ray diffraction studies to examine the change in clay structure on absorbing K and thus to estimate K fixation (e.g. *Mortland & Gieseking [1951])*.

Quémener [1979] listed the methods used currently to measure fixation. The most popular is still to measure the amount of potassium remaining exchangeable to ammonium ions following the addition of K to the soil. *Van der Marel*'s method *[1954]*, widely used in France, involves measuring the K exchangeable to magnesium rather than ammonium because ammonium ions are thought to replace some fixed K, the opposite of *van Diest*'s criticism.

More recently *Quémener [1986]* summarized work done at SCPA to relate fixation capacity (as measured by *van der Marel*'s method) to various properties of some European soils. Previously he had made the point *(Quémener [1979])* that although a lot of work has been done to measure fixed K and the process of fixation, little has been done to devise a systematic method of analysis. This is urgently required. *Van Diest [1979]* pointed out the difficulty of extrapolating laboratory measurements to predict field behaviour, and in particular, that K which is found to be fixed in the laboratory may well be readily available to a crop in the field.

4.1 Recent developments in measuring K fixation

Ross & Cline [1984] measured the fixation of K in Canadian soils conventionally against NH_4^+ exchange and compared this with the vermiculite content of the soils. They also measured the fixation of K^+ and NH_4^+ in a vermiculitic soil in the field following 6 years of slurry application *(Ross et al. [1985])*. Measuring Rb fixation capacity (by adding 0.1 M RbCl, drying, washing with M NH_4Cl, and digesting with HNO_3-$HClO_4$-HF to determine fixed Rb) before and after slurry application showed that large amounts of K and NH_4 had been fixed, and x-ray diffraction studies showed that much of the vermiculitic mineral in the soil had been changed into a mica-like mineral; a form of reverse weathering.

Shaviv et al. [1985] measured K fixation against exchange with Ba, K fixed being calculated as either the decrease in CEC or the difference between initial Solution + Exchangeable K + Added K, and final Solution + Exchangeable K; a reasonable agreement was found between the methods with an r^2 of 0.88.

Yamada & Shoji [1982] used an electron microprobe to measure the K content of fresh and aged (*i.e.* from soil) volcanic glasses and found that these had fixed some K during agricultural use.

At Rothamsted, K release curves coupled with extraction by strong acid (20% HCl – constant boiling HCl) have been used to follow the long term balance of K in a number of soils. These two methods together provide estimates of exchangeable and non-exchangeable K, and separate the latter into fixed and mineral K. Using soil samples taken periodically from the long-term experiments at Saxmundham and the Rothamsted and Woburn Reference Plots it has been possible to see in which fractions the accumulated K is fixed, and from which fractions K is released. A qualitative balance and, in some cases a quantitative balance has been achieved. We have also attempted to assess K fixation by measuring changes in total K levels on the Classical experiments. However even on these very long term plots, only on those plots which have received very large amounts of K can a difference in total K be seen which is outside the standard error of the method *(Johnston, [1986])*.

5. The usefulness of methods of measuring K fixation and release

Novozamsky & Houba (this volume) critically evaluated soil test methods. Below are listed some important factors relating to the usefulness of methods of measuring K fixation and release, both for research and advisory purposes.

5.1 Research

The research scientist is seeking information on the amount and rate of release of various fractions of soil K which will enable him to understand the behaviour of K in soil and relate it to various soil properties; he may or may not be interested in relating these to K availability to crops. Those methods which provide the best means of relating K release and fixation to soil properties are ion exchange resins and NaTPB. Strong acid extractions are of some use, especially in combination with the detailed release curves obtained from resins and NaTPB. Q/I curves fall between the practical and research methods, being too complex for routine testing and not quite sensitive enough to soil changes for research purposes. EUF does give quite a lot of information but, as *Németh [1985]* admits, it will not «replace the highly informative K desorption curves, in particular not in basic research».

5.2 Advisory purposes

Beringer [1985] reviewed the usefulness of all analyses for soil K. He preferred simple methods involving extractants, although suggested that ion exchange resins (cation and anion) and EUF were useful in providing information on more than one nutrient at a time.

For purely advisory purposes balance sheets, as discussed at length at the 13th IPI Congress in 1986, present the simplest and most useful means of assessing soil K in the field. Regular monitoring of soil K using only ammonium acetate as an extractant, linked with analyses of crop yield and nutrient content, shows optimum levels of soil K and whether this is increasing or decreasing. From this one can develop a manuring policy to maintain soils at an optimum K level (optimum in terms of either crop yield or the best economic return) and which will increase, maintain, or decrease soil K reserves.

Field experiments on major soil types enable the potassium characteristics of soils to be determined and incorporated in advice given to those farming such soils. Alternatively, or simultaneously, laboratory methods which estimate the release/fixation of K would be useful to classify and map soil K reserves, providing good background data.

6. Comparing laboratory data with field data

This was discussed in detail by *Villemin* (this volume). Some points are pertinent to this paper.

Doll & Lucas [1973] listed some of the information an advisor needs to provide adequate instruction to the farmer and grower: *(i)* yield goals, *(ii)* crop requirements, *(iii)* root uptake ability, *(iv)* nutrient intensity related to that of other cations and the strength of adsorption of K, *(v)* the fixation/release properties of both the surface and subsoil, *(vi)* the time of year at which the soil sample(s) were taken and the way in which they were prepared for analysis. Measures of soil K availability form a rather small part of this. They concluded that there was no substitute for field trials.

But what is the main aim of the farmer: is it to increase yield at all costs, or is it to obtain the best economic yield. *Beringer [1985]* was of the opinion that both short- and long-term fertilizer experiments were required in which soil tests can be related to growth of crops in the field. Short-term experiments are important because they allow many soil types and climatic conditions to be compared. Long-term experiments smooth out the vagaries of climate and show when nutrient reserves are likely to limit yield.

In this context the work of the *All India Soil Test – Crop Response Correlation Scheme,* summarized by *Goswami & Singh [1979]* should be mentioned. This scheme was designed to improve the advice given to farmers and to allow them to make best use of the high yielding crop varieties that were becoming available when the scheme started in the yearly 1970s. Field experiments were carried out on selected important soil types. Soil test values were related to yield through multiple correlation and regression equations. Targetted yields were then set for each soil and critical limits for nutrient levels obtained. *Goswami and Singh* were well aware of the shortcomings of such a simple scheme, but it is commendable for its simplicity and clarity of purpose. These authors also noted the need to understand the effects of soil structure, water availability, root development and properties when giving advice on nutrient requirements.

7. Summary and conclusions

Many methods have been used to measure K release and fixation. A set of agreed standard methods would be a great step forward, but admittedly will be very difficult to achieve. The published proceedings of this conference may help towards that goal.

There are quite clearly methods which are useful for research purposes and methods which are useful for advisory work. There are few methods which can do both jobs. Methods for research must be precise and repeatable, and in particular provide information on all fractions of soil K. Methods for advisory work need to be simple and inexpensive and above all to be related to crop behaviour in the field. In this context we still need both short and long-term field experiments to calibrate our laboratory methods.

Cooke & Gething [1978] pointed out the need for laboratory methods which measured the rate of K release to crops, and *Bertsch & Thomas [1985]* recently reiterated this need to link kinetic with equilibrium measurements in studies of K availability. They suggested that EUF field strength may provide this link, and ion exchange resins may also provide an answer to this problem.

To make further progress, we need to take into account the perhaps dominating effects of soil heterogeneity and structure, root distribution and morphology, and climate. There have been few attempts to include the effects of wetting and drying and freezing and thawing on K release from field soils. Because the amount of K released by a few wetting and drying cycles is much greater than that which is released by those same soils when kept constantly moist, laboratory methods should aim to assess the magnitude of these effects in relation to the need of the crop for K during the growing season.

With regard to roots, most soil analyses are made on the surface 20 cm or less of soil, although subsoil K analyses are currently routine in the Delaware coastal plane of the United States. *Beringer [1985]* and *Haak [1981]* have presented data to show that up to 50% of the K taken up by a crop may come from the subsoil, and *McEwen & Johnston [1984]* showed that subsoiling can increase K uptake by improving root distribution. *Kuhlmann et al. [1985]* proposed a method for estimating root uptake of K from the subsoil using Rb labelling, but a suitable routine technique has yet to be established. It is also apparent from root studies that plant roots often explore very little of the soil available to them, perhaps sometimes less than 10%. This small volume will be stressed much more in providing enough K for the crop than would the whole soil. The magnitude of such effects will differ between crops; *Steffens [1986]* provided evidence of greater weathering of illite to smectite under grass than under clover and annual crops will generally exploit less of the soil than perennial crops. Equally it will be necessary to take into account diffusive flow of K to roots and how this varies with different soil parameters.

We therefore need a more complete understanding of the volume and distribution of roots of the main arable crops, which, together with their uptake characteristics and data on soil K release could be combined in a model which would cover every aspect of soil K availability.

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Adsorption and Exchange of K in Multi-Ionic Soil Systems as Affected by Mineralogy

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Summary

The adsorption characteristics of potassium in soils that received high applications of K-fertilizers in greenhouses were studied. By comparison to control soils that did not receive such high applications of fertilizers and by detailed potassium-calcium exchange isotherms, it was shown that both in the multi-ionic greenhouse soils and the binary Ca-K exchange in the soils, a pronounced decrease in adsorption affinity towards potassium is observed above a certain exchangeable potassium content. This content was defined as the *«Preferential Adsorption Capacity for Potassium» (PACP),* and was found to correlate strongly and linearly to the content of illite in the clay fraction of the soils. The contribution of mica-type minerals in the coarser fractions of the soil to the PACP was apparently smaller than that of illite in the clay fraction. Furthermore, montmorillonite, a major mineral in these soils did not affect profoundly the adsorption at low potassium contents. Reassessment of data from several previous studies of potassium adsorption in arid lands, including those reported by the *Riverside Salinity Laboratory* in the U.S.A., reveals that a similar abrupt change in the affinity towards potassium is present. It is recommended that it will be considered as an additional characterization parameter of potassium exchange in soils.

1. Introduction and background

Since the pioneering work of the *U.S. Salinity Laboratory* in Riverside on the adsorption relationships of cations in arid-zone soils it is tacitly assumed that the adsorption function of potassium in such soils (as that of sodium) is linear if presented as the exchangeable potassium ratio (EPR = EP/(CEC-EP)) *vs.* the potassium adsorption ratio (PAR), apparently showing a constant Gapon exchange coefficient K_G^K.

Although in the early 1960's it was shown by several European researchers *(Van Schouwenburg & Schuffelen [1963]; Bolt et al. [1963])* that the adsorption affinity of potassium, as measured by a Gapon-type coefficient in illitic soils, decreases steeply as the exchangeable potassium content increases, the use of the linear EPR-

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PAR relationship has continued, especially in the arid-zones that were traditionally influenced by the «Riverside approach» to soil and water management. Partial justification for the linearity assumption may have been found in the fact that the dominant clay mineral in many arid-zone soils is smectite-montmorillonite, for which potassium has been found to behave similar to sodium and have low affinity throughout the isotherm, when exchanged with divalent cations *(Banin [1968])*.

Adsorption of potassium onto minerals from the illite and mica groups is mechanistically different from that onto minerals from the smectite or kaolinite groups. In illitic clay, potassium ions may bind to planar surface sites, to edge sites, and to interlattice sites. The specific adsorption of the potassium ions on the edge and interlattice sites is due to a combination of electrostatic and crystal stability considerations due to the fitting of K into the hexagonal openings between the base oxygen of the tetrahedral layer *(Bolt et al [1963]; Van Schouwenburg & Schuffelen [1963])*. This gives rise to relatively high preference for potassium over divalent ions which is not predicted from electrostatic considerations. The «wedge zones» in dioctahedral vermiculites were also suggested as having preferential adsorption capacity for potassium *(Dolcater et al [1968]; Carson & Dixon [1972])*. Unlike the above minerals, ion exchange of potassium on montmorillonite is similar to that of other monovalent ions and is primarily controlled by the electrostatic parameters of valency ratio and ionic size *(Banin [1968])*. The exchange sites are on the planar surfaces and on the edges of the mineral layers. The edge sites of the montmorillonite layers are not specifically favored for potassium, thus their bonding energy for potassium is not particularly high. The slight changes in the adsorption preference of K *vs.* Ca throughout the isotherm were found by *Banin [1968]* as connected to changes in the packing and arrangement of the clay tactoids during the saturation of the mineral with potassium. It should be pointed out, however, that throughout the isotherm, calcium was preferred comparative to potassium and only relative changes in the degree of preference of the K ions were observed.

In many studies, exchange isotherms of K-Ca on various minerals or soil clay fractions, are presented. Since the exchange sites have different bonding energies for potassium, it was found that Gapon constants (K_G^K) would not have the same value along the isotherm, especially in minerals from the illitic group. In pure illite K_G^K values were found to decrease during the saturation of the mineral with potassium from an extreme value > 2000 to a final value of about 2 *(Schwertmann [1962]; Bolt et al [1963])*. In most of the studies with montmorillonite minerals, K_G^K values $((1/mol)^{1/2})$ were found to vary between 1 and 4 *(Dolcater et al [1968]; Schuffelen [1972]; Knibbe and Thomas [1972])*. Somewhat higher K_G^K values were presented in other works: *Krishnamoorthy and Overstreet [1950]* 4.00-4.76; *Banin [1968]* 4.12; *Carson and Dixon [1972]* 3.03-11.11; *Jensen [1973]* 3.57-5.16. The high values, generally observed at low levels of adsorbed potassium, were attributed to residual impurities of illite. In kaolinite, a decrease in the values of K_G^K was also found during its saturation with potassium *(Schwertmann [1962]; Jensen [1963])*.

Selectivity for potassium as measured by the Gapon constant in soils is influenced by the assemblage of soil minerals. In soil clay fractions which contain mainly illite, K_G^K varied between 40 and 2, generally decreasing with increasing saturation with potassium *(Bolt [1963]; Van Schouwenburg & Schuffelen [1963]; Rich [1964]; Carson and Dixon [1972]; Knibbe & Thomas [1972]; Schuffelen [1972])*. In montmorillonite-rich clay fractions which contain also illite, vermiculite or kaolinite, relatively high values of K_G^K were found at low exchangeable potassium percentages (EPP): 5.90 at EPP = 10% *(Deist & Talibudeen [1976])*, and 8.11 at EPP = 2% *(Kishk & El-Sheemy [1974])*. Again, the assumption was that the illite or kaolinite minerals contributed to the increase of K_G^K values in spite of their being secondary minerals in the clay fraction.

We have found in a detailed study that the EPR/PAR relationship in several greenhouse soils from Israel receiving high applications of potassium fertilizers is composed of two linear segments. High preference for potassium, under realistic conditions of multi-ionic exchange in soils at low adsorbed potassium percentages, contributes to what may be defined as *Preferential Adsorption Capacity for Potassium (PACP)* which is linearly correlated to the illite content in the soil. These relations are of importance because former research *(Chen et al [1983])* has suggested that high EPR values may be deleterious to the physical properties of soils in greenhouses cultivated for long periods of time.

Reevaluation of published data shows that such a preferential capacity, amounting to 3 to 10 percent of the cation exchange capacity of the soil, is characteristic in many arid-zone soils, and should be considered when potassium state and availability is evaluated.

2. Materials and methods

Greenhouse soils

Soils from eight greenhouse sites from the Lachish and Rehovot districts in Israel were studied. Greenhouse and control samples were taken from inside the greenhouses and from a virgin soil outside the greenhouses, respectively. In the case of transported greenhouse soils, the control samples were taken from the site of original sampling. Cation Exchange Capacity (CEC) and adsorbed cation composition were determined after displacement with 1N sodium acetate and 1N ammonium acetate, respectively *(U.S. Salinity Laboratory Staff [1954])*. The potassium adsorption ratio (PAR) was calculated as:

$$\mathrm{PAR} = \frac{c_K}{\sqrt{\frac{c_{Ca} + c_{Mg}}{2}}} \tag{1}$$

where C is the concentration in solution (me/1), of the respective ions.

Gapon's constant for potassium exchange in the soil (K_G^K) was calculated as:

$$K_G^K = \frac{\mathrm{EPR}}{\mathrm{PAR}} \tag{2}$$

where EPR is the exchangeable potassium ratio ($\mathrm{EPR} = q_K/(q_{Ca} + q_{Mg})$) and where q is the concentration of the exchangeable cation (me/100 g soil).

The dimensions of K_G^K in eq. 2 are $(1/\text{mmol})^{1/2}$, and it is converted to $(1/\text{mol})^{1/2}$ by multiplication by $\sqrt{1000} = 31.6$.

Potassium-calcium exchange isotherms

Exchange isotherms of potassium with calcium were determined for five soils, varying in texture and representing the common soils in greenhouses throughout Israel.

The upper horizon (0-25 cm) of each soil was sampled. The samples were air-dried, crushed and sieved through a 2 mm sieve. Chemical and physical properties of the soils were determined as follows: cation exchange capacity and adsorbed cation species as described with the greenhouse soils; particle size analysis by the hydrometer method *(Van der Wolt [1966]);* organic matter by a wet-combustion method *(Black et al [1965]);* $CaCO_3$ content by the calcimeter method *(Black et al [1965]).* The mineralogical composition of the clay fraction was determined using methods described by *Gal et al [1974].*

Exchange isotherms were determined using a double-analysis technique after equilibrating the soil in suspension with a solution at a given K/Ca ratio and a constant total electrolyte concentration *(Deist & Talibudeen [1967]; Tucker [1967]; Banin [1968]; Knibbe and Thomas [1972]; Carson and Dixon [1972]; Schalscha et al [1975]).* Changes were measured in the soluble phase every three days when the external solution was replaced, and in the adsorbed phase after equilibrium was reached. Using this technique, it was possible to measure exchange reactions at a constant total electrolyte concentration and to characterize the complete ($\overline{X}_K$ = 0-1.0) range of the equivalent ionic fraction of exchangeable potassium.

The equilibration dialysis was performed as follows: A stock suspension at a concentration of 2% soil in distilled water was prepared for each soil. The suspension was shaken 10 hrs and then aliquots of 150 ml were taken into dialysis bags, and immersed in an excess of the appropriate solution at 27° C. Nine equilibrating solutions were used, in 4 replicates each. The total electrolyte concentration was constant at 20 me/1. The PAR values were calculated so that a desirable EPP value can be achieved according to the following equation *(U.S. Salinity Laboratory Staff [1954]).*

$$\text{PAR} = \frac{1.036\ \text{EPP} - 3.6}{0.1051\ (100 - \text{EPP})} \tag{3}$$

The concentrations of the salts were calculated from the following equation:

$$c_K + c_{Ca} = 20 \tag{4}$$

$$\text{PAR} = \frac{c_K}{\sqrt{\frac{c_{Ca}}{2}}} \tag{5}$$

Desired EPP, calculated PAR and composition of the solutions used are listed in Table 1. The dialysis bags were shaken gently and the equilibrating solutions were renewed every 2-3 days. After 15 days, when changes in ionic concentration in solution were minimal, the soil suspensions were centrifuged. Potassium and calcium concentrations were determined in the supernatant solution and, after displacement, in the soil sediment.

Table 1. Desired EPP, calculated PAR and K^+ and Ca^{2+} concentrations in the equilibrating solutions.

Solution No.	Desired EPP %	Calculated PAR	K^+ concentration (me/1)	Ca^{2+} concentration (me/1)
1	5	0.16	0.50	19.50
2	10	0.72	2.14	17.86
3	15	1.34	3.82	16.18
4	20	2.04	5.50	14.50
5	30	3.74	8.85	11.15
6	40	6.00	12.00	8.00
7	60	13.93	17.02	2.98
8	80	37.72	19.47	0.53
9	100	∞	20.00	0.00

From the analytical data, the equivalent ionic fraction in solution, X, and adsorbed in the soil, X, and the selectivity coefficient, K^K_{Ca}, were calculated by using the following equations:

$$X_K = c_K/(c_{Ca} + c_K); \; X_{Ca} = c_{Ca}/(c_{Ca} + c_K) \tag{6}$$

$$\overline{X}_K = q_K/(q_{Ca} + q_K); \; \overline{X}_{Ca} = q_{Ca}/(q_{Ca} + q_K) \tag{7}$$

and

$$K^K_{Ca} = \frac{\overline{X}_K^{\,2} X_{Ca}}{\overline{X}_{Ca} X_K^{\,2}} \tag{8}$$

3. Results and discussion

The greenhouse soils

It was generally found that values of PAR, EPP and ESP + EPP (data not shown) were higher in the greenhouse samples than in the control samples from the same site. However, the Gapon constants found in the greenhouse samples were lower than in control samples. The conclusion of the survey was that intensive fertilization, in both local and transported greenhouse soils, had led to enrichment of exchangeable potassium. Particularly large enrichment percentages of exchangeable potassium were recorded, in greenhouse samples relative to control samples, in sandy soils.

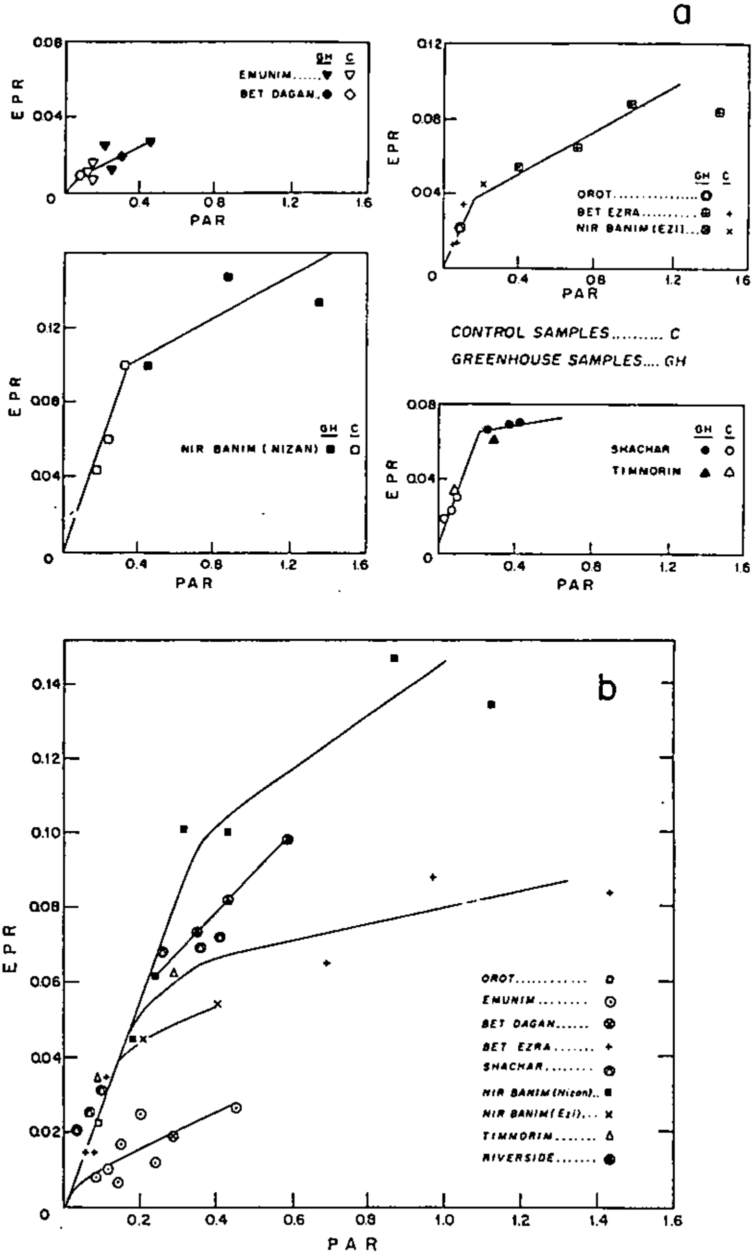

Fig. 1. EPR-PAR function for several greenhouse soils from Israel: (a) Detailed plots; (b) Combined plot, including data for 59 soils from the Western U.S.A. («Riverside»; from U.S. Salinity Laboratory Staff [1954]).

Plots of EPR vs. PAR for the greenhouse soils are given in Figure 1. Note that the slopes of the lines are the K_G^K values calculated according to Equation 2. Generally the curves can be divided into two parts. The first part (range I) is characterized by a steeper slope, which is rather similar for all the soils. This range of high K_G^K, represents the *Preferential Adsorption Capacity for Potassium (PACP)* of the exchange complex. In the second part (range II) the slope is not as steep as in the first range and it varies between soils. We suggest that the transition from the first to the second range indicates the saturation of the PACP and the beginning of an adsorption process that is controlled mostly by electrostatic-double layer forces. The PACP comprises the edges and interlattice sites that have high affinity towards potassium, and it may depend on the illite content in the soil. This dependence will be discussed later.

PACP values for the soils were obtained from the intercept on the EPR axis ($=EPR_s$) of the linear regression line fitted to the points in range II, by the equation

$$\text{PACP}\ (\%) = \frac{\text{EPR}_s \cdot 100}{1 + \text{EPR}_s} \qquad (9)$$

PACP is given in % of the sum ($q_K + q_{Ca} + q_{Mg}$). It was converted to meq/100 g by

$$\text{PACP} = \frac{\text{PACP}\ (\%) \cdot \text{CEC}}{100} \qquad (10)$$

neglecting the small contribution of exchangeable sodium to the CEC. PACP values, and the Gapon constants in range I and II are presented in Table 2.

In all the greenhouse soils studied here, PACP was found equal to or greater than the EPR values of the control samples (Figure 1a). Furthermore, exchangeable potassium in all the greenhouse soils fell in the second range. The data for all the soils could be fitted with one line, giving a high Gapon constant of 8.74 $(1/\text{mol})^{1/2}$ for range I (Figure 1b and Table 2). Although in range II the various soils had different $^{II}K_G^K$ values (Table 2), all these values were lower than $^{I}K_G^K$ and were in the range reported for mono-divalent ion-exchange reactions on clays.

Reassessment of the data presented by the *U.S. Salinity Laboratory [1954]* clearly shows that the EPR/PAR relationship of 59 soils of the arid zones of the U.S.A. has two straight-line segments. From the intercept of the line fitted by the Riverside laboratory to the data, an average PACP (%) of 3.5% is calculated (Eq. 9 and Table 5). The accepted and widely used relationship EPR = 0.1051 PAR + 0.036, will not hold for exchangeable potassium percentage below 3 to 4% which is a fairly common range in arid zone soils. Interestingly, the $^{I}K_G^K$ estimated from the slope of the first segment of the Riverside plot is in the range of 8-9 $(1/\text{mol})^{1/2}$, similar to the values obtained in our detailed survey.

Table 2. Potassium exchange constants (Gapon type) and preferential adsorption capacity for K^+ (PACP) in the greenhouse soils.

Soil location	Range I				Range II				Preferential adsorption capacity for potassium (PACP)	
	n	Regression equation	r	$^{I}K_G$ $(1/mol)^{1/2}$	n	Regression equation	r	$^{II}K_G$ $(1/mol)^{1/2}$	% of CEC	me/100 g
Bet-Dagan		–			8	EPR = 0.046PAR+0.006	0.709	1.47	0.6	0.024
Emunim								1.47	0.6	0.024
Orot	6	EPR = 0.222PAR+0.002	0.932	7.00	6	EPR = 0.055PAR+0.031	0.985	1.75	3.0	0.190
Bet-Ezra								1.75	3.0	0.180
Nir Banim (1)								1.75	3.0	1.260
Nir-Banim (2)	5	EPR = 0.297PAR−0.004	0.985	9.39	4	EPR = 0.057PAR+0.080	0.798	1.80	7.4	2.440
Shahar	5	EPR = 0.284PAR+0.005	0.931	8.99	4	EPR = 0.024PAR+0.061	0.891	0.77	5.7	1.530
Timmorim								0.77	5.7	1.530
All soils of the present study	16	EPR = 0.276PAR−0.001	0.950	8.74		–				

n = number of observations included in calculation of regression equation.
r = regression coefficient.

Potassium-calcium exchange isotherms

To study in more detail the potassium exchange behavior of soils customarily used in greenhouses in Israel, five soils were selected. Some chemical and physical properties of the soils and the mineralogical composition of their clay fractions are presented in Tables 3 and 4, respectively. The divalent ions, calcium and magnesium, comprise the major fraction of the CEC of the natural soils, ranging from 93% of the CEC in the light clay soil (Timmorim) to 99% in the heavy clay (Bet-Netofa). The dominant clay mineral is montmorillonite accompanied by kaolinite and illite.

Table 3. Some characteristics of soil samples.

Location	Soil texture class	Cation exchange capacity (me/100g)	Exchangeable cations (me/100 g)				Exchangeable potassium percentage (%)	$CaCO_3$ (%)	Particle-size analysis (%)			Organic matter (%)
			K	Na	Mg	Ca			clay	silt	sand	
Rehovot	Loamy sand	10.9	0.2	0.2	1.5	9.0	2.2	2.6	13.8	1.3	85.0	0.7
Givat Brener	Light clay	34.0	0.8	0.5	9.1	23.7	2.2	7.6	40.0	12.5	47.5	1.4
Timmorim	Light clay	34.5	2.0	0.5	9.4	22.6	5.8	15.8	40.0	16.2	43.8	2.1
Yagur	Heavy clay	53.7	0.9	0.7	15.4	36.7	1.6	12.5	48.7	25.0	26.3	3.7
Bet-Netofa	Heavy clay	62.5	0.6	0.6	5.5	56.6	1.0	5.0	51.2	21.3	27.5	3.7

Table 4. Mineralogical composition of the clay fraction.

Soil location	Illite (%)	Montmorillonite (%)	Kaolinite (%)	Free oxides (%)					$CaCO_3$ (%)
				SiO_2	Fe_2O_3	Al_2O_3	MnO_2	Total	
Rehovot	10	56	26	1.9	4.2	0.4	0.03	6.5	1.5
Givat-Brener	9	56	21	3.5	1.6	0.3	0.02	5.4	7.7
Timmorim	16	47	19	2.6	2.2	0.3	0.04	5.1	13.5
Yagur	11	58	17	2.7	2.3	0.4	0.02	5.4	9.0
Bet-Netofa	8	57	22	2.5	6.3	0.6	0.06	9.4	2.7

Detailed exchange isotherms for K-Ca exchange are presented in Figure 2, and the variation of the selectivity coefficient (K^K_{Ca}) as a function of $\overline{X}_K$ is shown in Figure 3. In all the soils, the selectivity toward potassium decreased with an increase of $\overline{X}_K$ and in all of them selectivity reversal *(i.e.* change from $K^K_{Ca} > 1$ to $K^K_{Ca} < 1$) was

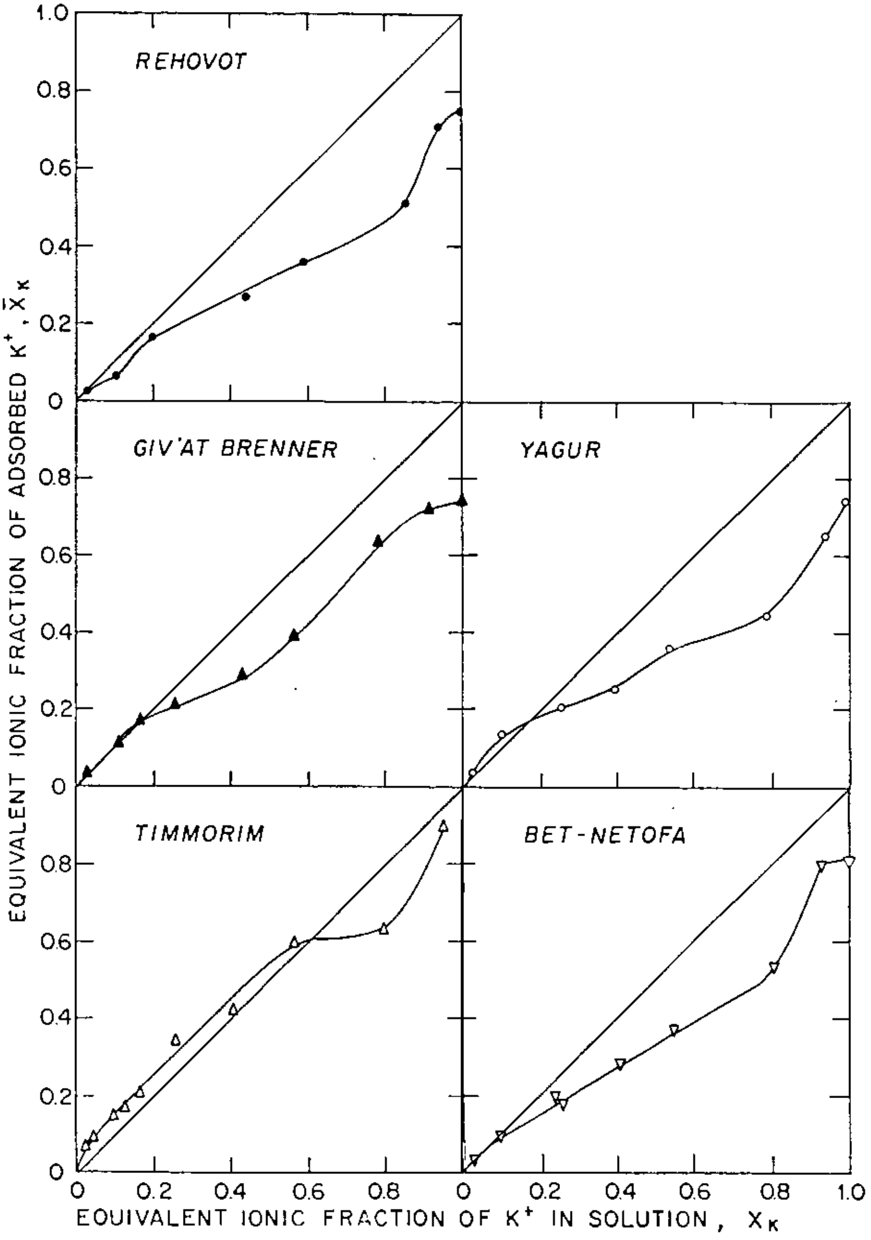

Fig. 2. Potassium-calcium exchange isotherms of five soils at 27° C and constant total electrolyte concentration of 20 me/L.

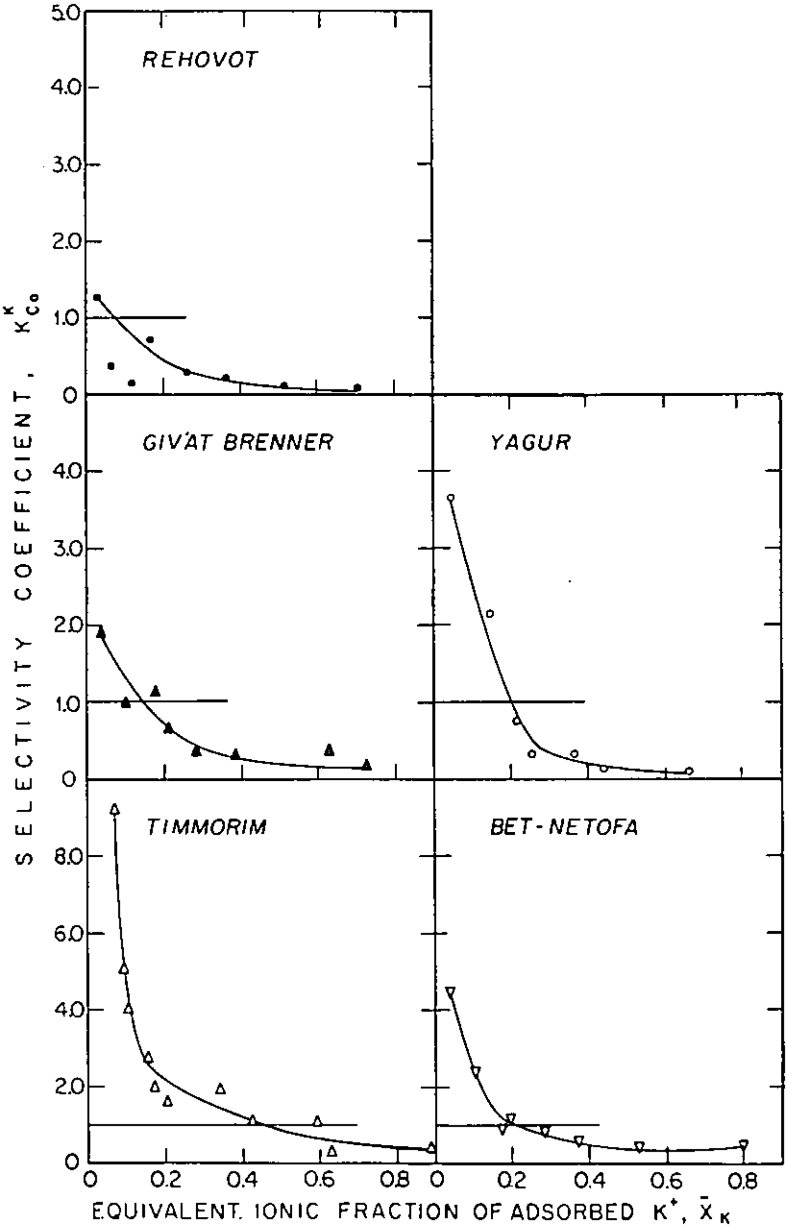

Fig. 3. Dependence of selectivity coefficient, in potassium-calcium exchange in five soils, on the equivalent ionic fractions of adsorbed K^+ (from isotherms shown in Figure 2).

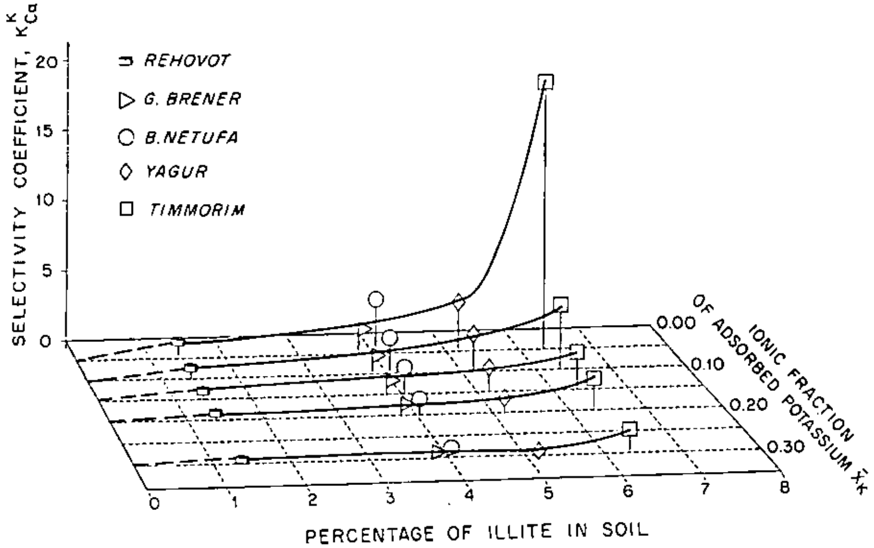

Fig. 4. The variation fo the selectivity coefficient in potassium-calcium exchange of five soils, with the illite percentage in the soil, at various equivalent ionic fraction of adsorbed potassium.

observed. The reversal occurred at $\overline{X}_K < 0.1$-0.2 except for one soil (Timmorim), where it took place at $\overline{X}_K = 0.4$. The selectivity coefficient was strongly dependent on the illite content of the clay fraction (Figure 4), especially at low $\overline{X}_K$, indicating that at this range, potassium is mostly adsorbed on illite sites, probably the edge-sites, having high preference for this cation over the diavalent calcium ion.

From the data obtained in the isotherm studies the EPR/PAR function could be obtained. It is presented in Figure 5 along with similar data for soils and soil clays obtained from the literature. In all cases a break in the curve is observed at EPR of 0.15 or less. Again, it is found that the first part of the curves for field soils can be unified into one curve, which is similar to the first part of the curves for greenhouse soils (Figure 1b). These findings show that the energy of adsorption at low levels of exchangeable potassium is relatively high and similar in all the soils that were studied. At higher exchangeable potassium contents (range II, Table 5), K^K_G values were lower and fell in the range of 2.4-3.8 $(1/\text{mol})^{1/2}$, as typical for mono-divalent exchange reactions on smectite-montmorillonite minerals. PACP values for the various soils were calculated from Figure 5 as explained above and are given in Table 5.

The dependence of PACP on the percentage of illite in the soils is presented in Figure 6 using data from the present work and from *Carson & Dixon [1972]*. The illite content of the greenhouse soils was estimated from the clay content in the soils and the percentage of illite in clay fractions of similar soils *(Gal et al [1974])*. A positive and fairly high correlation was found for 14 soils (Figure 6). This indicates that there is a connection between the preference for potassium and the illite content of the soil. The average contribution of illite to the PACP is 0.75 me/g illite, as estimated from the slope of the regression line in Figure 6 (0.75 meq/100 g soil per 1% of illite). This is a relatively high contribution, which indicates that the potassium exchanged may include not only that which is adsorbed on the planar surfaces, but from edge and interlattice sites as well.

Linear correlations of PACP *vs.* percentage of illite, or PACP *vs.* percentage of illite+mica, for the five soils that were tested for their K-Ca adsorption isotherms were calculated. The equations were as follows:

$$\text{PACP} = 1.022 \times \%\ \text{illite} - 0.33 \qquad (r = 0.892);$$

and

$$\text{PACP} = 0.612 \times \%\ (\text{illite+mica}) - 0.08 \qquad (r = 0.777).$$

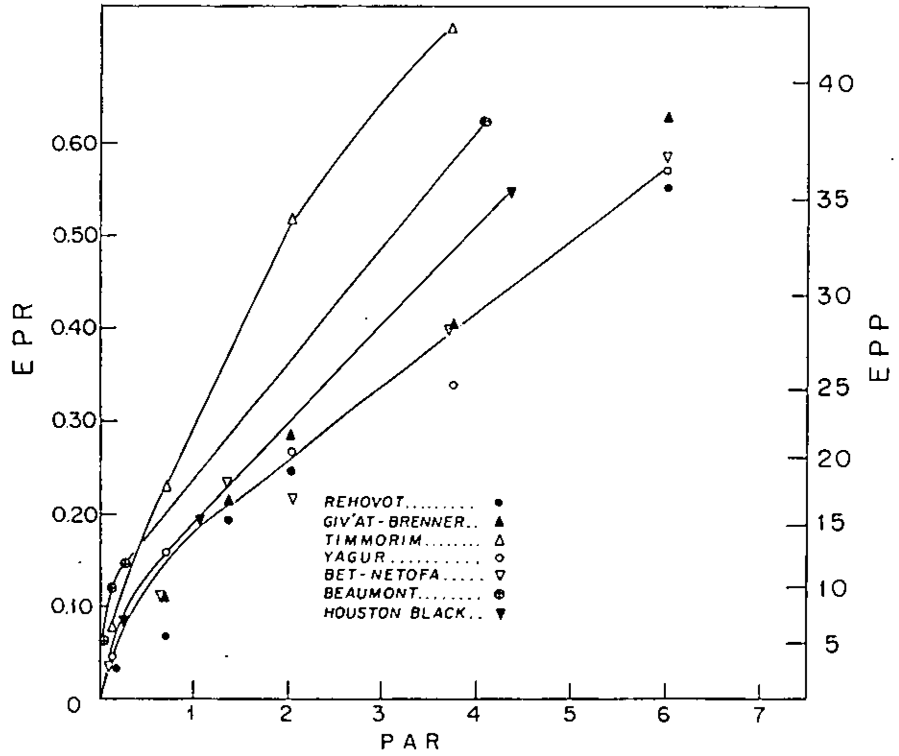

Fig. 5. EPR-PAR function for several soils, from the present work and reported in the literature.

Table 5. K_G^K and PAPC in several soils

Soil location	Range II n*	 Regression equation	 r**	 ${}^{II}K_G^K$*** $(1/\text{mol})^{1/2}$	PACP %	 me/100g	Reference and remarks
Rehovot	4	EPR = 0.077PAR+0.088	0.999	2.44	8.1	0.88	This study;
Givat Brenner	5	EPR = 0.088PAR+0.092	0.997	2.78	8.4	2.85	(soils)
Timmorim	4	EPR = 0.120PAR+0.220	0.975	3.80	18.0	6.21	
Yagur	4	EPR = 0.079PAR+0.085	0.972	2.48	7.8	4.18	
Bet Netofa	5	EPR = 0.081PAR+0.094	0.983	2.55	8.6	5.38	
Beaumont	4	EPR = 0.120PAR+0.110	0.945	3.80	9.9	3.37	*Carson & Dixon [1972];*
Houston Black	4	EPR = 0.105PAR+0.080	0.995	3.30	7.4	3.33	(Clay fraction)
Western U.S.A.	59	EPR = 0.105PAR+0.036	0.972	3.30	3.5	–	*U.S. Salinity Lab. Staff [1954] (soils)*

*n = number of points in regression.
**r = correlation coefficient.
***${}^{II}K_G^K$ = calculated from the slope of the second part of the curves in Fig. 5.

A comparison of the slopes in the two equations shows that the contribution of mica to the PACP is much lower than that of the illite indicating, as expected from literature data, limited exchangeability of crystalline potassium in mica and preferential exchange/adsorption of potassium on illite.

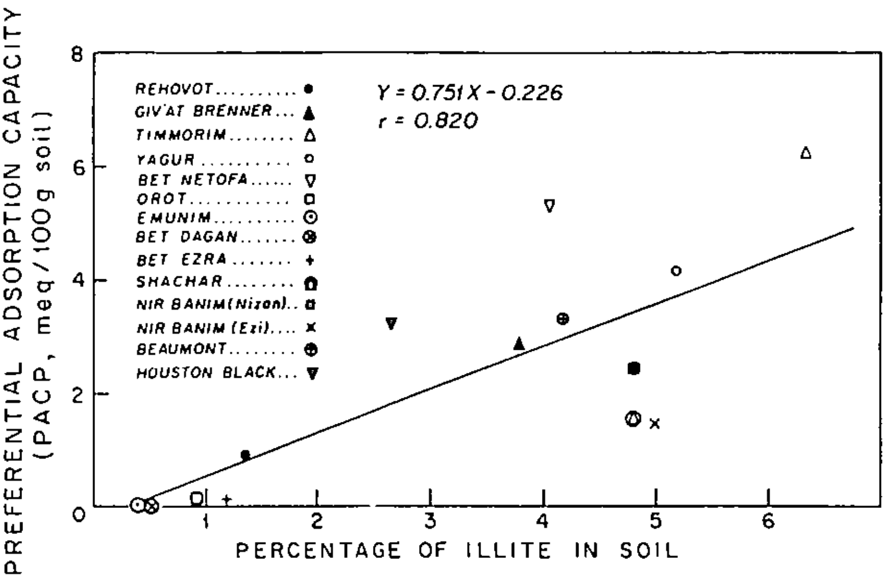

Fig. 6. Dependence of the preferential adsorption capacity for potassium (PACP) values in soils on the illite content of the soil.

4. Conclusions

In many soils from the arid zones, the initial part of the EPR/PAR function shows an abrupt change in slope dividing it into two ranges. From the intercept of the straight line fitted to the data points in the second range, the preferential adsorption capacity for potassium (PACP) may be quantitatively estimated. It was found to correlate well with the illite content of soils. The adsorption behavior of potassium in soils, its availability to plants and its participation in other soil processes will be profoundly affected by the transition from preferential to less preferential adsorption.

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The Surface Mobility of Exchangeable Cations in Soil.

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Summary

It is well established that in pure clays exchangeable cations are mobile and make an important contribution to the total diffusive flux through clay pastes. On the other hand in soils the evidence has been that diffusion occurs very largely through the soil solution; the exchangeable cations contributing little. Using an accurate pulse labelling method for determining self-diffusion coefficients, we have recently obtained evidence in a variety of soils that exchangeable cations may have considerable mobility. This means that estimates of the diffusion coefficients of these cations in such soils need to be increased.

The understanding we now have of the movement of nutrients towards roots, away from fertilizers, and down a profile, has emphasized the need for us to know their diffusion coefficients. Unfortunately, the diffusion coefficient of an ion, such as potassium, in a soil varies greatly with the nature of the exchange complex, its degree of saturation by the cation, the cation concentration in the soil solution, and the water content of the soil. Further, in passing from the bulk of the soil to the surface of the root, for example, the concentration of the potassium ion in the soil solution can change greatly, and correspondingly its diffusion coefficient will change. To attempt to determine the diffusion coefficient experimentally over this wide range of conditions for a given soil is a considerable and skilled task. It is therefore essential if diffusion coefficients are to be used in dynamic nutrient models that we have a ready means of predicting their values from easily measured soil properties.

The diffusion coefficient is defined by the equation

$$F = -D \frac{dC}{dx} \qquad (1)$$

where F is the solute flux, x is distance in the direction of diffusion and C is the concentration of diffusible cation in the whole soil. The total flux can be conveniently

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divided into two components. One depends only on the movement of ions through the soil solution

$$F_L = -D_L \theta f_L \frac{dC_L}{dx} \tag{2}$$

where

D_L is the diffusion coefficient of the ion in free solution
θ is the soil moisture content
f_L is an impendance factor that accounts for the tortuosity of the diffusion pathway, and the influence of the solid on the viscosity of the solution near changed surfaces
C_L is the concentration of the ion in the soil solution.

The other component, F_S, involves the mobility of the exchangeable ions on the solid surfaces in the direction of diffusion.
It is convenient to define a surface phase impedance factor by the equation

$$F_S = -D_L f_S \frac{\varrho dC_S}{dx} \tag{3}$$

where ϱ is the dry density of the soil (wt of solid/unit vol whole soil)
C_S is the exchangeable cation content (equiv. cation/unit wt of solid)
f_S is equivalent to f_L, it not only depends on the geometric tortuosity of the sorbed cation, but also contains the effect of the solid on the mobility of the exchangeable cations. We know that movement of exchangeable ions solely via a surface phase pathway is slight since diffusion of ions through dry soil is very slow. Hence f_S also allows for the cooperation between liquid and solid pathways. It is likely that within a given system there will be a range of mobilities of sorbed cations, depending on the nature of their bonding with the surface. f_S may thus be thought of as a measure of the average mobility of exchangeable cations, relative to their mobility in free solution.

$$\text{Now } F = F_L + F_S \tag{4}$$

Substituting equations (1), (2), (3), in (4)

$$D \frac{dC}{dx} = D_L \theta f_L \frac{dC_L}{dx} + D_L f_S \frac{\varrho dC_S}{dx} \tag{5}$$

$$D = D_L \theta f_L \frac{dC_L}{dC} + D_L \varrho f_S \frac{dC_S}{dC}$$

The main purpose of this paper is to discuss the component f_S.

Determination of f_S

f_L is readily measured by determining the diffusion coefficient of a non-absorbed ion such as Cl^- in the soil. This makes the assumption that the liquid pathway for Cl^- and cations are the same. Since the term $\frac{dC_L}{dC}$ is readily determined from the cation exchange isotherm the term $D_L\ \theta\ f_L \frac{dC_L}{dC}$ can be calculated.

If D is determined by experiment the value of f_S can be calculated.

Earlier work, reviewed by *Nye [1979]*, led to the conclusion that the mobility of exchangeable cations in soils was only a small fraction of their mobility in free solution, and hence to the view that the diffusion coefficient could conveniently be estimated from the first term in equation (5)

$$D = D_L\ \theta\ f_L \frac{dC_L}{dC} \qquad (6)$$

An example of the experimental evidence for potassium is shown in Figure 1. *(Vaidyanathan, Drew & Nye [1968])*. When values of D measured experimentally are plotted against values of $\frac{dC_L}{dC}$,

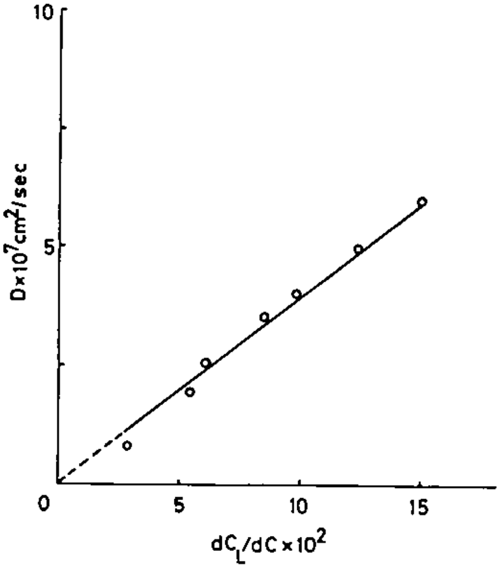

Fig. 1. D for potassium in Coral Rag clay soil related to the slope of the potassium sorption isotherm.

obtained from the slope of the sorption isotherm, a straight line is obtained which, when extrapolated, passes very close to the origin.

Equation (6) has been successfully used to estimate K uptake from soil by whole plants *(Claassen & Barber [1976])* though the estimates are not very sensitive to the exact values of the potassium diffusion coefficients.

The assumption that the surface mobility of sorbed cations is negligible is also commonly made in setting up the mass balance equation in convection-dispersion models of solute leaching. The apparent slight mobility of exchangeable cations in soil was unexpected, because many experiments with pure clay pastes and suspensions have shown that exchangeable cations have considerable mobility in these conditions. Table 2 summarizes this evidence. Since the proportion of soil cations in the surface phase is usually greater than in the liquid phase, the surface contribution to the total flux might often be expected to outweigh the liquid phase contribution.

Very recently the self-diffusion coefficients of Na and Ca have been measured over a wide range of soil types *(Staunton & Nye [1987])*. These measurements have shown that the ions in the surface phase make a very significant contribution to the overall diffusive flux. Table 1 shows the clay mineralogy of the soils studied, and the values of f_S (Na) and f_S (Ca) and f_L which were determined. f_S for sodium was between 1/5 and 1/2 of the liquid phase impendance factor f_L; f_S for calcium was between 1/9 and 1/20 of f_L. These values are in general agreement with the mobilities of exchangeable sodium and calcium determined in experiments with pure clay systems. The values of f_S were not obviously related to the mineralogy of the clay fraction of the soil, the moisture content, or the pH.

Table 2 shows the proportion of the mobile sodium and calcium ions that where in the sorbed form, the remainder being in the soil solution. It also shows the relative contribution of the sorbed ions to the total flux, F_S/F. Although the mobility of the sorbed ions is considerably less than it is in the soil solution, because most of the ions are sorbed their contribution to the total diffusive flux is greater than that contributed by the flux through the liquid phase alone. This study did not include potassium ions, because a suitable isotope was lacking. However the studies with pure clays, summarized in Table 1, show the mobility of the sorbed potassium ions usually lies between that of sodium and calcium.

This work leads to the conclusion that cation diffusion coefficients calculated

from the simple formula $D = D_L \, \theta \, f_L \, \frac{dC_L}{dC}$

must be treated as minimum values. The true values may be several times greater. Unfortunately we have not yet been able to relate the mobility of the sorbed ions to any soil property, and for the present can only advise that calculated values of the diffusion coefficients of the alkali and alkaline earth cations in soils should be used cautiously.

Table 1 Mobility of ions in salt-free clay gels relative to solution at 25 °C

Method	Clay concentration	Ion							
		Li	Na	K	Rb	Cs	Ca	Sr	Ba
					Montmorillonites				
Conduction	0.1-10 g clay/100 ml soln		0.37			0.19	0.13		
Diffusion	15-28%		0.27			0.19	0.22		
Diffusion	4-6 g clay/100 g gel		0.37						
Diffusion	4.9-10.6 g clay/100 g gel						0.08		
Diffusion	3 g clay/100 ml soln		0.25	0.23		0.06	0.08	0.09	0.04
Conduction	60 g clay/100 g gel		0.13	0.06	0.02	0.01	0.08		
					Kaolinites				
Diffusion	56 g clay/100 g gel		0.28						
Conduction	70 g clay/100 g gel	0.19	0.18	0.08		0.03			
Conduction	31-35 g clay/100 ml gel		0.14					0.05	
Self-diffusion coefficients in water at infinite dilution ($m^2/sec \times 10^9$)		1.04	1.35	1.98	2.07	2.11	0.78	0.78	0.84

Table 2 Clay mineralogy and the surface phase impedance factors

Soil	Clay mineralogy	f_S (Na)	f_S (Ca)	θ	f_L
Banbury	Micaceous, very ferruginous	0.044	0.011	0.28	0.23
Batcombe	Complex vermiculite components	0.105	0.016	0.29	0.24
Denchworth	Montmorillonite	0.095	0.026	0.39	0.25
Tedburn	Micaceous	0.129	0.020	0.46	0.24
Teigngrace	Kaolinite	0.189	0.041	0.38	0.36

Table 3 The proportion of sorbed sodium and calcium ions, and their relative contribution to the total flux.

	Sodium		*Calcium*	
	$\varrho S/C$	F_S/F	$\varrho S/C$	F_S/F
Banbury	0.911	0.66	0.995	0.90
Batcombe	0.690	0.49	0.965	0.64
Denchworth	0.850	0.68	0.993	0.94
Tedburn	0.836	0.73	0.996	0.96
Teigngrace	0.758	0.66	0.989	0.91

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Critical Evaluation of Soil Testing Methods for K.

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Summary

Various methods and approaches for determining available soil potassium are discussed and compared. It is concluded that a theoretical model describing K behaviour in soil is not yet applicable in practical soil testing, and that extraction methods supplying information on exchangeable K are useful in soil testing only when the values obtained are corrected with the use of soil parameters affecting exchange reactions in soils.

A 0.01 *M* $CaCl_2$ extraction procedure was tentatively compared with more established extraction procedures (0.1 *M* HCl and Electro-Ultrafiltration). Since different fractions of soil potassium are extracted with the three methods, different correction parameters are needed for estimating available K. With the use of such correction factors, all three methods appear equally useful. Preference for anyone of them can therefore be based on economic factors, such as ease and speed of operation and costs involved.

1. Introduction

A wide range of soil extractants has been used, and is still being used, for the assessment of that portion of soil K which is «available» to plants. Probably most widespread is the use of neutral 1 *M* NH_4Ac solution. Other extractants frequently used are Bray solution, $NaNO_3$, NH_4NO_3, $CaCl_2$, $NaHCO_3$, buffered or unbuffered NH_4-oxalate, Ca or NH_4-lactate, double acid (HCl-H_2SO_4), Morgan's extract (NaOAc-HOAc), dilute H_2SO_4 (Truog), 0.1 *M* HCl + 0.2 *M* oxalic acid, NaTPB (Na-tetraphenylborate) in various concentrations, hot HNO_3, etc.

Our laboratory organises a world-wide sample exchange programme for plant material. Knowing that several member laboratories are also involved in soil analysis, we have asked by means of a questionnaire which methods are used for the determination of available potassium. The methods reported are listed in Table 1. It is clear that even for the same extracting solution rather different extraction conditions are being used.

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Table 1 Methods for the determination of available potassium in different countries

Country	Solution	Extraction procedure Ratio	Time	other elements
Australia	1*M* Ammonium acetate		30 min.	Na, Mg
Austria A	1 *M* Ammonium acetate		90 min.	Na, Mg, Mn
Austria B	Calcium acetate lactate (CAL)	1:20	120 min.	
Austria C	EUF		0-30, 30-35 min.	NO_3, NH_4, Al, Na, K, Mg, Ca, P
Brasil A	0.05 *N* HCl + 0.025 N H_2SO_4 (Mehlich)	1:10	5 min.	P
Brasil B	Resin extraction	2.5 cm^3 soil + 25 ml H_2O + 2.5 cm^3 cation + anion resin	16 hours	P, Ca, Mg
Brasil C	0.5 *M* H_2SO_4		15 min.	
Burkina Faso	HCl + oxalic acid		60 min.	Na
China (Taiwan)	1 *M* Ammonium acetate		30 min.	Mg
Finland	0.5 M CH_3COOH + 0.05 *M* CH_3COONH_4 (pH = 4.65)	1:10 (V/V)	60 min.	Mg
Germany A (FRG)	Double lactate or Calcium ammonium lactate			
Germany B (FRG)	EUF		0-30, 30-35 min.	NO_3, NH_4, Al, Na, K, Mg, Ca, P
Great Britain A	1 *M* NH_4NO_3	1:10	30 min.	Mg
Great Britain B	1 *M* Ammonium acetate		150 min.	
Great Britain C	1 *M* Ammonium acetate	1:10	30 min.	Mg
Honduras	1 *M* Ammonium acetate pH 4.8-7.0		10 min. pH = 4.8 30 min pH = 7	Na, Ca, Mg
Hungary	Ammonium lactate/acetic acid (pH = 3.75)	1:20	120 min.	
Ireland	Sodium acetate/acetic acid (Morgan's solution)		30 min.	P, Mg
India	1 *M* Ammonium acetate		5 min.	
Indonesia	1 *M* Ammonium acetate	1:20	30 min. (perc.)	
Jamaica	1 *M* Ammonium acetate		30 min.	Na, Mg
Jordan	1 *M* Ammonium acetate	1:5	30 min.	
Kenya	1 *N* HCl + 0.025 *N* H_2SO_4	1:5	1 hour 10 min.	Na, Mg, Mn

Table 1 Continued

Country	Solution	Extraction procedure		
		Ratio	Time	other elements
Malaysia A	1 *M* Ammonium acetate		5-6 hours (perc.)	Mg, Na, Mn
Malaysia B	1 *M* Ammonium acetate		120 min.	Na, Mg
Mauritius	1 *M* HNO_3	1:10	10 min. boiling	
Mexico	1 *M* Ammonium acetate	1:5	30 min.	
Netherlands	0.1 *M* HCl + 0.2 *M* oxalic acid	1:10	120 min.	Na
New Zealand A	1 *M* Ammonium acetate		2 min.	Na, Mg
New Zealand	1 *M* Ammonium acetate		30 min.	Na, Mg, Mn
New Zealand C	1 *M* Ammonium acetate		1 drop/10 sec.	Na, Mg
Pakistan A	1 *M* Ammonium acetate		30 min.	Na
Pakistan	1 *M* Ammonium acetate		60 min.	Na
Papua New Guinea A	1 *M* Ammonium acetate	1:10	about 30 min. leaching	Na, Mg, Mn
Papua New Guinea B	1 *M* Ammonium acetate		leaching over-night	
Peru	1 *M* Ammonium acetate	1:2.5	30 min.	Na
Philippines A	1 *M* Ammonium acetate		leaching	Na, Mg
Philippines B	1 *M* Ammonium acetate		5 min.	Na, Mg
Portugal	Ammonium lactate/acetic acid (pH = 3.75)	1:20	120 min.	
South Africa A	1 *M* Ammonium acetate	1:10	30 min.	Na, Mg, Ca
South Africa B	0.5 *M* Ammonium acetate		30 min.	
Spain	1 *M* Ammonium acetate		60 min.	Na, Mg
Surinam	3% acetic acid (pH = 2.6)		30 min. night over	Na, Mg
Sri Lanka	1 *M* Ammonium acetate		30 min.	Na, Mg
Swaziland	1 *M* Ammonium acetate	1:10	20 min.	Mg
Sweden	Ammonium lactate/acetic acid (pH = 3.75)	1:20	90 min.	Mg
Virgin Islands	0.25 *N* $NaHCO_3$ + 0.01 *M* EDTA + 0.01 *M* NH_4F	1:10	10 min.	P, Mn

From the different extractants in use it can be inferred that slowly an understanding is developing of the processes involved in the supply of nutrients to plants, in this case K.

It can be observed that a number of extractants are «multipurpose», and that in most cases, both water-soluble and exchangeable forms of potassium are determined. Obviously, mineral acids and complexing agent (s) like NaTPB will also extract more tightly bound forms of potassium, in contrast to neutral electrolyte solutions.

Efforts to correlate the results obtained with those of field experiments were certainly not always rewarding. Contradictory results were often reported and a useful fertilizer recommendation scheme could often be constructed only when a number of correction factors derived form statistical analysis of the data, were introduced.

2. Theoretical considerations

It is nowadays recognized that ion accumulation in plants is related to the activity or concentration of that ion in the soil solution *(Fox [1979]; Pavan et al. [1982]; Mengel [1982])*. For that reason, in soil testing it would be important to devise techniques with which estimates of nutrient concentrations in soil solutions could be obtained. It must, however, be realized that it is technically difficult to collect a representative sample of a soil solution, and that, in case such a sample has been obtained, its chemical composition is not more than a reflection of a momentary situation.

It is known that the activity or concentration of K-ions in the soil solution is sustained by the solid-phase potassium *i.e.* a combination of exchangeable and non-exchangeable K in secondary minerals and K in primary minerals. Furthermore, use could be made in soil testing of the fact that cation exchange phenomena in a soil system can be sufficiently described by Gapon's equation *(Gapon [1933])*. In case all complementary adsorbed cations are divalent ones, the Gapon equation for K reads:

$$\frac{\text{Exch K}}{\text{CEC} - \text{Exch K}} = K_g \frac{a_K}{\sqrt{a_M^{2+}}} \qquad (1)$$

in which:

Exch K = exchangeable K content in cmol (+) kg^{-1}

CEC = cation exchange capacity in cmol (+) kg^{-1}

a_M^{2+} = activity of cations involved in $molL^{-1}$

a_K = activity of potassium in $molL^{-1}$

K_g = Gapon cation exchange selectivity coefficient in $(Lmol^{-1})^{1/2}$

The lefthand side of this equation supplies information on the degree of saturation of the adsorption complex with K. The righthand side depicts the so-called «reduced» ratio of the cations present in the bulk solution and involved in exchange reactions. Thus, the activity of K^+ in the soil solution is a function of the degree of K saturation at the exchange complex, of the square root of the sum of the activities of all divalent cations *(e.g.* Ca + Mg) and of the numerical value of Kg. In other words, a value on exchangeable K, when expressed as fraction of the total exchange capacity, could yield an estimate of the K-concentration in the soil solution, provided that values on Kg and a_m^{2+} are available.

2.1 Selectivity coefficients (Kg values)

With respect to Kg, it is generally known that, even among soils of identical clay-mineral type, Kg values are far from constant. Soil material is usually a blend of various exchangers, each with its own Kg value. For instance, organic matter, often making an important contribution to the CEC, has a very low affinity for K, resulting in low Kg values compared with clay minerals. Similarly various clay minerals differ in their affinity for K resulting in Kg values varying by a factor 5 *(Bruggenwert and Kamphorst [1979]).*

Even within one type of clay mineral one must count on the presence of different types of sites, differing in their affinity for cations. Such a heterogeneity of site-types leads in practice to gradual changes in Kg values as a function of K-loading of the exchange complex. In addition, there is some evidence that even within a particular type of site *(e.g.* that on oxidic surfaces) a range of values for binding strength pertaining to a given cation is to be expected. The influence of such heterogeneities on the exchange process was tentatively described mathematically by *van Riemsdijk et al. [1986]).*

For a composite exchanger such as soil, it can be attempted to arrive at a weighted mean of Kg values, with each adsorbent contributing according to its relative prevalence. Thus, *Harmsen [1979],* using exchange equations slightly different form those used by *Gapon,* defined the average selectivity coefficient for heterovalent ion exchange in a simple two-site system for mono- and divalent cations as:

$$\overline{K}_g = \frac{\sqrt{a_M^{2+}}}{a_K} \times \frac{\text{Exch K(H)} + \text{Exch K(L)}}{\sqrt{\{\text{CEC} - \text{Exch K(H)} - \text{Exch K(L)}\}}} \qquad (2)$$

in which:

$\overline{K}_g$ = average cation selectively coefficient in $(\text{Lmol}^{-1})^{1/2}$

a_M^{2+} = activity of divalent cations involved in molL^{-1}

a_K = activity of potassium in molL^{-1}

CEC = cation exchange capacity in cmol (+) kg^{-1}

Exch K(H) = exchangeable K content in cmol (+) kg^{-1} at high-affinity sites

Exch K(L) = exchangeable K content in cmol (+) kg^{-1} at low-affinity sites.

For a soil as a whole, the average Kg can assume very extreme values, as was demonstrated by *Ehlers et al. [1967].* Determination of such a value can be contemplated, but may prove of limited practical usefulness. Whereas clay and silt contents may be seen as relatively stable parameters, such is not the case for organic matter, content and nature of which depend on type of soil management.

Probably the most convenient estimation of variations in Kg values is obtained by determining (a) exchangeable K (= Exch K(L), see equation 2) with neutral electrolytes, and in the same sample (b) exchangeable + «fixed» K (= Exch K(L) + Exch K(H) by HCL−, HNO_3−, or NaTPB extractions, or with electro-ultrafiltration (EUF).

2.2 Complementary cations

When estimates of K activity in soil solution are to be obtained through the use of Gapon's equation, the activities of divalent cations need to be measured or their values should be constant. This condition of constancy is, however, hardly never met. It is clear from equation (1) that any change in degree of K saturation automatically leads to changes in both a_K and $a_M{}^{2+}$. Only in special cases, such as calcareous soils with Ca not only as a dominant, but also as well buffered cation, is the constancy of (M^{2+}) nearly assured.

In acid soils, exchangeable Al appears as complicating factor. Still, for practical purposes this last aspect may prove less important than it seems, since at pH values prevailing in agricultural soils, Al ions are often present in divalent form.

In humic sandy soils with low pH, sizeable portions of the exchange complex may be occupied by protons constituting an additional obstacle to the practical use of the Gapon equation. The influence of pH is reflected in a change in the actual CEC as such.

In summary, it can be concluded that most parameters needed to estimate the K-concentration in a soil solution are too complex to be used in practical soil testing for a model description of all exchange processes occurring in a soil. Nevertheless, it is useful to know which factors influence the exchange reactions, and to realize that knowledge of these factors can be helpful in converting laboratory data on extractable K into estimates of K available under field conditions to crops.

3. Practical consequences

The question remains how a realistic estimate of available K can be obtained in the laboratory. Since K uptake by plants appears to be most directly dependent on K concentrations or -activity in the soil solution, it seems logical to try to determine this parameter in the laboratory. This, however, is technically rather difficult to perform. Addition of pure water always leads to exchange between solution and adsorption complex. For an optimal approximation, the amount of water added should be kept to a minimum. In this line of thinking, a potentiometric determination of K directly in the soil paste, similar to pH measurement, comes to mind. To our knowledge, such an approach has never been made, probably because of its analytical complexicity.

Rather close to determining the concentration of K in the soil solution stands the original EUF technique *(Németh [1980])*, in which 7 different fractions are distinguished. The first fraction is supposed to represent the soil solution potassium. We analysed a number of soils for solution K with the EUF method and compared the results with those obtained in a procedure involving an addition of water in a ratio 1:2.5 (w:v) soil to solution. The values found were generally very low and no particular differences were found between the values obtained with these two methods, which makes it clear that even the EUF extraction does not give a true picture of soil solution potassium.

The empirical determination of the so-called intensity parameter, being the value of the activity ratio of cations in the soil solution as defined in equation (1), has been tried by several authors. This approach, together with that of the so-called Q/I curves which combines information on intensity parameter with that on buffering capacity of soils was reviewed by *Goulding [1983]*. The laboratory procedure for determining activity ratios (AR_0) and/or Q/I curves is very cumbersome and the relevance of the results to nutrient uptake is not convincing. Examination of equation (1) reveals that determination of the fractional saturation of the exchange capacity by potassium yields a parameter which is related to the above-mentioned activity ratio. The laboratory determinations of exchangeable potassium and of the CEC are easily performed. Because of variations in K_g values, as discussed above, the relevance of such a parameter to nutrient uptake should theoretically be worse than that of activity ratio solely.

4. Proposed methods

Because of cost aspects, easy-to-perform extraction procedures with which the largest possible number of nutrients can be determined are looked for in practice. In such extracts usually only the easily exchangeable forms of potassium are present. Considering the above discussion, it is our opinion that such extraction procedures would be adequate for all practical purposes involving fertilizer recommendations, provided the values obtained are considered together with other soil parameters directly or indirectly relevant to the exchange properties of soils, such as pH, clay (type and content) and organic matter. In such an approach, the effects of variations in CEC and Kg are empirically taken into account.

The procedure used for making fertilizer recommendations in the Netherlands can serve as an example of such an approach, except that due to historical developments only two elements (Na and K) are determined in the extract obtained. The relation between quantities extracted in a laboratory procedure and quantities absorbed by crops was determined by means of field expermiments on different soil types. The evaluation has led to different formulas employed to calculate a so-called K-number as index of K-availability.

The method consists of an extraction of soil with 0.1 *M* HCl, with which the easily and a portion of less easily exchangeable potassium *(de Vries and Dechering [1960])* are withdrawn. The «corrected» value for potassium is called the K-number for that particular soil, and the formulas used for calculating these numbers for different soil types are given in Table 2. It can be seen that the soil characteristics affecting potassium availability and incorporated in the formulas are based on soil type and land use. Correlation with nutrient uptake by different crops has been well verified.

Table 2 Empirical formulas used for converting values of K extracted with 0.1 *M* HCl into estimates of K available to crops.

Soil type/land use	K-number calculation
Arable land on sandy soils, reclaimed sandy soils, and peat soils	$\text{K-number} = \dfrac{20 \times \text{K-HCl}}{10 \pm \%\ \text{organic matter}}$
Arable land on clay soils with less than 10% organic matter (if pH > read pH = 7)	$\text{K-number} = \dfrac{\text{K-HCl} \times b}{0.15 \times \text{pH-KCl-}0.05}$
Arable land on clay soils with more than 10% organic matter	$\text{K-number} = \text{K-HCl} \times b$
Grasslands on all soils	$\text{K-number} = \dfrac{10 \times \text{K-HCl}}{f \times \%\ \text{organic matter}}$

in which:
K-HCl = mg K_2O/100 g soil extracted with 0.1 *M* HCl

b = factor determined by fraction < 16 micro meter

f = correction factor

Another example of a method originally designed for estimating potassium availability is the so-called EUF method developed by *Németh [1972, 1979]*. For this method the advantage is claimed that simultaneously a number of other nutrients can be determined in the same extract. The principles of the method are simple. Soil is suspended in water in a compartment with on two opposite sides membrane filters and behind these platinum electrodes. On the electrodes a potential difference is applied of 200 V during 30 minutes and 400 V for the next 5 minutes. As a result the cations migrate towards the cathode and the anions towards the anode. After having passed the filters the cations and anions are collected and measured. In the case of potassium the first fraction (200 V; 0-30 min.; 20 °C) is said to represent the easily exchangeable and water soluble potassium; the second fraction (400 V; 30-35 min.; 80 °C) contains (part of) the more difficultly exchangeable K. Here again the analytical values are not used as such but are in fact corrected by taking into account the ratio of the second and first fraction, and the sum of extractable Ca and Mg *(Wiklicky and Németh [1981])*. The ratio of K and Ca + Mg in the two fractions supplies information on the mean selectivity coefficient as well as on the cation exchange capacity.

In our laboratory we have applied a very simple extraction with 0.01 *M* $CaCl_2$ (*Houba et al. [1986]*). This extracting solution differs slightly in concentration from the one used originally by *Schachtschabel [1954]* for the determination of Mg, Ba, Sr, K and pH. We preferred 0.01 *M* as concentration because it is widely used for determining pH *(Page et al. [1982]; Woodruff, [1961])* and for the determination of N-availability indices *(Fox and Piekielek, [1978]* a and b; *Stanford, [1968]; Stanford and Smith, [1971, 1976]; Stanford and DeMar, [1969, 1970])*.

5. Comparison of the proposed methods

For a comparison, 84 soil samples were collected at 21 locations (4 sites per location). Roughly half of the soils were sandy soils and the other half clay soils (Table 3). For as broad a comparison as possible, not only potassium, but also other nutrients determined in the «universal» extraction procedures (EUF and 0.01 *M* $CaCl_2$) were considered (Table 4).

The results obtained with the various extraction procedures are presented in Tables 5, 6 and 7.

5.1 Potassium

A comparison of data on K extracted with 0.01 *M* $CaCl_2$ and 0.1 *M* HCl shows that the degree of correlation depends on soil type, with clearly different results obtained for sandy soils and for clay soils. Such a divergence is to be expected, as 0.1 M HCl also extracts portions of the difficultly exchangeable and primary-mineral K from clay soils. The relations are shown in Figure 1 for all analytical values at hand. The relation between the sets of data obtained with the two methods is very good for sandy soils, whereas the values for clay soils are much more scattered. Hence, it is reasonable to assume that in clay soils the readily exchangeable potassium is extracted with both methods but that, depending on type and amount of clay minerals, varying portions of more tightly bound K, as extracted by HCl, are responsible for both scattering and higher values.

Table 3. Location of trial fields and chemical characteristics of soils used in the investigation (means of 4 samples per location).

Soil number	Location	Soil type	Organic matter (%)	Fraction < 16 μm (%)	Fraction > 50 μm (%)	$CaCO_3$ (%)
1	Emmercompascuum	Reclaimed peat subsoil	16.7	–	–	–
2	Drouwenermond	Reclaimed peat subsoil	18.7	–	–	–
3	Valthermond	Reclaimed peat subsoil	12.5	–	–	–
4	Stadskanaal	Reclaimed peat subsoil	15.7	–	–	–
5	Gieten	sandy soil	5.1	–	–	–
6	Aalden	sandy soil	6.9	–	–	–
7	Odoorn	sandy soil	5.1	–	–	–
8	Oude Schans	marine clay loam soil	4.3	71	25	0.7
9	Kloosterburen	marine clay loam soil	2.5	45	46	8.7
10	Wieringerwerf	marine clay loam soil	3.0	29	56	12.4
11	Biddinghuizen	marine clay loam soil	3.7	58	29	9.5
12	Zeewolde	marine clay loam soil	4.3	41	42	13.3
13	Lelystad	marine clay loam soil	4.3	51	36	8.8
14	Colijnsplaat	marine clay loam soil	1.9	31	62	5.6
15	Westmaas	marine clay loam soil	2.4	32	58	8.0
16	Ovezande	marine clay loam soil	3.7	35	59	3.1
17	Ravenstein	river clay soil	3.3	39	57	0.1
18	Langenboom	sandy soil	3.4	–	–	–
19	Rips	sandy soil	5.0	–	–	–
20	St. Hubert	sandy soil	2.2	–	–	–
21	Wijnandsrade	löss soil	2.0	28	70	0.1

Table 4 Standard procedures for soil testing in the Netherlands

Parameter	Extraction solution	Remarks
pH	1 *M* KCl	1:5 (v/v); air-dry soil
K, Na	0.1 *M* HCl and 0.2 *M* $H_2C_2O_4$	1:10 (w/v); air-dry soil
Mg	0.5 *M* NaCl	1:20 (w/v); air-dry soil
P	water	1.2 ml of air-dry soil is incubated with 2 ml water at 20 °C for 22 hours. Next 70 ml of water is added and P is extracted
N-min ($NO_3 + NH_4$)	0.5 *M* NaCl or 0.5 *M* KCl	1:2.5 (w/v); field-moist soil

Table 5 Values of nutrients as exacted with EUF (means of 4 replicates).

Soil Number	P mg P kg^{-1}	Mg mg Mg^{-1} kg^{-1}	K mg K kg^{-1}	Na mg Na^{-1} kg^{-1}	Mn mg Mn^{-1} kg^{-1}	NO_3-N mg N kg^{-1}	NH_4-N mg N kg^{-1}	EUF-N[XX] mg N kg^{-1}
1	25/15[X]	60	162/ 23	58	2	8/0.2	5.1/0.3	33/ 7
2	31/24	50	188/ 29	72	2	13/0.3	1.5/0.1	38/11
3	26/19	46	187/ 29	35	4	18/0.2	3.8/0.1	41/ 8
4	22/20	48	85/ 18	83	2	19/0.8	1.8/0.2	42/ 7
5	13/11	28	51/ 17	18	1	5/0.5	3.3/0.3	12/ 3
6	28/29	60	77/ 22	35	2	14/0.2	1.5/0.1	35/11
7	12/ 8	27	60/ 18	23	3	3/0.4	1.0/0.1	12/ 3
8	18/ 5	45	92/ 77	46	1	13/0.7	3.3/0.7	35/ 7
9	15/ 8	29	117/ 66	39	1	5/0.5	1.0/0.1	26/ 5
10	4/ 5	26	85/ 49	27	1	4/1.0	1.5/0.3	19/ 7
11	10/ 4	48	155/100	33	1	4/0.4	6.3/1.0	23/ 6
12	6/ 5	52	131/ 77	31	1	5/0.5	1.8/0.4	24/ 5
13	5/ 5	42	142/ 90	59	1	7/1.0	6.8/1.8	24/ 7
14	15/14	27	85/ 48	36	1	3/0.0	1.3/0.2	20/ 6
15	10/ 8	25	78/ 51	23	1	6/1.0	1.5/0.4	20/ 4
16	28/20	49	162/ 88	34	1	6/1.0	2.5/0.7	37/ 9
17	11/19	35	73/ 31	38	6	8/1.0	0.5/0.2	32/ 8
18	59/53	36	108/ 28	17	1	5/0.3	2.0/0.5	22/ 8
19	60/50	36	132/ 20	16	2	10/0.1	2.5/0.1	31/ 5
20	45/28	22	145/ 38	17	7	2/0.0	2.5/0.6	18/ 6
21	13/22	29	107/ 36	21	10	8/1.0	1.0/0.2	35/ 7

[X] Two values listed stand for 1st fraction and 2nd fraction; one value stands for the sum of 1st and 2nd fraction.

[XX] These values are based upon 8-16 replicates.

Table 6 Values of pH and nutrients as extracted with standard procedures in use in the Netherlands

Soil	pH	K-HCl	Mg-NaCl	P_w	
Number	1 *M* KCl	mg K kg^{-1}	mg Mg kg^{-1}	mg $P_2O_5 l^{-1}$	mg P kg^{-1}
1	5.2	143	171	49	26
2	5.1	164	166	64	34
3	4.8	166	94	46	19
4	5.3	95	139	46	26
5	5.4	58	65	25	9
6	5.2	92	94	52	21
7	5.1	75	42	22	8
8	7.1	247	195	31	13
9	7.4	251	86	25	10
10	7.5	145	39	19	8
11	7.3	326	170	30	12
12	7.4	247	146	20	8
13	7.3	309	120	21	8
14	7.4	141	65	23	9
15	7.4	145	48	18	7
16	7.4	247	118	53	21
17	6.6	98	121	37	14
18	6.2	129	48	116	39
19	5.5	125	54	112	40
20	6.7	141	39	89	32
21	6.8	112	69	46	17

It is claimed that the EUF-procedure can distinguish between readily exchangeable and tightly bound potassium fractions. This could mean that K in the first fraction obtained with EUF is closely related to K extracted with 0.01 *M* $CaCl_2$ and that K in the combined first and second EUF fractions is comparable to K extracted with HCl, independent of soil type. That this is really the case, can be seen from the analytical results (Figures 2 and 3).

It is clear that $CaCl_2$ extracts only easily exchangeable K (Exch K(L), see equation (2)). Hence, this method provides less information necessary for the evaluation of available K than the other two methods discussed. Information on Exch K(H) can be obtained by either taking into account soil type or, still better, by determining Exch K(H) which value is little dependent on soil management and therefore needs to be determined only once. CEC could be determined directly, or could be estimated from values of pH, clay content and/or organic-matter content.

Table 7 pH values and quantities of nutrients as extracted with a 0.01 *M* $CaCl_2$ solution (means of 4 replicates)

Soil		P	Mg	K	Na	Mn	NO_3-N	NH_4-N	Soluble organicN	Total N
Number	pH	mg P kg^{-1}	mg Mg kg^{-1}	mg K kg^{-1}	mg Na kg^{-1}	mg Mn kg^{-1}	mg N kg^{-1}	mg N kg^{-1}	mg N kg^{-1}	mg N kg^{-1}
1	5.0	10.0	145	133	46	8.7	8.4	12.4	16	36
2	5.1	9.0	125	135	58	8.2	14.9	9.2	21	45
3	4.8	7.1	88	147	24	15.2	18.2	12.1	11	41
4	5.2	5.8	125	77	76	6.4	24.3	12.4	16	52
5	5.5	0.5	60	41	8	3.8	4.0	6.2	5	15
6	5.2	4.0	93	61	22	4.3	13.0	7.4	11	31
7	5.3	0.8	53	50	11	7.0	3.3	5.5	4	13
8	7.4	0.8	127	69	34	0.6	12.5	4.7	10	28
9	7.4	0.9	70	86	27	0.6	5.0	5.2	8	18
10	7.3	0.6	37	81	17	0.9	3.1	5.2	7	15
11	7.4	0.7	126	122	21	0.6	3.5	5.3	11	19
12	7.6	0.6	110	107	17	0.7	4.6	6.1	11	22
13	7.3	0.5	95	127	44	0.5	7.4	5.9	7	21
14	7.2	0.9	55	60	20	0.5	3.3	2.9	5	11
15	7.3	0.4	40	65	12	0.7	5.4	4.8	10	20
16	7.4	2.5	87	113	19	0.4	7.2	4.0	12	23
17	6.6	1.2	109	44	27	5.6	8.4	4.9	12	25
18	6.0	13.3	51	88	6	1.8	5.7	5.6	11	23
19	5.5	9.9	59	110	7	5.1	15.0	6.6	7	29
20	6.5	8.0	41	101	4	3.2	2.5	4.7	7	14
21	6.7	1.9	67	107	10	5.2	6.9	5.8	5	18

5.2 Sodium

Sodium was determined with the $CaCl_2$ and EUF procedures only. As expected, the relation between the results obtained with the two procedures is very close, meaning that in both methods solely the readily exchangeable Na is extracted. From the values listed in the Tables 5 and 7 the following relation was calculated;

$$\text{Na-CaCl}_2 = 1.0 \times \text{Na-EUF} - 12 \ (r = 0.993).$$

The relatively large negative intercept is due to Na contamination of glass cuvettes and filters of the EUF apparatus. The blank values, for which no corrections were made, accounted for the intercept value.

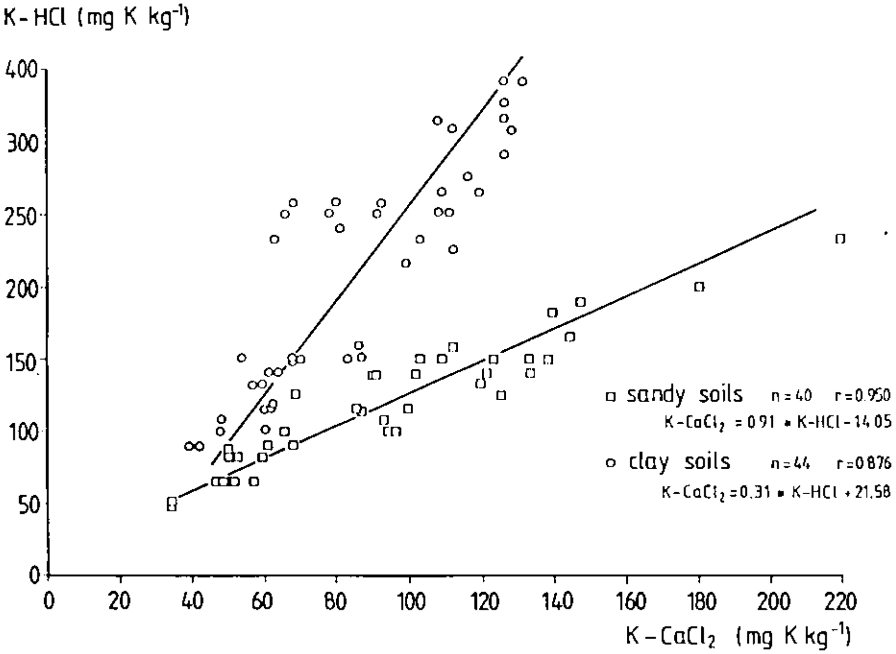

Fig. 1. Relation between extractable K with 0.1 *M* HCl (K-HCl) and 0.01 *M* $CaCl_2$ (K-$CaCl_2$).

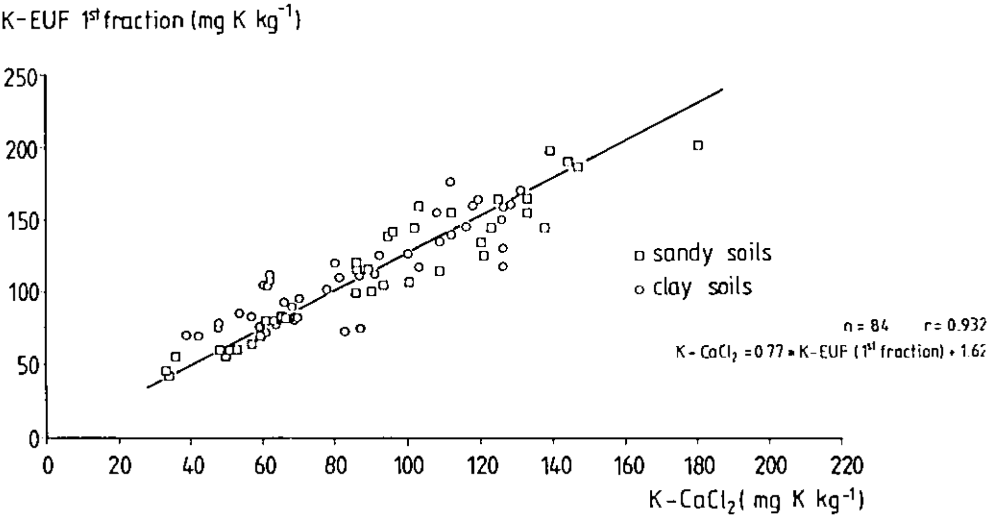

Fig. 2. Relation between extractable K with EUF-1st fraction and 0.01 *M* $CaCl_2$ (K-$CaCl_2$).

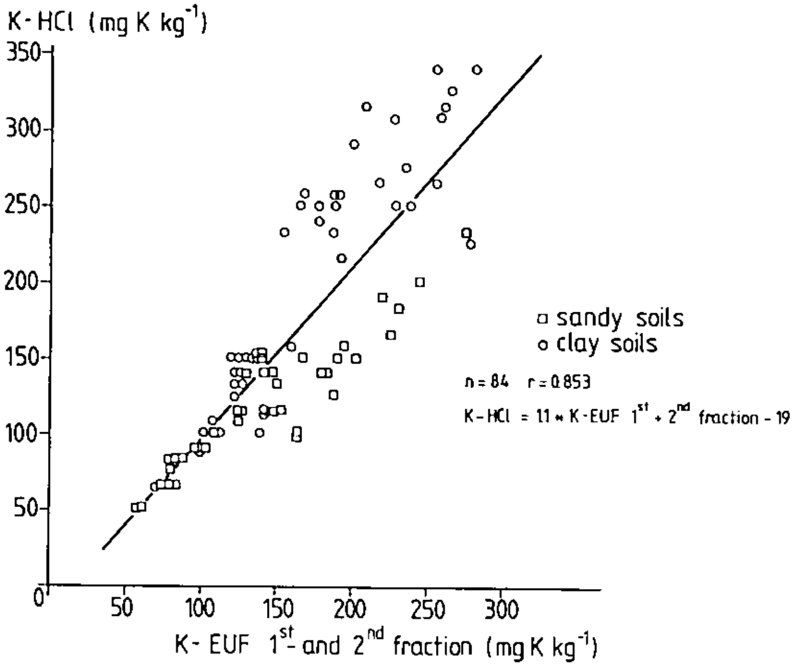

Fig. 3. Relation between extractable K with 0.1 *M* HCl (K-HCl) and EUF-1st and 2nd fraction.

5.3 Magnesium

From the Tables 6 and 7 it can be seen that up to about 100 mg Mg per kg of air-dry soil almost equal amounts of Mg were extracted with 0.5 *M* NaCl (standard Dutch procedure) and 0.01 *M* $CaCl_2$. Above this value, $CaCl_2$ extraction yielded lower values due to incomplete exchange. It is to be expected that the location of this boundary value depends on the total CEC of the soil and on the percentage Ca saturation of the adsorption complex. Since for fertilizer advisory purposes on arable land only values up to about 50 mg kg^{-1} Mg are of interest, the exchanging power of 0.01 *M* $CaCl_2$ as used here is sufficient. Since Mg contents of the soils under investigation proved to be rather high, an additional series of 7 sandy soils with Mg contents in the range of 10 to 40 mg kg^{-1}, was analysed with the two methods. The regression analysis of all results up to 100 mg kg^{-1} (extracted with NaCl) showed that

$$\text{Mg-CaCl}_2 = 0.91 \times \text{Mg-NaCl} + 2 \ (r = 0.976).$$

It is clear that both procedures are equally useful in predicting Mg-availability in soil.

The values obtained with EUF-extraction were consistently lower than those obtained with NaCl. Regression analysis showed that:

$$\text{Mg-EUF} = 0.2 \times \text{Mg-NaCl} + 21 \ (r = 0.770).$$

The rather poor relation between EUF- and NaCl values may be ascribed to analytical difficulties encountered with the EUF-extraction method. During the EUF-extraction, magnesium hydroxides are formed on the cathode. This precipitate only partly dissolves in the corresponding filtrate, resulting in low values for Mg measured in the filtrate.

5.4 Phosphorus

Normally the P_w value used for fertilizer recommendation in the Netherlands is expressed in mg P_2O_5 per litre of air-dry soil. For the sake of comparison, however, all results for the different extraction procedures are given here in mg P per kg air-dry soil. P_w was determined according to the Dutch procedure (Table 4). Thereafter the density of the dry soil was determined and the values converted (Table 6).

Extractions with both water and 0.01 *M* $CaCl_2$ solution can roughly be considered as yielding intensity parameters. However, the use of 0.01 *M* $CaCl_2$ solution leading to a pH lowering in the equilibrium suspension and the introduction of Ca ions into the system influence the solubility of Ca phosphates. Accordingly, when the absolute amounts of P extracted with the two procedures are compared, we find less P with 0.01 *M* $CaCl_2$ than with water extraction. Since the processes leading to the establishment of equilibria in $CaCl_2$-extracts are different for calcareous and non-calcareous soils, separate comparisons were made for these two groups of soils.

In Figures 4 and 5 the relations between the amounts extracted with 0.01 *M* $CaCl_2$ and with water are displayed for all available values. In both cases acceptable correlations were found. The somewhat higher variability for the non-calcareous soils is probably caused by the higher organic matter content of certain soils, introducing additional uncertainties during the conversion from volume to weight for the water extraction data.

With the EUF method two successive extractions were performed: first 30 minutes at 20 °C, followed by 5 minutes at 80 °C. The first-fraction values and the ratios of 1st and 2nd-fraction values are, together with other parameters, used for fertilizer recommendation purposes *(Wiklicky and Németh [1981]).*

In Figure 6 the summed values are shown in relation to the values found for water-extractable phosphorus. A reasonably linear correlation between the two sets of data was found. From the regression relation it further follows that with EUF about 2.4 times more phosphorus is extracted than with water. In both methods the extraction ratio is comparable so that the values expressed per kg of soil should not differ too much.

The regression analysis pertaining to the first fraction of EUF leads to:

P-EUF (1st fraction) = 1.2 × P_w − 2.5 r = 0.912 (n = 84).

It follows that roughly equal amounts are extracted with both methods, indicating that with these methods similar intensity parameters are obtained. If we take the second fraction of P-EUF separately, the same conclusion can obviously be drawn, on the basis of the following equation:

P-EUF (2nd fraction) = 1.1 × P_w − 1.5 r = 0.862 (n = 84).

It appears that EUF-extractable P is just double the quantity obtained as intensity parameter. Thus, little additional information is obtained with an extended extraction procedure at 80 °C.

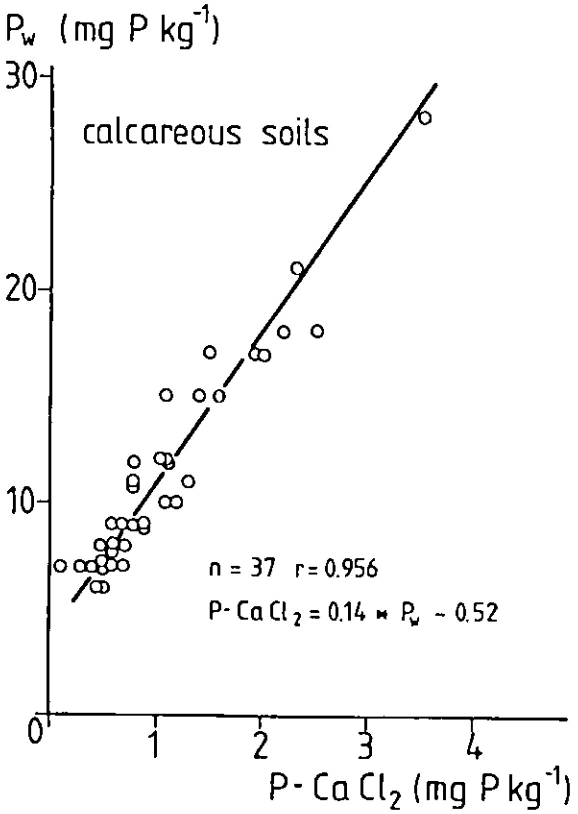

Fig. 4. Relation between extractable P with water (P_w) and 0.01 *M* $CaCl_2$ (P-$CaCl_2$) in calcareous soils.

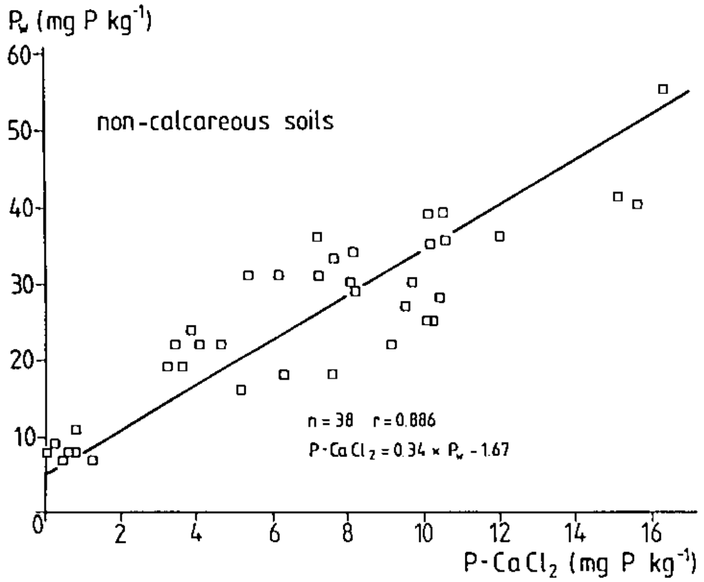

Fig. 5. Relation between extractable P with water (P_w) and 0.01 *M* $CaCl_2$ (P-$CaCl_2$) in non-calcareous soils.

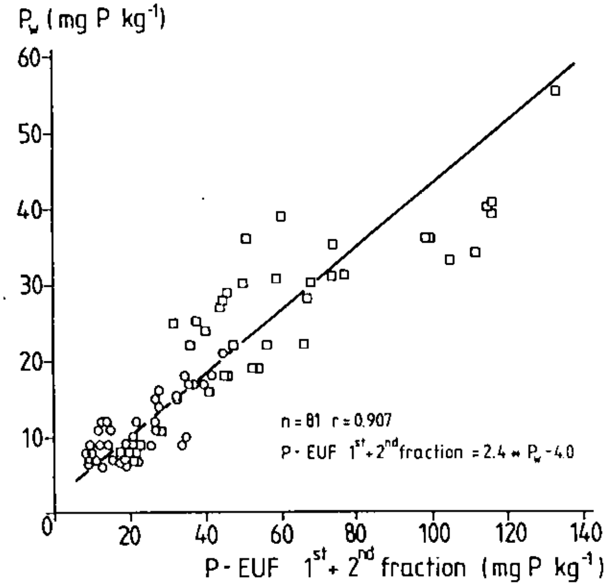

Fig. 6. Relation between extractable P with water (P_w) and P-EUF- 1st and 2nd fraction.

3.5 Nitrogen

The current fertilizer advisory scheme used in the Netherlands is based on levels of inorganic N forms extractable from fresh soil material sampled to a depth of about 1 meter. Such deviating sampling conditions make a comparison of results obtained with the various methods rather meaningless.

Next to the inorganic ions NO_3^- and NH_4^+, an additional mobile organic-N fraction is extracted with the EUF procedure, which fraction is claimed to make an additional contribution to a proper assessment of N-availability in soils *(Németh, [1985])*.

A comparison of the EUF-total N values of the first fraction with those of total soluble N in 0.01 *M* $CaCl_2$ extracts (Tables 5 and 7) leads to the following relation:

$$\text{Total-N } (CaCl_2) = 0.99 \times \text{EUF-total N } (1^{st} \text{ fraction}) - 2.5 \ (r = 0.82).$$

The conclusion can be drawn that virtually identical fractions of soil nitrogen, *i.e.* NO_3-N and soluble organic N are determined with both methods. This conclusion is further supported by a comparison of the NO_3-values only:

$$NO_3\text{-N } (CaCl_2) = 1.1 \times NO_3\text{-N (EUF)} - 1 \ (r = 0.96).$$

It should be pointed out that the EUF values are poorly reproducible. The values of the total EUF-N shown in Table 5 are the means of 8-16 replicates, for which the coefficient of variation varied from 8 to 63%. Especially in clay soils the variability was large. The corresponding coefficients of variation in the $CaCl_2$-procedure varied from 4 to 25% based upon 4 replicates.

The quantity of nitrogen recovered in the second EUF fraction was not considered here, as if falls within the experimental error range and therefore supplies no additional information. One of the causes of excessive variability encountered with the EUF-method could be contamination occurring in filters, and furthermore analytical uncertainties in the determination of soluble organic N. The contamination was avoided in the $CaCl_2$-procedure by centrifugation. Such a contamination was probably also the reason behind an absence of correlation between NH_4-N values found with the two methods, contrary to the expectation based upon the good correlation found in the cases of potassium and sodium.

6. Conclusions

1. In our opinion, theoretical models intended to describe the behaviour of K in a multi-variate exchanger system, such as a soil, cannot yet serve as useful tools for making K-fertilizer recommendations.

2. With the aid of empirical correction factors based on various soil characteristics involved in exchange reactions, estimates of exchangeable K, as determined with various methods, can be converted into estimates of plant available K needed for making K-fertilizer recommendations. Examples of useful methods are the 0.1-M HCl extraction procedure and the electro-ultrafiltration procedure.

3. Like the electro-ultrafiltration method, the newly proposed 0.01-M $CaCl_2$ extraction method can serve as a universal extraction procedure, supplying information on K, Mg, Mn, Na, P, NO_3, NH_4, soluble organic N, and pH. In comparison with the EUF method, the $CaCl_2$ extraction method is cheaper and more rapid, and is less burdened with interferences.

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Translation of Laboratory K-Data into K Fertilizer Recommendations

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Summary

Following a review of present methods for interpreting soil analysis, the methods now used at the Aspach Research Centre are explained. While exchangeable K does not fully describe the K supplying power of a soil, the inclusion of modifying factors reduces uncertainty in the relation between soil potential as indicated by response to K fertilizer and soil analysis results. Such factors are estimates of those forms of potassium which are not exchangeable but which contribute to the nutrition of plants. Fertilizer advice so derived is then described as well as the consequences of such a philosophy for field experimentation.

1. Introduction

Though the effects of fertilizer nutrients were discovered over a century ago the first attempts, in Anglo-Saxon countries *[20, 31]* or in France *[3, 24]* alike, at rational fertilizer advice were not made until the period 1940-1960.

This paper is limited to potassium and by reference to recent reviews discusses questions of the interpretation of soil analysis with reference to three points of current interest:

- K saturation of the cation exchange capacity,
- the desired level of K,
- Compensation for crop removals.

Each of these will be considered individually and in combination with one or both the others *[13, 16, 17, 20, 29]*.

– K saturation of the CEC is very widely used for diagnostic purposes. It is based on the concept of an ideal soil in which the cations are present in ideal proportions. One serious defect of this approach is that it has to be significantly modified in relation to soil type, in particular as between calcareous and non-calcareous soils.

– Definition of a desirable soil K level originated in *van der Paauw's [33]* work confirmed by *Barbier [4, 32]*. They stressed the concept of residual value which

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was indicated in interaction between newly applied fertilizer and the effect of soil enrichment by historical dressings.

> «On a soil well provided with a nutrient (*e.g.* phosphorus or potassium) moderate dressings of a fertilizer will produce results superior to those given by much more generous dressings on a soil without residues.»

– The careful replacement of K removed in crops is based on the idea that avoidance of running down the soil reserve of a nutrient will ensure that it will function as a reserve buffer throughout the growing period.

The SCPA has integrated these three ideas in a general concept of rational fertilization which uses soil analysis with regional information pertaining to the site, soil type and cropping objectives.

2. A basis for interpretation

Description of the nutrient supplying power of the soil is based on one or more analytical determinations. Necessary basic data are provided:
- first by field experimentation investigating response curves,
- second, by soil analysis: for potassium, exchangeable K content, % saturation of the CEC, clay content etc.

2.1 Expression of results

Soil K levels are plotted against indices of K response *[24, 30]* (Figure 1). The response index is given by:

$$I_R = \frac{\text{Yield at } K_X - \text{Yield at } K_0}{\text{Yield at } K_0}$$

This is easily translated into economic terms.

It is best only to include in the figure positive or nil responses on the assumption that negative responses are not caused by depressive effects of the nutrient under test but by negative interaction, *e.g.* too little N fertilizer or deficiency in Mg or some other nutrient.

2.2 Reduction of data

In order to eliminate some of the variability it is advisable to set up soil K classes within which the frequency of response F_R (ratio of responsive situations to the total) can be calculated (Figure 1). F_R is then plotted as ordinate against the midvalues for the soil K classes on a graph like that of Figure 2 *([2])*. When soil K is lower than a specific level t_1 there is always response to K fertilizer ($I_R > 0$); above another level (t_2) response is always nil. Between the two levels response varies from year to year and field to field. In general, F_R decreases as soil K increases. There are limitations of such a method:

- one approach places the desired soil K level at t_1 to ensure that there is always a response to K fertilizer,
- a less conservative approach places it at t_2 to ensure that there is no possibility of missing a response ($100 - F_R$).

To resolve this quandary, various proposals can be made to take into account the probability of response and thus to introduce an economic element into the choice of desirable K level *[12]*.

All the above reasoning must take account of soil type *[18, 25, 27]*. To establish Figure 2, at least ten points are needed, each of these being the number of response situations in relation to the total, which should again be at least ten. Thus it is necessary to have for each soil and cropping system a minimum of 100 values. (It is known that beet and potatoes respond in a different way from cereals.) On this latter point one is again faced with a decision as to the desirable soil K level for a rotation including both row-crops and cereals. Some opt for the higher level required by the more demanding crops, others prefer to take into account the frequency of the different crops in the rotation *[26]*.

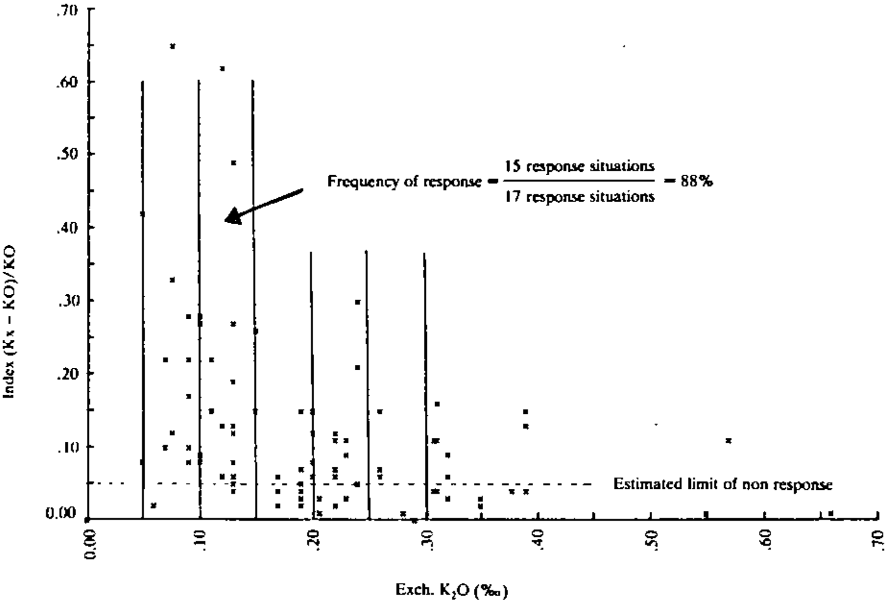

Fig. 1 Experimental field SCPA: relation between exchangeable K and response index.

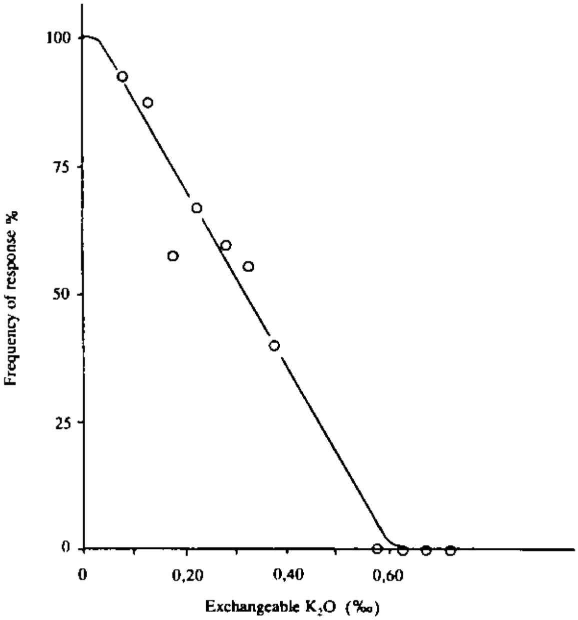

Fig. 2 Relationship between exch. K_2O and frequency of response.

2.3 Modification – CEC

There is usually a great spread of results even after reduction of the data as above. The reason is that, even on a particular soil type, exchangeable K is not the sole criterion of K supplying power. Response is a function of two or more variables. There are two possibilities for interpretation:

- Use of Discriminatory Factorial Analysis (DFA) as described by *Laurent et al. [12]* in their work on copper deficiency. This procedure is useful when it is not known what qualifying variables should be used. As far as concerns potassium, the literature *[29, 34]* shows that supply of K to the root depends on a number of phenomena all related to the exchange complex. DFA looses some of its attraction because it is difficult to use with only modest facilities for computing.
- The alternative is less rigorous. However, it allows verification of the significance of data without the risk of misinterpretation through poor statistical control.

The response indices I_R from the various experiments are plotted in their appropriate positions on a diagram whose coordinates are exchangeable K and CEC (or clay content). This may appear to be a retreat from the proposition above to work with frequency of response. Frequently there is insufficient data to allow use of the more certain method.

A main difficulty with this method is to distinguish between responsive and non-responsive situations and there are two reasons for this:

- «abnormal» results (A and B on Figure 3) may lead one to place the desired level of soil K too high; such points will be weighted by taking into account frequency of response (Section 2) and should be eliminated by re-examining the original experiment to find the reason for aberrant behaviour *[7]*.
- very frequently, experiments are sited where a response to K fertilizer is to be expected so there are few results from trials showing an absence of response and, therefore, fixing the desirable level in the higher range of soil K is a delicate matter.

With increase in CEC (or clay content), the supply of exchangeable or intermediate K, and consequently the soil's K supplying power, increases. The K fixation capacity also increases; the first phenomenon generally affects the latter and the curve representing the desirable level is concave to the base. This has the effect of reducing the desirable K level *[7, 24]*.

The limits of soil K classes other than the desirable level aid in interpretation. The lower classes seperate subjectively classes for response index (0 < I_R < = 20% < I_R < = 40% for example). The upper limit defines a class of high K content at which a strategy to reduce fertilizer application might be applicable (see below section 4).

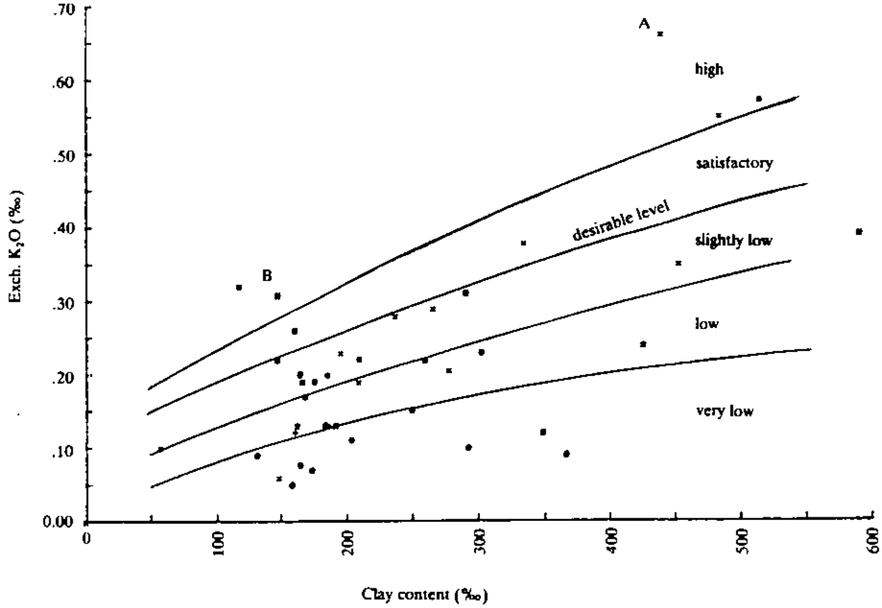

Fig. 3 Interpretation diagram for fixing desirable exchangeable K_2O level.

3. Adjustment of interpretation diagrams

The difficulties in establishing a soil analysis interpretation diagram like that of Figure 3 and its inadequacy under some conditions *[2, 15]* remind us that the relation Yield = f (K exch., CEC) does not explain all the variability encountered. Detailed investigation *([23]; [34])* has shown the importance of the mineral component of CEC, as estimated by a technique suggested by *Addiscott [1]* in explaining the K dynamics. Several pieces of work have shown that the general relation between mineral CEC and total CEC [*Metson* for example] has important deficiencies. Thus:

Mineral CEC = 0.95 total CEC − 24.6 ($r^2 = 0.91$) for 380 samples of soils of very different origins,

or

Mineral CEC = 0.85 total CEC + 1.3 ($r^2 = 0.88$) for 213 samples of Lorraine calcareous brown soils

One might conclude therefore that total CEC (or clay content) gives only a rather general indication of behaviour of potassium as compared with mineral CEC. One can use a modifying coefficient:

General: Mineral CEC = a × total CEC + b
For a particular soil: Mineral CEC = a^1 × total CEC + b^1
Modifying coefficient: a/a^1
(Usually, b and b^1 do not differ significantly from 0)

Then the diagram is modified for the particular soil by multiplying by a/a^1. If this ratio is less than unity, *e.g.* 0.8, the diagram will be modified parallel to the abscissa. This means for example that a value for CEC of 150 on the general diagram indicates a mineral CEC of 120 for the soil under study. So far this procedure has only been used experimentally.

In a similar way the ordinates can be modified by taking into account the amount of intermediate K *[2]* particularly for cereal or grass based systems. Thus one considers that exchangeable K is an indicator of all the K shown in a biological extraction *(Stanford and de Ment [21])* or by a chemical method like NaTPB extraction *[22]*. Using similar reasoning to that applied to CEC we mention some examples described elsewhere *[35]*.

General norm NaTPB extracted K = 1.92 × exch. K − 18.8^{ns} $r^2 = 0.83$
Champagne rendzinas NaTPB K = 1.46 ″ + 10.0 $r^2 = 0.90$
Modifying coefficient = 1.92/1.46 = 1.32
Calcareous brown soil
on Lorraine Lias NaTPB K = 2.21 × exch. K + 37.5 $r^2 = 0.81$
Modifying coefficient = 1.92/2.21 = 0.87

The diagnostic diagram is then shifted orthogonally parallel to the ordinate. These two kinds of modification are shown in Figure 4.

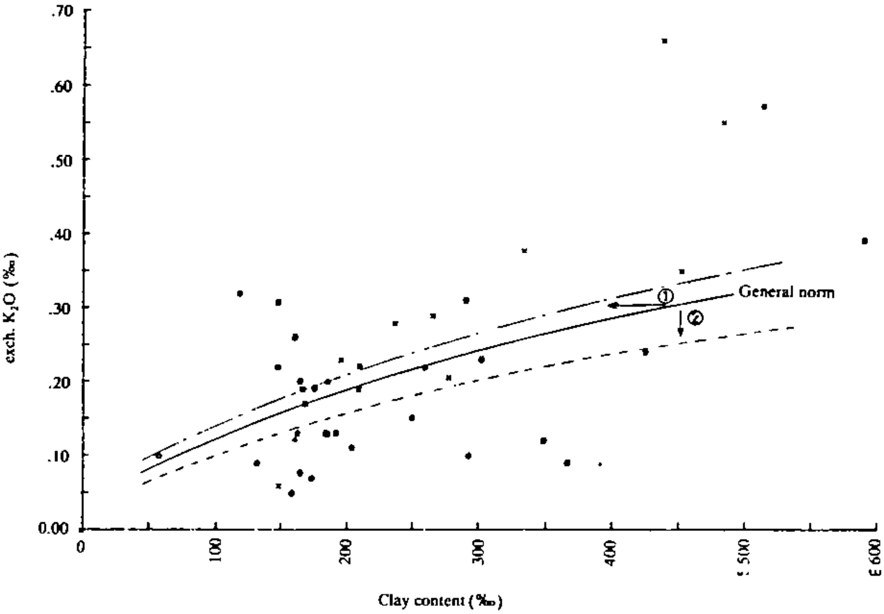

Fig. 4 Examples of modification of interpretation diagram
1. by ratio mineral CEC/total CEC 2. by ratio exch. K/ NaTPB K.

One could consider using mineral CEC and intermediate K directly in diagnosing K supplying power but unfortunately these two determinations are not suitable for routine use, because they are expensive and difficult to automate. They are concerned only with the dynamics of K and should be used only as an addition to routine soil analysis which is used to indicate other mineral or organic characteristics of soils. The difficulty is overcome by confining such investigations to samples representative of a particular soil type. Then the relations and modifying coefficients described above are determined statistically. All routine analysis is then interpreted via the diagram with the sufficient care given by regression equations */2, 15/*.

In the above, intermediate K is taken into account in modifying the interpretation diagram. This value, being a point on an extraction curve */8, 22/* indicates release of non-exchangeable soil K. However, it is only one, empirical, aspect of buffering capacity which governs the equilibrium between K retained on the clay colloids and that in the soil solution */25, 27/*. Buffering capacity has been described in various ways */5, 11/* but none of these are suitable for routine use in diagnosis. ***Loué and Quémener*** suggested a method for the «Groies» soils of central western France */15/*. These red rendzinas have a buffer capacity scarcely higher than that of a sand. K fertilizer causes a marked increase in solution K resulting in good responses to K fertilizer. This is particularly the case with maize which covers most of the irrigated areas in this region where the climate is favourable and K demand is high.

4. Fertilizer advice

This has been described in detail elsewhere *[7, 9, 35]* and only the main points are mentioned here.

When soil K is above the critical level it should receive fertilizer to replace the various losses: removal in crop, fixation and leaching:

- *Crop removal:* this is the product of estimated K content, on a regional basis, with the target yield in the light of local potential and technical competence of the farmer.
- *Leaching:* this is measured for each soil by lysimeter studies or estimated from the granulometric composition. It depends greatly on rainfall distribution and is modified on a regional basis.
- *Fixation:* Pot studies at Aspach have shown that in the course of a cycle where the balance (fertilizer applied – crop removal) is zero, the balance indicated by exchangeable K is negative *[23]*. In other words, that part of fertilizer K fixed is not re-utilised by the crop within its growth period; the plant uses preferentially the exchangeable portion and the rest is accounted for as intermediate K. In calculating fertilizer need it is necessary to take this into account; it is expressed as a percentage. Fixation at these levels of soil K often varies between 10 and 20% of maximum uptake by the plant. Precise estimation is made in pot trials or through field experiments on different soil types.

In the special case where the indicated soil K level is high, fixation is negligible and K fertilizer application can be reduced by 30%, *i.e.* omitting K fertilizer for one year in three.

When soil K is below the desired level, corrective measures are called for. Corrective requirement is calculated as follows:

Corrective dressing = Difference between soil K determined and desirable level
×
mass of soil in which the application will be diluted
×
Fixation coefficient

The soil mass depends on soil type and rooting depth and is approximates to plough depth.

The fixation coefficient defines the supplementary fertilizer needed to obtain the desired enrichment, taking into account fixation. For potassium at least this is generally proportional to the rate applied and is expressed as a percentage thereof. For example a soil fixing 35% retains 35% of applied K in the intermediate form, 65% remaining exchangeable *[23, 28]*.

5. Consequences for experimentation

The use of norms such as we have described for the interpretation of soil analysis defines the necessary experimental approach. Here we shall only present an outline of the relation between experimentation and regional enquiry.

Before deciding to embark on a long term experiment it is necessary to define the objective in terms of soil and cultural system. The enquiry should follow the course outlined:

- Examination of the bank of soil analytical data for the region. If this is insufficient, analysis of sufficient soil samples to represent the region.
- Description of data (statistical basis, histograms ....) from which the ‹modal› soil can be described. This will serve as a reference for the detailed studies which follow and can be used to identify the soil type *[34, 36]*.
- Investigation in detail of K dynamics in representative soil samples: intermediate K, K fixation, mineral CEC, Q/I curves, diffusion ...
- Statistical determination of regression equations to estimate elements of K dynamics mentioned above from routine analyses.

At this stage of the work it is possible:

- To place the soil with regard to the general interpretation of soil analysis and so calculate the required modifications as described above (section 3).
- To define one or more sites representative of the soil type for experimentation.

Field experiments investigate crop response to applied nutrients at different levels of soil enrichment and/or response to increasing rates of K fertilizer.

There are two ways of going about things. One approach is to set up, by applying differential K dressings, different levels of soil K and to compare crop response to increasing dressings of K on the variously enriched soils. This will indicate the critical level of soil K and will measure the value of residual K in the soil. The other, is to proceed directly to investigation in detail of crop response. If the experiment runs over a lengthy period, there will be a cumulative effect of K dressings applied to preceding crops. Account should be kept of the K balance and this with annual soil analysis will also indicate the level of soil K which should be aimed for.

Details of the methods used are available elsewhere *[6, 19, 27]* and an up-to-date summary is in course of preparation, so they will not be discussed here. Suffice it to say that all factors should be controlled in such a way that the aim of the experiment will be realisable. Among other things it is important that:

- N fertilizer should be sufficiently high and soil magnesium at an adequate level, N × K and Mg × K interactions being considerable.
- There should be sufficient replication to allow proper statistical treatment.

6. Conclusion

Rational fertilizer use is one of the essential requirements for the improvement of crop productivity. Too high rates increase costs and may result in nutrient disequilibrium to the detriment of yield. Too low rates makes it impossible to realise the full potential of the soil – cultural technique – crop combination.

Methods of interpreting existing methods of soil analysis as indicating soil fertility have been discussed. The current philosophy of the *Aspach Research Centre* is based on identifying a desirable level of exchangeable K in relation to cation exchange capacity (or clay content) at a degree of saturation of the CEC. The resulting advice allows for replacement of crop removals plus a correction to bring the soil to the desired K level.

Further efforts must be made in the future to continue or develop experimentation to verify the effect of the numerous factors which influence the interpretation of soil analysis.

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Coordinator's report on the 2nd working session

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The topic of the second session «*K release and K fixation*» has important implications for practical agriculture. It is clear that for their direct K requirements plants depend on the K that can be readily released by the soil. *Goulding,* however, rightfully claimed that in the long run plants also benefit from the fact that many soils are capable of retaining K that was applied to them and was not absorbed by the first crop grown after application.

In fact, it should not be forgotten that the boundary line we draw between exchangeable and non-exchangeable portions of soil K is an arbitrary and artificial one, and that during one growing season crops often manage to withdraw from soils quantities of K which are several times larger than the quantity of K originally present in so-called exchangeable or available form.

Goulding pointed out that in practical agriculture we are faced with the dilemma that many laboratory techniques capable of describing and predicting the behaviour of K in soils are too cumbersome and too expensive for practical use. In their survey of methods in use for determining available K, *Novozamsky* and *Houba* could only list simple extraction methods, none of which can shed any light on the behavior of K in soil.

Staunton in her paper made it clear that for a proper evaluation of the rate of supply of K to plant roots not only diffusion through soil solution, but also diffusion along exchange sites will have to be taken into account. When soils differ in the ease with which such diffusion processes can take place, one must realize that simple laboratory extraction procedures will never be able to account for such differences.

In many West European countries the study of K-behaviour in soil may be simplified by the circumstance that only one type of clay mineral is involved. In their contribution to this Colloquium, *Bar and co-workers* pointed out that the adsorption characteristics of soils may be far more complex when more than one type of clay mineral is present.

Another important issue is the choice between a one-nutrient and a multi-nutrient extracting agent. Both systems are in use and both have their advantages and disadvantages. *Villemin's* contribution is an example of a system in which only potassium is under investigation. When every nutrient has its own extracting agent, soil testing can become so expensive that farmers may show a reluctance to regularly submit samples for testing. In order to avoid such an unsatisfactory situation, I think that multi-nutrient extracting agents will become more important in the near future.

Also with the use of such multi-nutrient extractants, the disadvantage remains that the multitude of soil characteristics affecting the availability of K in soil cannot be properly evaluated in a laboratory extraction procedure. For further progress in this field I can visualize a system in which a farmer places a number of strips of cation- and anion exchangers in his soil and, after a certain period of contact between soil and exchangers, recovers the strips and submits these to a soil-testing laboratory for analysis. After recharging, the strips could be returned to the farmer for repeated use. In such a procedure, the time-consuming collecting and handling of soil can be avoided. The quantities of nutrients collected on the exchangers are a function of more soil characteristics than can be evaluated in laboratory extractions of soil material, and can therefore serve as better estimates of nutrient availability than those obtained with the conventional soil-testing procedures.

Even with such a more natural system of nutrient withdrawal, a number of factors influencing the behaviour of soil K will be overlooked. For instance, the effects that root systems have on the availability of nutrients will not be fully evaluated, and weather conditions during the growing season may differ from those in the extraction period.

Nevertheless, I expect that in the near future progress will be made in the realm of more natural techniques employed to withdraw from a soil those fractions of nutrients which under field conditions make a contribution to the nutrition of our crops. In that way, the gap may be breached between knowledge compiled by mineralogists and the analytical ease and efficiency required by agronomists. It is in my opinion the task of agronomists to devise rapid and simple extraction methods that still allow full use to be made of knowledge acquired by mineralogists on the behaviour of K and other minerals in their natural habitat, namely the undisturbed soil exposed to regular climatic fluctuations.

Chairman of the 3rd Session

Prof. Dr. *U. Kafkafi*, Field Crops Department, Faculty of Agriculture, The Hebrew University of Jerusalem, Rehovot/Israel; member of the Scientific Board of the International Potash Institute

3rd Session

Potassium Dynamics in the Rhizosphere

Potassium Dynamics in the Rhizosphere and Potassium Availability

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Summary

Diffusion is the main process supplying K to the root. Methods for study of K concentration distribution near the root are briefly described. The extent of K depletion can be influenced by factors which affect diffusivity and results show that:

> Plants use both exchangeable and non-exchangeable K. Non-exchangeable K is taken up from within 1-2 mm of the root surface while exchangeable and non-exchangeable K is desorbed and transported further. Fertilization of salts not containing potassium and/or proton excretion influence availability of both, exchangeable and non-exchangeable K.
>
> K fertilization increases K availability because:
> (1) Concentration gradients steepen and K flux towards the root increases;
> (2) Spatial access for K is increased due to higher mobility in soil.
>
> Transport of K to the root is facilitated as soil water content increases.

The plant itself is an important factor in K availability.

1. Introduction

It is often postulated that soil nutrient content is the main factor limiting potassium availability. Soil tests based on mainly K concentration are used as indicators of fertility level in soil. It is trivial but often ignored that there are three prerequisites for nutrient uptake:

(i) the soil must contain nutrients,
(ii) roots have to be in the soil to take up the nutrients,
(iii) nutrients must be mobile to reach the root surface.

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It is well established that only a small fraction of soil K, if any, can come into contact with the root surface without being transported via soil water to the root. Hence, transport mechanisms are involved in supplying K, *e.g.* mass flow and diffusion as shown by *Barber [1962]*.

Mass flow, induced by water transpiration by the plant causes transport of K ions in soil water towards the root surface. Accordingly the amount of K supplied to the plant depends on flow rate of soil water and solution K concentration. *Barber [1962]* calculated for soils collected in the USA that mass flow could contribute from 5 to 200 percent of the amount of K taken up by the plant. If mass flow results in a higher rate of transport than the plant can take up, nutrient accumulates at the root surface. If transport through the soil is not sufficient to meet the plant's needs, soil solution concentration at the root surface is reduced. This causes a net diffusive flux towards the concentration sink, that is the root surface. The flux rate is dependent on the size of the diffusion coefficient of potassium in soil and the gradient between solution concentration at the root surface and the surrounding soil. Nutrient flux towards the plant root can thus be expressed mathematically as the sum of mass flow and diffusion (equation 1).

For most of the German soils we studied diffusion was the main process of K supply to the plant because of low soil solution concentration relative to plant absorption. Consequently soil solution is depleted during the course of time of K uptake, being buffered at the same time against this change in concentration by desorption of K from the solid phase. Schematically this process is shown on the lefthand side of Figure 1. If concentration distribution perpendicular to the root were measured at intervals the result would be a graph as given on the right side of Figure 1. The amount of nutrient absorbed by the plant root thus is given by two parameters:

(i) degree of depletion at the root surface which is the result of the interaction of root K absorption and potassium flow towards the root, and
(ii) the extension of the depletion zone.

How far the depleted soil zone extends from the root surface depends on the size of the effective diffusion coefficient (equation 2) and thereby the amount of soil that feeds a unit of root surface area. The effective diffusion coefficient is given by multiplication of the diffusion coefficient in water (specific for each element) with factors that modify flow of K through soil as compared to pure water (equation 3).

$$F = D_e \frac{dc}{dr} + v\, c_l \qquad (1)$$

$$x = 2\sqrt{D_e t} \qquad (2)$$

$$D_e = D_l\, \theta\, f/b \qquad (3)$$

F = nutrient flux towards the root surface; D_e = effective diffusion coefficient; dc/dr = concentration gradient: change in concentration of the nutrient, dc, with distance from root surface, dr; v = water flux; c_l = concentration of soil solution; t = time; D_l = diffusion coefficient in water; θ = volumetric water content; f = tortuosity (impedance) factor; b = relation between change in concentration of diffusible ions, dc, and change in concentration of ions in solution, dc_l.

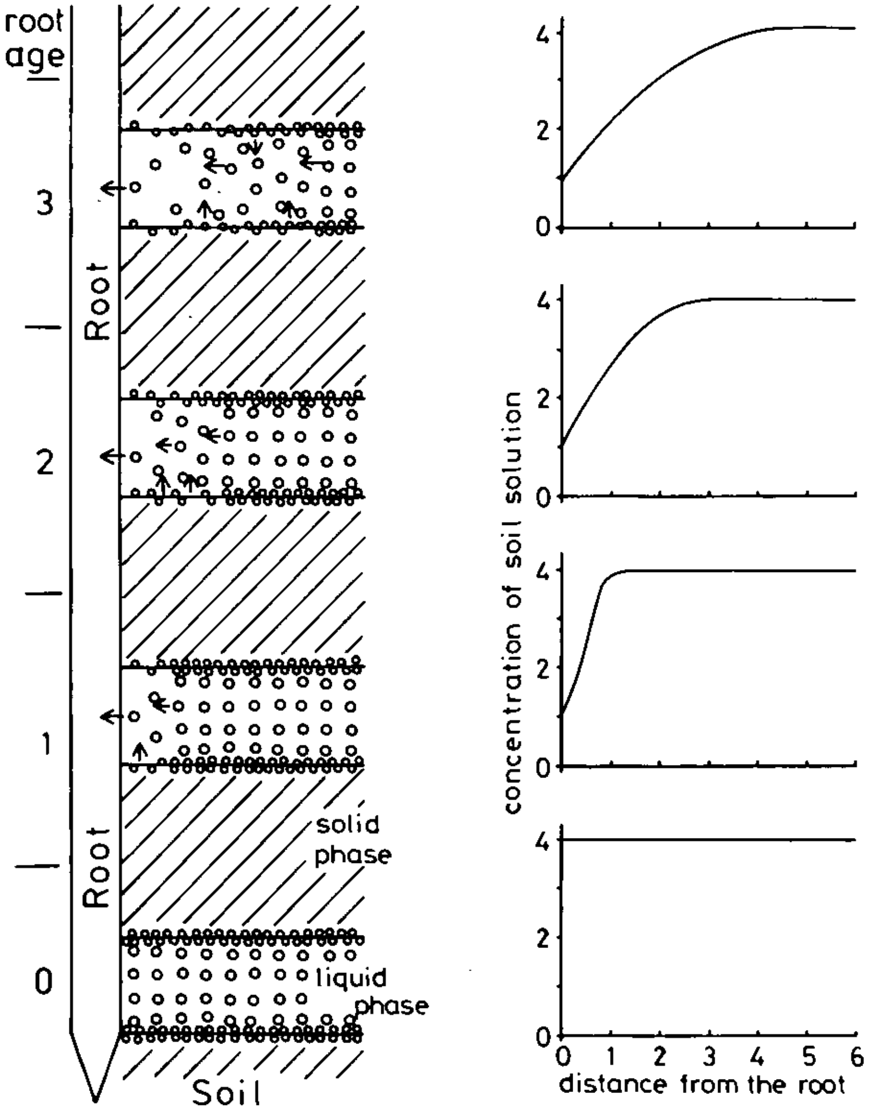

Fig. 1 Schematic representation of the process of nutrient uptake from the soil by diffusion controlled process and resulting concentration distribution around roots (after *Claassen*, unpublished)

This shows that to understand K availability in the soil-root-system one has to measure potassium concentration distribution in the vicinity of roots. Such measurements allow quantification of degree of depletion and extension of the depletion zone in the vicinity of roots. Bulk soil measurements are only satisfactory if *(i)* mobility is high compared to uptake, and hence no or only small concentration gradients are developed; this may be the case in highly fertilized soils with a low buffer power, and/or *(ii)* when plant roots are so close together that the soil between them is depleted almost uniformly, which may be the case in pot experiments or under cereal crops.

The aim of this paper is

- to introduce and briefly discuss methods that are used in rhizosphere research to measure and calculate potassium concentration distribution close to the root surface,
  and
- to show factors and their significance for K availability.

2. Methods to study K concentration distribution near roots

Several methods with their advantages and disadvantages are described.

2.1 Analysis of soil adhering to roots

This method tries to separate soil adhering to roots or root hairs form the bulk soil. Usually plants are grown in pots with finely soil. After the experiment roots with adhering soil are carefully separated from the bulk soil. The soil is then carefully washed from the roots or the roots are shaken gently to loosen the soil. This method was used by *Starkey [1931], Riley and Barber [1969, 1970], Hoffmann and Barber [1971], Sinha and Singh [1976] and Hendriks and Jungk [1981]).* Elements studied were calcium, magnesium, sodium, phosphate, and potassium.

Advantage of the method: *(i)* no additional equipment needed, *(ii)* fast and uncomplicated analyses of soil material possible *(iii)* comparison of rhizosphere and non-rhizosphere soil possible in pot and field experiments with standard soil test procedures.

Drawbacks of the method: *(i)* restricted to finely sieved soil, preferably with high sand content, *(ii)* no well defined cylinder of soil around roots, especially on coarse textured soils and plants with short root hairs, *(iii)* problems associated with root axes in rhizosphere soil that contain high concentrations of the nutrient under investigation and may cause experimental and analytical error, *(iv)* differences between rhizosphere and non-rhizosphere soil have to be pronounced to be consistent.

In summary this method gives qualitative information about changes in concentration close to the root.

2.2 Autoradiography

In this method soil is mixed with an active isotope of the element to be studied. A root growing into this soil will take up the isotope. If the soil is exposed to a x-ray film, regions with high activity will result in a higher film density (blackening) than regions where the plants did take up some of the isotope and where consequently the film density is lower. Concentration distribution perpendicular to the root is measured densitometrically from this autoradiography. The method was used in studies on potassium mobility in soil by *Bhat and Nye [1973], Claassen, Hendriks and Jungk [1981], Claassen and Jungk [1982].* For potassium rubidium was used as a tracer, except in the work of *Claassen et al. [1982].*

Prerequisites of the method: *(i)* root sections to be measured have to be at the soil surface, *(ii)* radioisotope has to be homogeneously mixed with the soil, *(iii)* optimum activity necessary for autoradiograph with high resolution. The nuclide has to be of low energy for high resolution of the autoradiograph and half life has to be long enough to carry out the experiment.

Advantages of the method: *(i)* undisturbed measurements of soil-root system, *(ii)* time course measurements possible on same root section, *(iii)* two tracers with different half life can be used simultaneously to investigate interaction.

«Crossfire» is a problem generally associated with autoradiography. Emission of radiation in all possible directions causes the image of the emitter to be larger than the emitter himself. Hence, film density is not a correct measure for activity. The problem becomes critical where there are big differences in activities, *e.g.* where a root has a much higher activity than the surrounding soil, or *vice versa.* In this case film density may be very much different from activity. Hence, densitometric measurements have to be corrected for crossfire if film density is not proportional to activity. One way to do this is described by *Claassen, Hendriks and Jungk [1981].* Soil containing the isotope is separated from inactive PVC material. The film density on the inactive side of the system being caused by crossfire from the active side is measured. With distance from the border between the two compartments film density declines. Using a mathematical procedure suggested by *Passioura [1972]* coefficients can be calculated to convert film density values into activity values. This procedure depends on a laborious empirical approximation *(Claassen et al. [1981]).* If one wants to convert activity distribution of an autoradiogram into concentration values this can be done by a procedure described by *Fried and Dean [1952]* or *Broadbent [1970].* Isotopically exchangeable potassium has to be calculated (for details see *Claassen and Jungk [1982]);* if the relation of activity to isotopically exchangeable K is constant, concentration can readily be calculated from the activity. However, this relation in many cases is not constant. In this case isotopic dilution studies can be conducted *(Claassen and Jungk [1982]).* The intention is to calculate the relation between ^{43}K activity and isotopically exchangeable K for different levels of K depletion. To do this soil containing the isotope is diluted successively with a solution similar to the soil solution, but devoid of K. Isotopically exchangeable potassium can be calculated for each desorption step. This gives information about the dynamics of potassium as the soil solution is depleted by the plant root. For more detailed description see *Claassen and Jungk [1982]*.

2.3 Soil samples from defined distance from root

Papavizas and Davey [1961] described a method to obtain soil samples from defined distance from sunflower seedling roots. *Helal and Sauerbeck [1981]* separated soil layers of known thickness and distance from a central soil volume which contained actively growing roots. Problems associated with both methods is a spatial resolution not high enough for nutrients of low mobility and difficulties in defining the start of the uptake period.

Thin slicing rhizospheric soil: The method produces a plane root surface by arranging individual roots to form a root mat. Roots and soil are brought into contact to allow root axes or root hairs to take up nutrients. The soil adjacent to the roots is cut into slices of defined thickness. The soil samples then can be analysed with standard procedures. *Farr, Vaidyanathan and Nye [1969]* used roots of onion and oilseed rape plants in contact with soil blocks to measure diffusion in soil towards a plane root surface. This method does not take root hairs into consideration which may be of importance for nutrient uptake for elements like phosphorus and potassium. *Kuchenbuch and Jungk [1982]* developed a method of separating roots from soil while allowing root hairs to penetrate the soil and take up water and nutrients.

Advantages of the method: *(i)* soil samples at defined distance from the root are obtained, *(ii)* can be analysed with standard soil test or other procedures, *(iii)* conditions influencing mobility, *e.g.* water content or soil bulk density can be changed easily, *(iv)* many elements can be analysed at the same time; *(v)* balance sheets of nutrients taken up from soil *versus* accumulated in the shoot are possible.

Drawbacks of the method: *(i)* conditions of diffusion are one-dimensional rather than two-dimensional, as is the case for roots growing in soil; as a result less soil is feeding one unit of root surface in experimental pots and the drop in concentration at the root surface is accelerated; *(ii)* in case of experimental design of *Kuchenbuch and Jungk [1982]* root hair density is very much higher than under cylindrical conditions of a single root; this may exaggerate the importance to some degree.

2.4 Desorption studies

Aim of the procedure is to simulate the process of nutrient uptake by the plant in a system without plant roots. Basic assumption is that plant roots take up nutrients from soil solution only and that this decrease in concentration causes desorption of nutrients from the solid phase. These values, *e.g.* solution equilibrium concentration and amount of K desorbed may be used to calculate the buffer power of the soil (equation 3), or can be used to calculate isotopically exchangeable potassium *(Fried and Dean [1952]; Broadbent [1970])*. Usually soil samples are diluted in low concentration salt solution, thus initiating a new process of equilibration between exchange sites of minerals and solution *(Claassen and Jungk [1982])*.

2.5 Modelling potassium transport to the root and uptake into the plant

Mechanistic mathematical models that account for the processes involved in nutrient flow through the soil towards the root and uptake into the plant have been developed on the basis of work by *Nye and Marriott [1969])*. The models describe diffusion and mass flow mathematically and combine these processes with nutrient uptake calculated with Michaelis-Menten kinetics. Several authors extended this basic approach to calculate uptake of a growing root system by changing boundary conditions and/or mathematical procedures *(Claassen and Barber [1976]; Cushman [1979]; Barber and Cushman [1981]; Cushman [1984], Syring, Claassen and Jungk [1986])*. The models have been tested for validity of mathematical solution *(Cushman [1979])* and for agreement of calculated results with measured uptake. Verification of the model predictions as summarized by *Barber [1984]* and shown by *Claassen et al. [1986]* and *Kuchenbuch, Claassen and Jungk [1986b]* indicate that the basic approach is realistic and the main processes of nutrient uptake from soil are represented in the model.

Advantages of the method: *(i)* after verification of the model the individual processes that led to the result can be investigated; a sensitivity analysis showing the effect of change of one parameter on the overall result can be conducted as in sensitivity analyses carried out by *Silberbush and Barber [1983]; (ii)* if model predictions do not agree with reality, research on the cause of this result may lead to new working hypotheses and consequently to new understanding of the soil-plant-system; mechanistic models are thus valuable research tools at the moment.

Problems of this approach: since some parameters required by the model are not very well known at the moment, assumptions often are necessary; these assumptions may influence the result as much as measured data that go into it. One must avoid believing the assumptions giving good agreement of calculated with observed results to be identical with – or better than – results obtained from an experiment. Even though the mathematics of the models are quite complex and an accidental verification of the model seems to be very unlikely – there is no substitute for experimental evidence for the assumptions.

Barraclough [1986] calculated the concentration gradients around roots that are necessary to allow uptake rates measured in the field. His calculations are based on the steady state model of *Baldwin, Nye and Tinker [1973]* that accounts for root competition and needs input data that are similar to the model of *Claassen et al. [1976]*.

3. Potassium depletion of the rhizosphere soil

3.1 Potassium availability in the rhizosphere

Plants take up potassium from soil solution only. This process usually decreases soil solution concentration and potassium is desorbed from the solid phase. Figure 2 shows the concentration distribution of potassium, ^{43}K, measured with autoradiography after 1.5 days of uptake on «Herrenhausen» soil *(Claassen and Jungk [1982])*.

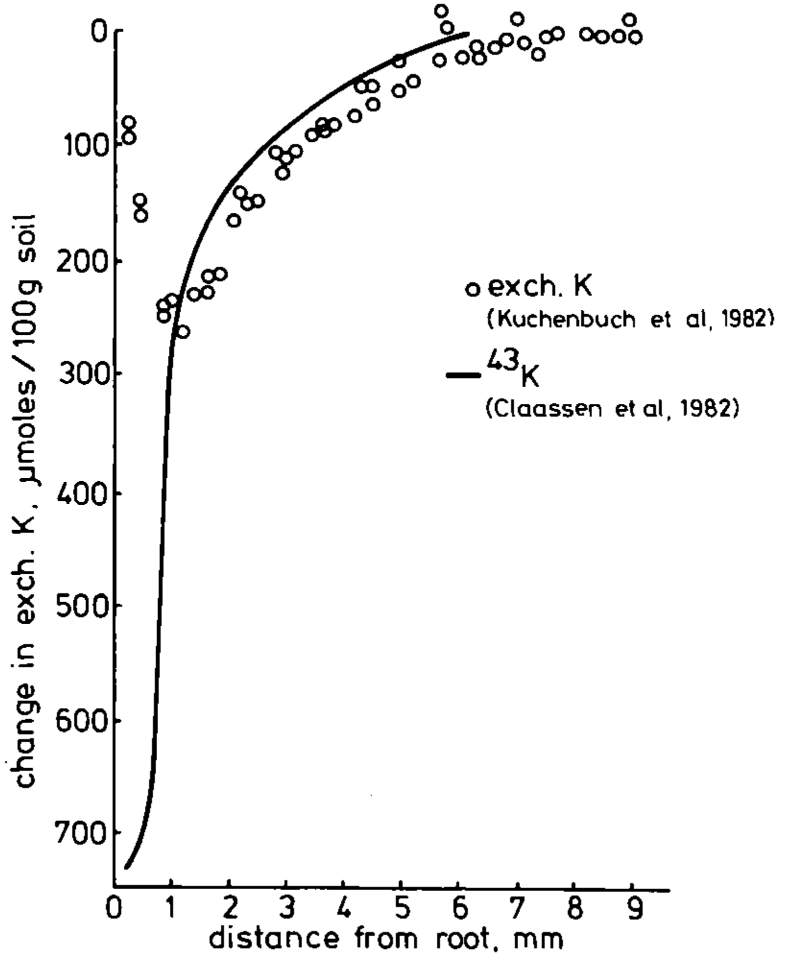

Fig. 2 Potassium concentration distribution in the vicinity of plant roots measured with different methods

The graph shows that at about 6 mm from the root surface concentration is identical with initial soil level. Closer to the root concentration decreases, most of the change occurs within 2 mm from the root surface. Total change in concentration is approx. 700 µmol K/100 g soil, whereas initial concentration of exchangeable potassium was 374 µmol/100 g soil. The authors conclude from this that non-exchangeable potassium is released as a result of potassium uptake by the plant. The same soil was used in a study by *Kuchenbuch and Jungk [1982]*; the concentration distribution of exchangeable K as measured with the method of thin slicing rhizospheric soil is given in Figure 2. A comparison of the two graphs shows that the extension of the depletion profile as measured with the two methods is the same, as well as the concentration distribution from 6 to 3 mm. Closer to the root autoradiography shows stronger depletion of the soil than exchangeable potassium. The difference in amount of K extracted with the two methods can be interpreted as amount of potassium from non-exchangeable sources that was taken up by the plant. Almost all of the uptake from non-exchangeable K sources occurs within 2 mm from the root surface. Similar results are given by *Kuchenbuch [1984]*. Obviously spatial access to non-exchangeable potassium is restricted to a soil layer very close to the root only, but within this region large amounts of non-exchangeable K are chemically available.

3.2 Influence of exchange processes on potassium availability

So that potassium can be desorbed from exchangeable or non-exchangeable sources into soil solution ion exchange is necessary. Since calcium in arable European soils is the dominant ion it will balance most of the exchange. However, if a salt is added to the soil, the cation will exchange potassium from the soil particle into soil solution, thus reducing K buffer power. Figure 3 shows an example of the result of NaCl fertilization on concentration distribution of exchangeable potassium in the vicinity of roots. As would be expected the extension of the depletion zone increased, increasing the soil volume feeding the root. Degree of depletion at the root surface is not changed. Hence, potassium availability is not only dependent on K content of the soil but may be influenced by factors that usually are not considered in fertilizer experiments, *e.g.* exchange processes.

It has been shown that plants are able to use non-exchangeable K in the vicinity of roots where potassium concentration is low (Figure 2). Generally all ions are able to desorb non-exchangeable potassium, however, there are differences in efficacy. Very effective are protons, having a small ion radius and being able to penetrate into interlayer spaces of illites more readily than other ions *(Rich [1964]; Rich and Black [1964])*. Acidification of a silt loam soil in a system without plant roots resulted in an increase in concentration of exchangeable potassium and in soil solution concentration, and consequently in a higher diffusion coefficient (Table 1, after *Kuchenbuch [1983]*). Adding lime reversed some of the proton effect. Table 1 thus shows that protonation of the soil that does not change soil pH very much, *e.g.*

from 7 to 6.7, may set free non-exchangeable K and change K mobility, D_e, more than 4-fold.

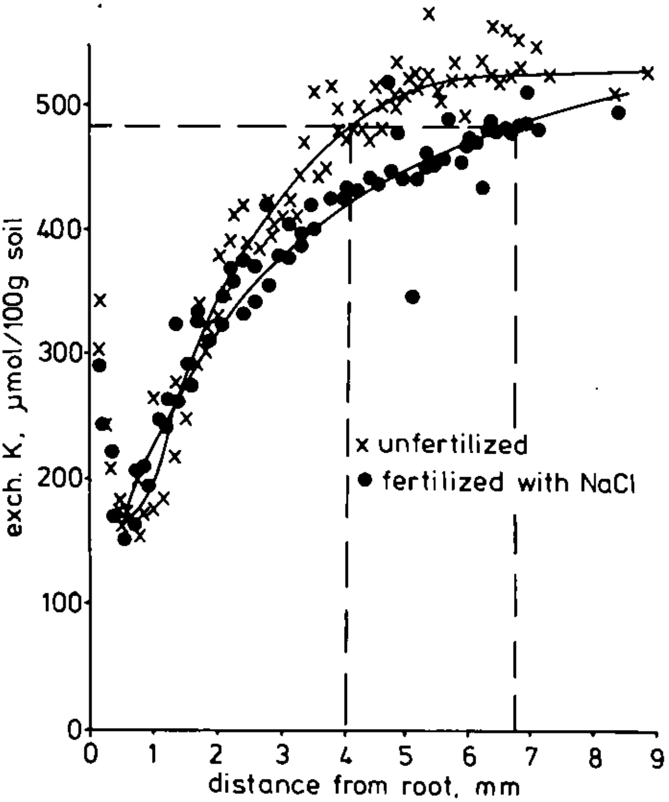

Fig. 3 Influence of NaCl application on the potassium depletion profile in the rhizosphere soil of rape seedlings (0.36 me NaCl/100 g soil)

Table 1 Influence of acidification and liming the acidified soil on parameters of potassium availability

treatment	pH	exch. K µmol/100 g	soil sol. conc. µM	D_e 10^{-7} cm^2 s^{-1}
untreated	7.0	522	620	5.3
acidified*	6.7	625	2800	18.0
acidified+ lime**	7.6	494	1550	6.8

* 5 µmol H^+/100 g soil
** 5 µmol H^+/100 g soil + 5 µmol CaO/100 g soil

It is difficult, however, to interpret the changes of exchangeable K, soil solution concentrations and effective diffusion coefficient in terms of potassium uptake by the plant. The reason is that the measurements represent an equilibrium situation, whereas the plant root disturbs the equilibrium and initiates changes during the course of time. Hence, the conclusions from Table 1 have to be considered qualitatively rather than quantitatively. A sensitivity analysis of potassium uptake carried out by *Claassen [1986]*, however, indicates that under conditions of low root density (cm root/cm^3 of soil) the concentration of soil solution largely determines potassium uptake by the plant. Soil solution concentration was influenced more than exchangeable K when the soil was acidified, and hence an increased potassium uptake would be expected.

It is well known that plant roots can change the pH of the surrounding soil and influence availability of macro- and micronutrients *(Miller, Mamarial and Blair [1970]; Riley and Barber [1971]; Smiley [1974])*. To investigate the change of pH in the vicinity of roots *Kuchenbuch [1983]* measured pH in soil samples at a known distance from the roots. The results are given in Figure 4, showing that oilseed rape plants decrease pH from 7 to 6.3, about the change that was used in Table 2 to show the effect of protonation of the soil on potassium availability. We conclude from Table 1 and Figure 4 that excretion of protones may be a factor in the availability of non-exchangeable K. This thesis is supported by the fact that the soil layer that is acidified extends about as far into the soil as the layer that contributes most of the non-exchangeable K as can be seen from Figure 2.

Table 2 summarizes the effect of liming an acid soil on potassium uptake from exchangeable and non-exchangeable sources *(Kuchenbuch [1983])*. The experiment was carried out with the method of thin slicing rhizospheric soil, and a balance sheet was calculated from data for K uptake as measured by plant analysis *vs.* exchangeable potassium being lost from the soil. Liming increased pH considerably, at the same time reduction in exchangeable potassium was observed. Similar results were reported by *Mehlich [1943]* and *Thomas and Coleman [1959]*. *Németh and Grimme [1972]* attribute the decrease of exchangeable K to an increase of selective sorptive sites within the minerals due to a reduced blocking of K-selective sites by aluminium compounds.

Table 2 Effect of liming on pH, exchangeable K and potassium uptake by oilseed rape plants (soil «Hoya», 1S; plants 4 days old)

treatment	pH	exch. K µmol/100 g	(1) K uptake µmol/pot	(2) exch. K$^+$ lost from soil, µmol/pot	nonexch. K^{++} taken up µmol/pot
unlimed	4.8	360	33.7	8.9	24.8
limed	7.5	330	22.1	6.8	15.3

$^+$ calculated from depletion profiles $^{++}$ difference between (1) and (2)

However, the effect of liming in terms of change in concentration of exchangeable K is not very strong, nor is the change in potassium uptake from exchangeable K *e.g.* 8.9 *vs.* 6.8 µmol K. The plants did take up 22.1 µmol/pot on the limed treatment as compared to 33.7 µmol/pot on the unlimed soil. This reduction in K availability is due to a reduction in availability of non-exchangeable K, as can be calculated as the difference between plant uptake and exchangeable K lost from the soil. Even though exchangeable K did not change much, the reduction in availability of non-exchangeable K may be another explanation for the observation that liming may reduce potassium concentration in plants besides ion competition for uptake at the root surface.

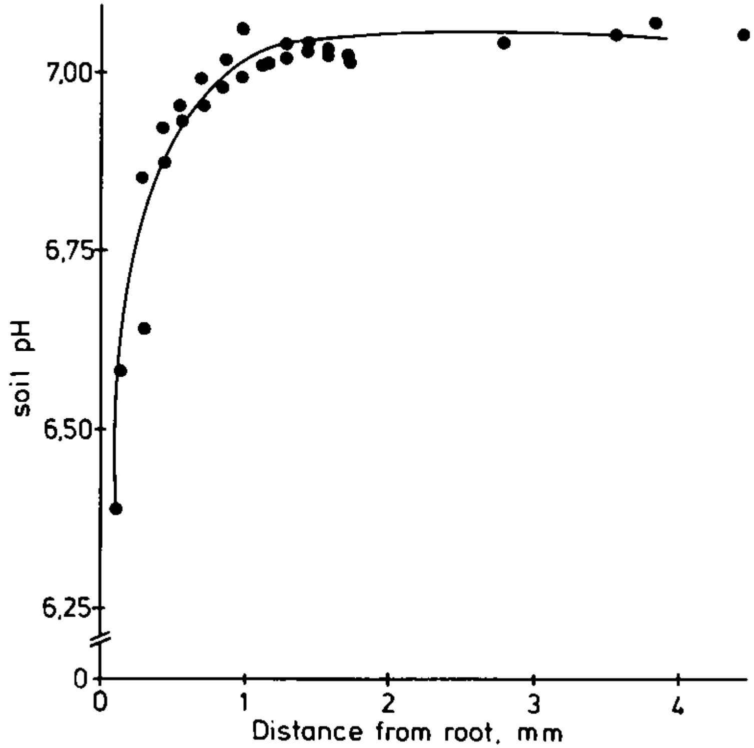

Fig. 4 Soil pH in the vicinity of oilseed rape plants. Plants are 4 days old, pH measurements in 0.05 M $CaCl_2$, soil: solution ratio = 1:50

3.3 Influence of soil K content on K availability

In a study by *Kuchenbuch et al. [1984]* a silt loam soil was precropped with maize to decrease soil K level (−K), left unchanged (K_o), and fertilized with KCl (+K). Table 2 shows that as a result of the pretreatment exchangeable K increased, consequently buffer power decreased and the effective diffusion coefficient increased.

The effect of these changes on concentration distribution is shown in Figure 5. Within a distance of 1 mm from the root surface exchangeable potassium is decreased to the same level; this is an indication that not all exchangeable potassium is available to the plant. The higher the K content of the soil, the higher the change in concentration close to the root surface, so that chemically available potassium increases quite strongly. On the other hand, the depletion zone extends further into the soil as the soil is fertilized; the reason is an increased mobility as the result of increased effective diffusion coefficient (Table 2), allowing for a diffusion from points further away from the root (equation 2). The result is an increase in soil volume feeding one unit of root surface area, *i.e.* an increased spatial access to soil K. This can be calculated on the assumption of cylindrical conditions for Figure 5.

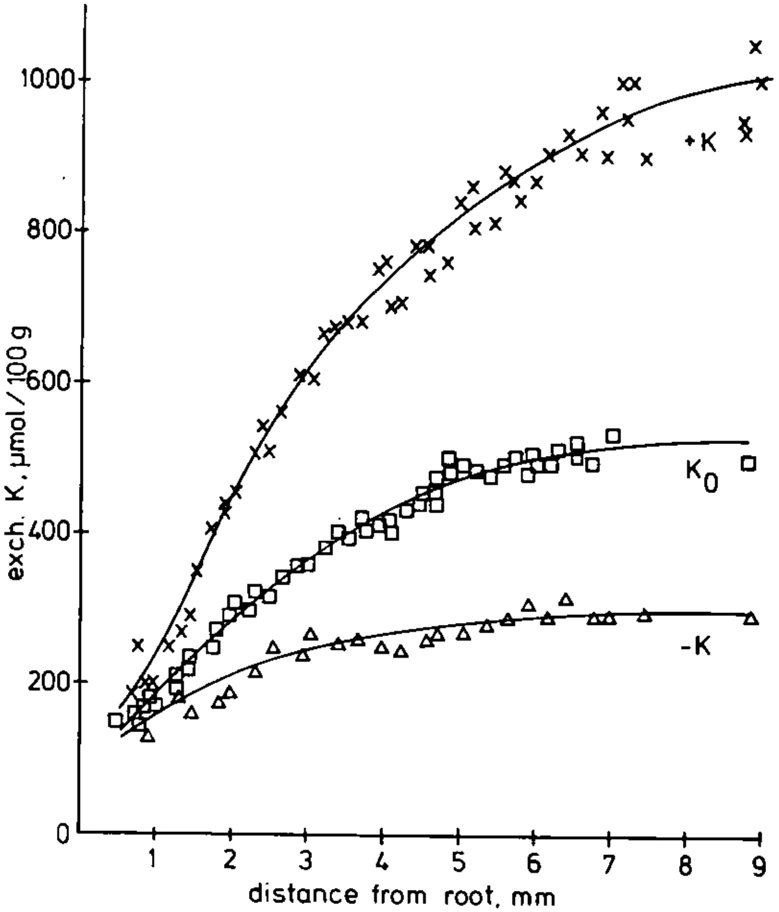

Fig. 5 Potassium depletion profiles in the rhizosphere soil of rape seedlings at different soil K levels after 7 days

The results are given in Table 3. As the extension of the depletion zone increases from 4.6 mm to 6.3 mm, the soil volume feeding 1 cm of root doubles from 0.66 to 1.24 cm^3.

Table 3 Influence of soil K content on soil parameters of potassium availability (Rape 7 days old)

soil	exch. K µmol/100 g	b$^+$	D_e 10^{-7} cm^2 s^{-1}	extension mm	depletion zone volume^{++} cm^{-3}/cm	avail. K^{++} µmoles/cm
− K	295	24.5	1.2	4.6	0.66	0.42
K_0	517	9.0	5.3	5.3	0.88	1.32
+ K	1365	2.6	27.0	6.3	1.24	9.10

$^+$ units for b, buffer power, are $\dfrac{\mu\text{mol K/cm}^3\text{ soil}}{\mu\text{mol K/cm}^3\text{ soil solution}}$

$^{++}$ calculated from 1-dimensional depletion profiles of Figure 5 under the assumption of cylindrical conditions for 1 cm of root

The combined effect of increased soil volume and stronger depletion within this volume results in an increase in available K for one cm of root from 0.42 to 9.10 µmoles K. We conclude from these results that fertilization acts in two ways: it increases the soil volume that feeds one unit of root, *e.g.* increases the spatial access for soil K, and it increases chemically available K, allowing for a stronger depletion of K at the root surface. Both factors result in an increase of K availability that is higher than exchangeable K would indicate.

Extension of the depletion zone has been found to be a factor of K availability because it limits the soil volume feeding a root segment. However, this is true only if no inter-root competition for potassium takes place. If the depletion zone extends further into the soil than the half distance between neighboring roots, the depletion zones will overlap. As a result, soil volume will be restricted by the distance between the roots, and the amount of available nutrients will be strongly determined by the second factor of availability, this is amount of chemically available K. If one compares the extension of the depletion zone on the low K soil in Figure 5, which is 4.6 mm, with half distances between roots that have been measured in the field, one must conclude that with root densities of 3 or greater (half distances < 4 mm) almost all the soil will feed the root under a cereal crop with root densities from 5 to 15 cm/cm^3 for the topsoil layers *(Barraclough and Leigh [1984])* and a large portion of the topsoil soil layers at root densities from 1 to 4, as reported for field grown maize by *Mengel and Barber [1976]* and *Kuchenbuch and Barber [1987]*.

3.4 Influence of soil water content on K availability

Equation 3 shows that mobility of soil K, *e.g.* the diffusion coefficient, is determined by volumetric water content and its interdependence with the tortuosity factor. This has been shown by *Rowell, Martin and Nye [1976], Barraclough and Tinker [1981]*, and *Kuchenbuch et al. [1986a]*. The effect of soil water content on potassium uptake, plant growth, and potassium uptake rate has been measured *(Mackay and Barber [1986])*. Results of *Kuchenbuch et al. [1986b]* show that potassium uptake rate is dependent on potassium mobility in soil, that is the product of θ and f. The higher the soil water content, θ, the higher the impedance factor, f, the higher the diffusion coefficient (equation 3). The higher the diffusion coefficient the higher the flow rate towards the root (equation 1), and consequently the potassium uptake rate. However, these conclusions are qualitative only. At the moment they cannot be quantified experimentally. Hence, mathematical models are used to describe the whole process, and these models are used after verification to get an overall picture of the processes and to investigate the importance of the factors involved.

Figure 6 depicts results of mathematical modelling of the influence of soil water content on soil solution concentration distribution around roots and the potassium uptake rate in the course of time *(Kuchenbuch et al. [1986b])*. For the dry soil with $\theta = 0.09$ soil solution concentration at the root surface drops to a value close to 0 within 7 days. Accordingly potassium uptake rate which is dependent on soil solution concentration also drops as quite rapidly from the start of the experiment. If soil water content is at a higher value no steep concentration gradients can be observed close to the root surface; concentration decreases in steps of the same size up to day 10, being higher at this than in the dry soil after 4 days. Consequently potassium uptake rate remains almost at maximum from day 0 to 10 of the experiment. We conclude from these calculations that water content of the soil modifies potassium availability appreciably; at low water content transport to the root may limit potassium uptake rate earlier than at high water content. The degree of influence depends on initial soil K content; we expect plants on a soil deficient of potassium to react much more strongly to changes in soil water content than on high K soils. Indications for the strong influence of soil water content on potassium uptake and yield of different crops are given by *Paauw [1958], Barber [1959]*, and *Mengel and Braunschweig [1972]*.

At the half distance between two neighboring roots, ca. 3 mm from the root surface in the examples of Figure 6, the soil is totally depleted of K in case of high water content, whereas there is some potassium left in the dry soil. However, the total soil volume is depleted of K even under dry conditions, showing that mobility of potassium is not a very important factor determining potassium uptake on this soil.

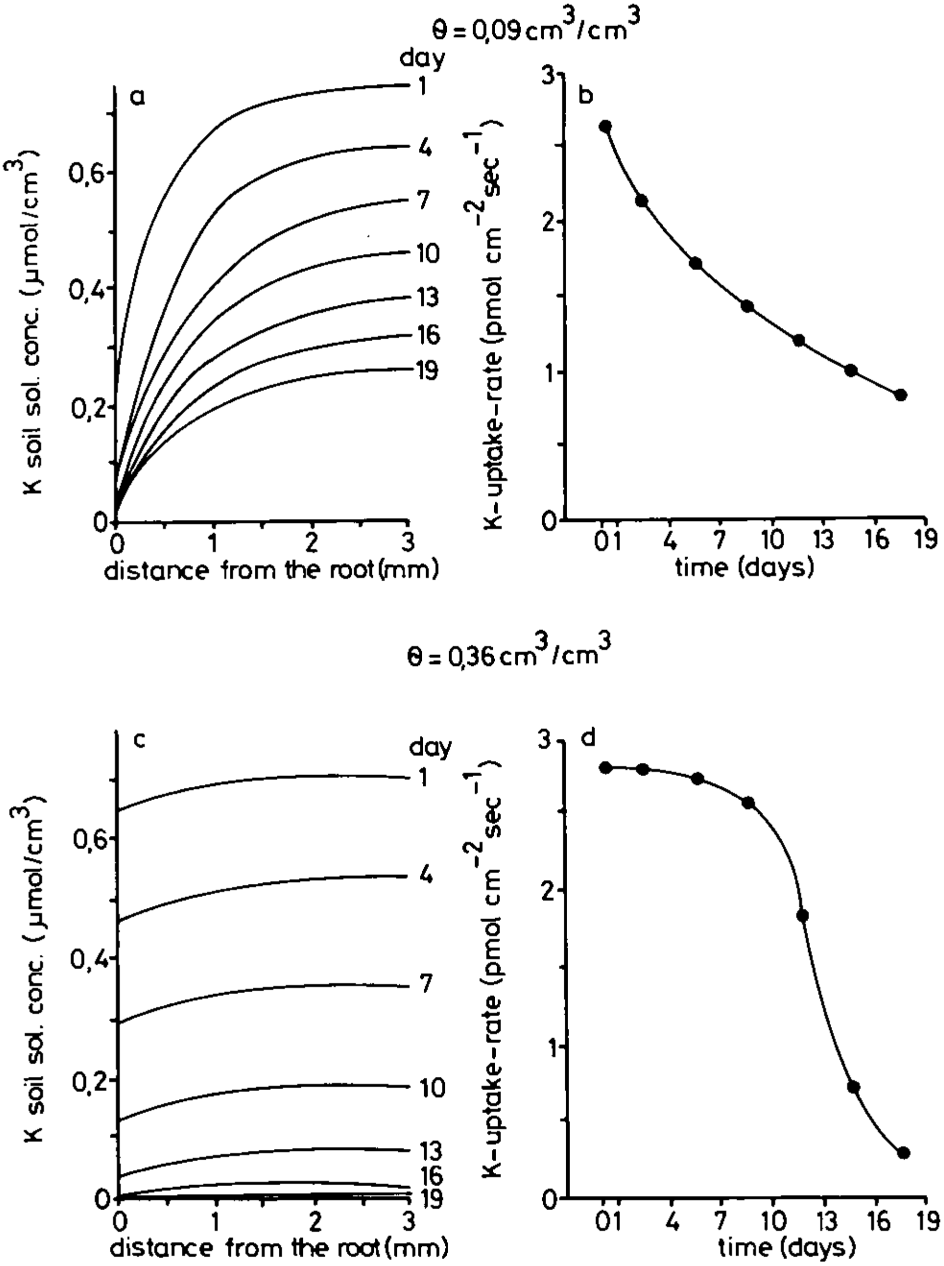

Fig. 6 Potassium depletion in the vicinity of onion roots and K uptake rate as a function of time of uptake at two moisture levels of the soil (Soederhof silt loam)

4. Conclusions

The data presented here support the view that potassium is transported towards the root mainly by diffusion. Depletion zones in the vicinity of roots measured by different methods (Figure 2) are a strong indication. Decrease of K concentration at the root surface (in soil solution, exchangeable or non-exchangeable) and extension of the depletion zone may be considered as the two parameters that determine the amount of K that is available to a root segment. These parameters are influenced by exchange processes between solid and liquid phase, and transport in soil water towards the root. Transport depends on buffer power, volumetric water content, and the tortuosity factor of the soil. Potassium flux rate into the root in addition depends on the size of the concentration gradient of K in the rhizosphere soil, being a result of plant nutrient uptake. Hence the plant itself becomes an important factor of nutrient availability – there is no available nutrient in soil unless the plant root disturbs the equilibrium in soil and induces the flux of nutrients towards the root. The amount of nutrient that may become available depends on spatial access, a soil factor, and degree of rooting, *i.e.* root density, a plant factor that modifies availability of nutrients and has not been considered in this paper.

However, under conditions of low K mobility in soil root density has been shown to be positively related to potassium uptake and yield of corn *(Kuchenbuch and Barber [1987])*. As a result of these interactions a single factor of nutrient availability – nutrient content of the soil, nutrient mobility, and rooting intensity – cannot be expected to be an accurate indication for soil fertility under all the different ecological conditions of farming.

More research is needed for a better understanding of the interactions between plant and soil in order to isolate and quantify the important parameters to describe soil fertility; the ultimate goal of rhizosphere research could be a better understanding of the whole system and development of a mechanistic model that has a high predictive value for potassium availability in the field.

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Methods of Sampling and Investigation of Rhizosphere Soil

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Summary

The rhizosphere is an area of intensive interactions between plant roots and soil. These interactions are of considerable significance for the nutrient availability to the roots. However, limited progress has been so far achieved towards clarifying and quantification of the nutrient dynamics in the rhizosphere. This is mainly attributed to the lack of appropriate methods. One of the most serious problems which retarded research progress in this field is the difficulty of separating and sampling the actual rhizosphere soil for analysis. This paper gives a comparative evaluation of various methods with special reference to the techniques developed by the authors.

1. Introduction: Root-microbe-soil interactions

Root influences on soil were already known to both soil microbiologists and agricultural chemists during the last century. *Sprengel* for instance described the architecture and functions of plant roots as early as 1839. He already considered selective nutrient uptake in connection with root exudations and plant allelopathy, pointing out that plants can prepare part of their food by releasing acids which dissolve otherwise insoluble mineral substances. Later on *Dyer [1894]* attributed this «feeding power» of plant roots to the acidity of the root sap while *Czapeck [1896]* confirmed that the carbonic acid excreted by roots makes available plant nutrients in the soil. *Hiltner* in 1904 coined the term «rhizosphere» to denote the sphere of influence of roots and referred to both its phytopathological and nutritional significance. However, progress towards further clarifying the processes governing nutrient availability in the rhizosphere was rather slow during the subsequent decades, mainly due to the lack of appropriate methods for sampling and analysis of the rhizosphere soil. As an alternative concept agricultural chemists devoted much effort to developing extractants for the «available» fraction of plant nutrients.

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The introduction of the concept of «nutrient mobility» by *Bray [1954]* revived interest in clarifying factors which govern the transport of nutrients to the root and establish nutrient gradients at the root-soil interface *(e.g. Barber [1962], Nye [1966], Passioura [1966])*. Along with these efforts, new techniques were developed or adopted from other research fields which made possible further progress in rhizosphere research in recent years. The rhizosphere now turned out to be a field of highly complex root-microbe-soil interactions. These are primarily attributed to three types of activity of the growing root:

1. fluctuating withdrawal of water and solutes,
2. physical stress on adjacent soil aggregates and
3. release of organic materials.

These primary processes initiate a series of secondary interactions *(Helal and Sauerbeck [1984, 1986a, 1987])* of considerable ecological and plant nutritional significance. Understanding these interactions is a basic requirement for further development and refining of methods in rhizosphere research. Therefore a brief discussion of important rhizosphere processes is given below through which reference to relevant methods and related problems will be made. It should be mentioned here, however, that comprehensive treatment or citation is impossible within the scope of this paper.

2. Water and solute gradients

The transport of water from the soil solution through the plants to the atmosphere is governed by the water potential gradient at both interfaces *(Slatyer [1967])*. Depending on the rate of water uptake by the plant relative to the water flow in soil to the root surface, the roots may strongly reduce the water potential of rhizosphere soil *(Dunham and Nye [1973])*. Consequently both rhizosphere and root water potential show periodic variations related to the change in transpiration rate *(Huck et al. [1970])*. Fluctuation of the rhizosphere water content affects in a complex way microbial activity, stability of soil organic matter and soil aggregates *(Agarwal et al [1971], Harris et al [1966], Reid and Goss [1982])*, as well as binding, diffusion and mass flow transport of nutrients to the root surface *(Nye and Tinker [1977])*.

Working with sieved soil in model systems under controlled conditions and near-constant soil water content enables detection of changes in solute concentrations in the rhizosphere. By the application of refined autoradiographic methods, for instance, nutrient concentration gradients have often been demonstrated *(Bhat and Nye [1973], Claassen et al [1981])*. It should be mentioned, however, that root turnover investigations *(Sauerbeck and Johnen [1977], Steen [1984], Helal and Sauerbeck [1986a])* indicated a highly dynamic system involving simultaneous breakdown of old and initiation of new roots. Accordingly, the active root-soil interface is continuously changing with limited possibility for the buildup of concentration gradients.

3. Physical root-soil interaction

Plant roots surrounded by a rigid medium can develop a considerable hydrostatic pressure *(Pfeffer [1893])*. This enables the growing root to displace soil particles from its path *(Whitely and Dexter [1984])*. Consequently, the magnitude of physical interaction between roots and soil will depend on the resistance of the soil to displacement and deformation *(Sprengel [1839])*. However, soil penetration resistance is a complex function of several soil properties including particle size distribution, aggregate stability and the characteristics of the void system in the soil *(Barley and Greacen [1967])*. Root observations *(Rogers [1939], Huck and Taylor [1982], Wang et al [1986])* show that roots tend to follow the way of least resistance and therefore grow preferencially along preexisting cavities (*e.g.* earthworm routes and channels of decaying roots) which are wider than their own diameter. Consequently roots under field conditions have only partial soil contact. Optical investigation of undisturbed soil-root interfaces *(Altemüller [1987], Altemüller and Haag [1983], Lund and Beals [1965])* confirm this view and demonstrate the difficulty of estimating the magnitude of the absorbing root surface. Considering the entire root surface as absorbing area, as usually assumed in root modelling *(Barber [1984], Cushman [1984])* is an obvious oversimplification of the situation.

In the absence of channels the root may be forced to displace the soil under pressure and therefore crush some soil aggregates *(Helal and Sauerbeck [1986b])*. Any such change in aggregation or density of rhizosphere soil is expected to modify a series of related processes such as soil-root contact and supply of nutrients to the root surface *(Phillips and Brown [1965], Parish [1971])*.

4. Exudation and turnover of roots

Plant roots release a great variety of substances into the soil. This includes leakage of diffusible compounds, active secretion of high molecular weight substances as well as lysis of sloughed cells and drying tissue *(Rovira and Davey [1974])*. A considerable part of our knowledge on root exudates came from simplified work with plants grown in sterile nutrient solution. This led to an underestimation of carbon release and the related root influences on soil for some time. It is known now that both microorganisms *(Vancura et al [1977])* and the physical interaction with the soil *(Barber and Gunn [1974])* have a considerable effect on the exudation and turnover of roots. A quantification of the carbon flow in the rhizosphere of plants growing in soil became possible only through the introduction of methods for homogeneous labelling of plants with ^{14}C (Figure 1). The most important feature of these methods is a gas-tight separation between shoot and root spheres in order to maintain a constant specific activity of the $^{14}CO_2$ supplied continuously to the shoots. The technique was originally developed to produce ^{14}C-labelled plant material for humus research *(Sauerbeck and Johnen [1971])*. It was then soon realized that it also offers a possibility for quantifying the carbon input into the soil by growing roots. The results of such experiments *(Sauerbeck and Johnen [1977])* show that a considerable part of the plant carbon is released from the rhizosphere as CO_2 originating either from root respiration or from microbial decomposition of root-derived organic material.

Experimental differentiation between these two components is difficult due to the complex interaction between plant roots and microbes, especially in view of the microbial production of substances which modify root physiology and exudation *(Brown [1972], Rovira and Davey [1974])*. These interactions throw much uncertainty on such estimates of the organic root carbon released into the rhizosphere which are based on comparisons between sterile and non-sterile roots *(Warembourg and Billes [1979])*. An alternative way is the short-term application of antimicrobial agents during the collection of exudates *(Minchin and McNaughton [1984])* and/or CO_2 *(Helal and Sauerbeck [1987])* from the rhizosphere of non-sterile plants. The results obtained in this way by the authors (Table 1) suggest that up to 84% of the root carbon input into the rhizosphere is in fact released from the roots in organic form with corresponding effects on the surrounding soil.

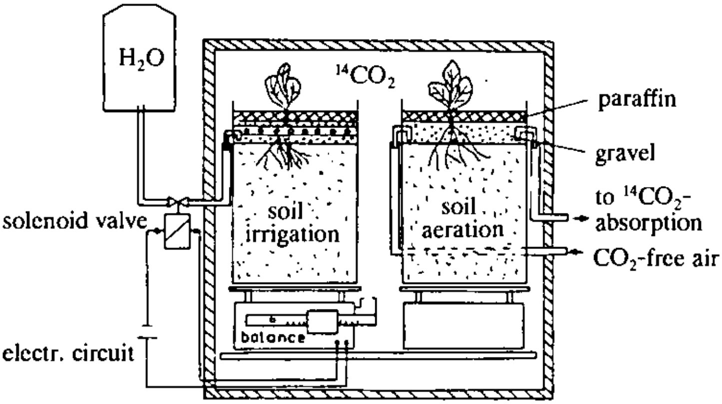


Figure 1 Production of uniformly ^{14}C-labelled plants (Sauerbeck and Johnen 1976)

Table 1 Effect of a short term treatment (6 hours) of the roots of ^{14}C-labelled, 3 weeks old plants grown in sand culture with p-hydroxymercuriphenylsulphonic acid (PHMPS) on the $^{14}CO_2$ development from the rhizosphere *(Helal and Sauerbeck [1987])*

	Phaseolus vulgaris		*Zea mays*	
	mg ^{14}C pot^{-1} h^{-1}	relative	mg ^{14}C pot^{-1} h^{-1}	relative
control	2.12	(100)	3.62	(100)
PHMPS (10 ppm)	0.51	(24)	0.58	(16)

5. Nutrient availability in the rhizosphere

Root exudates affect plant nutrient availability directly by modifying the solubility, sorption and diffusion of nutrient elements *(Nagarajah et al [1970], Jayman and Sivasubramaniam [1975], Kepert et al [1979], Gardner et al [1983], Morel et al [1986])*. In addition, extracellular root enzymes play a role in rhizosphere nutrient metabolism *(Chang and Bandurski [1964], McLachlan and Marco [1982])*. However, soluble exudates constitute only a minor fraction of root carbon released into the rhizosphere *(Rovira and Davey [1974])*. Furthermore, due to the considerable microbial activity in the rhizosphere, soluble exudates are only of low persistence. Their accumulation to concentrations necessary for a significant chemical interaction with the soil seems to be limited. The role of the root carbon in rhizosphere nutrient turnover should therefore be sought in its function as a source of energy, carbon and nutrients for the rhizosphere microbial population.

In addition to the development of techniques for homogeneous ^{14}C-labelling of plants and the differentiation between microbial and root respiration, the introduction of methods for the determination of the soil microbial biomass *(Jenkinson and Powlson [1976])* opened new ways for a quantitative treatment of carbon and energy flows in the rhizosphere. An example of the results obtained by combined application of these techniques is presented in Table 2. These results show that about 20% of the whole photosynthetic carbon was released by the growing roots in the soil, which confirms earlier findings of *Sauerbeck and Johnen [1977]*. Furthermore, these results demonstrate the utilization of root-derived carbon by the rhizosphere microbial biomass.

Table 2 The ^{14}C-balance of 30 d old maize plants.
$^{14}CO_2$ (35 μCi/g C) was supplied continuously to the shoots from day 7-30

	^{14}C-distribution on day 30 mg/pot	%
shoot	1692	57
root	712	24
root respiration and decomposition	484	16.3
rhizosphere microbial biomass	48	1.6
organic metabolites	33	1.1
sum	2969	100

6. Problems of sampling rhizosphere soil

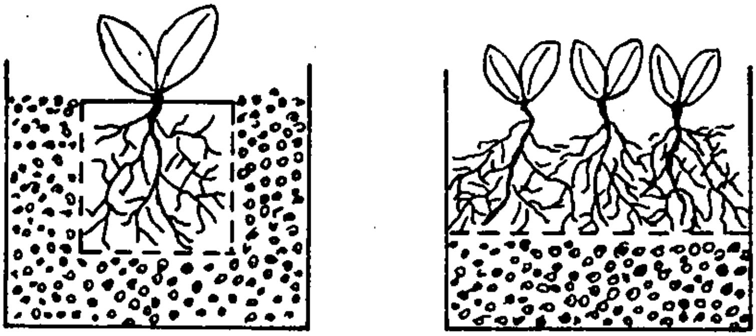
Considerable efforts have been devoted in recent years to developing techniques for sampling the rhizosphere soil. This would offer new possibilities for investigating root-microbial interactions related to rhizosphere nutrient turnover. However, most methods still suffer from technical or conceptual insufficiencies.

A classical, widely applied method for sampling involves careful removal of the roots from the soil after adjusting the soil moisture to a suitable level (40-50%

W.H.K.). Soil adhering to the root is considered rhizosphere soil. However, investigations of the P-turnover in soil isolated by this technique in the authors' laboratory yielded controversial results *(Helal and Sauerbeck [1981a])*. Therefore the authors *(Helal and Sauerbeck [1981b])* questioned the validity of this method and attributed its inadequacy mainly to two problems:

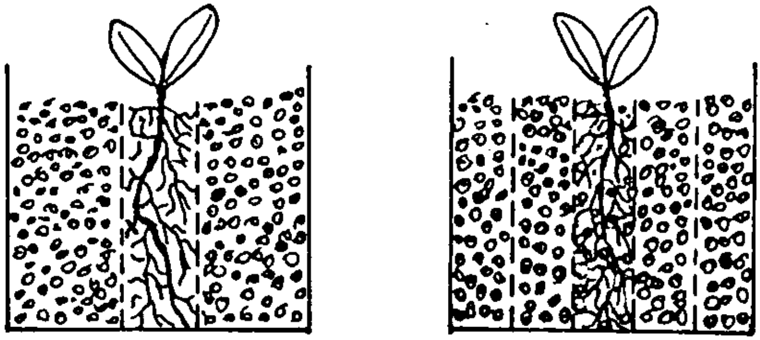
a) It is almost impossible to remove an intact root system with the adhering soil. By this method mainly old thick root axes and some primary branches withstand the isolation procedure. Fine root branches of higher orders which represent the functionally most active part of the root system are lost during the isolation. The soil fraction in contact with them is therefore left with the «nonrhizosphere soil».

b) This seperation method does not recognize the dynamic nature of the root system. Root studies *(Steen [1984])* indicate a simultaneous decay of some roots and the initiation and regrowth of others. Consequently, the contact of soil with the functional root surfaces is continuously changing.



A) Roots in a perforated metal box

B) Roots separated from soil by a horizontal membrane



C) Roots separated from soil by a vertical membrane

D) Soil layers differing in proximity to roots

Figure 2 Techniques for sampling rhizosphere soil

The idea of restricting root penetration by using a water permeable barrier and comparing soil modification on both sides seemed to offer a solution to these problems. *Harmsen and Jager [1963]* used a technique (Figure 2A) by which the roots were restricted to a chamber made from a nickel sheet perforated with holes 60 μm in diameter and considered the whole chamber as rhizosphere. However, it is clear that the soil directly outside the box, receiving diffusible exudates and metabolites through its pores must be by definition also considered as rhizosphere.

The model used by *Kuchenbuch and Jungk [1982]* involves a horizontal separation between roots and soil by a mesh screen (Figure 2B), leaving the whole root system outside the soil. A similar situation is encoutered in the techniques used by *Brown and Haq [1984]* and by *McLaughlin and Alston [1987]* who confined the roots inside a membrane (Figure 2C). It is evident that methods avoiding a regular soil-root contact take insufficient account of the already mentioned physical root-soil interactions, which have a significant bearing on both root turnover and root influences on the soil. *Boero and Thien [1979]* used a system of concentric cylinders made of nylon netting and confined the root system to the central core. This latter model accounts for physical root-soil interactions and makes possible the preparation of rhizosphere soil in a reproducible way. The main problem with this system, however, is the difficulty of preparing regular cylinders from nylon gauze and the breakthrough of roots at their joints. To avoid these difficulties the authors developed another technique (Figure 3) described below.

Appendix

7. Rhizosphere processes as a function of root proximity

The main feature of this technique is dividing the soil by stainless steel mesh fabrics into vertical planar layers (Figure 3). 4 such mesh fabrics are held in position by rectangular rods of plexiglass which are fixed with screws to the plexiglass side walls. This allows adjusting the distance between the individual mesh fabrics across the whole desired length. The whole set-up is placed on a sand layer (5mm) inside a suitable plastic container. This sand layer serves to supply water and at a later stage additional nutrients. The unit is then filled with soil and the central layer planted with two seeds. Root growth is thus restricted to this central layer. Only root hairs can penetrate to the adjacent (intermediate) layer, but never reach the outer soil layer. In this way the three layers reflect different intensities of root influences.

Work with several plant species has shown that the pore diameter should not exceed 30-40 μm in order to prevent roots from penetrating, but the open area of the mesh fabric should not be less than 20%, since otherwise water and solute transport to the roots may be impeded.

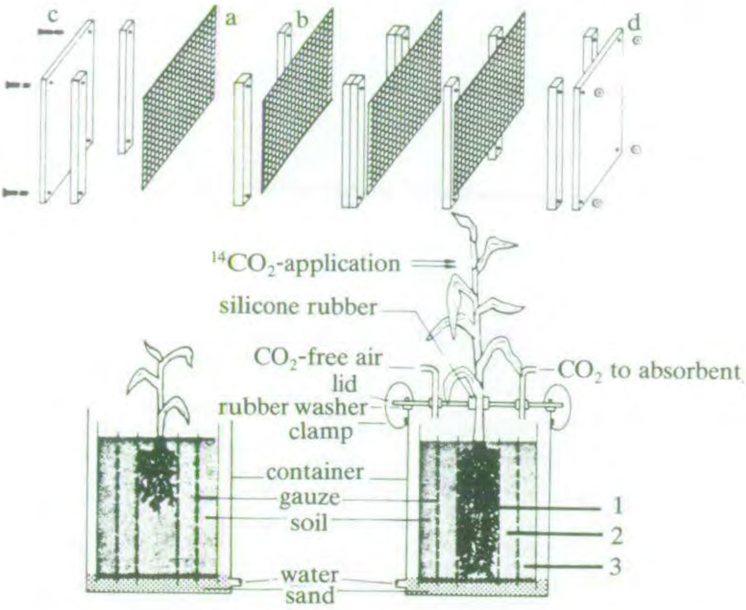


Figure 3 Arrangement for studying turnover processes in soil zones of different proximity to roots:
1) root zone, 2) intermediate zone, 3) outer zone
Dimensions = see text

A practical advantage of this system is that its dimensions may be varied to suit the desired duration of the experiment. This can be achieved by varying the area of the mesh fabrics and the distance between them. For short term experiments, the following dimensions are recommended:

- side area 90×105mm
- thickness of central layer 20mm
- thickness of half layers at both sides 10mm

A unit of these dimensions holds about 420g soil, *i.e.* 140g in each layer. When adequately fertilized, this is sufficient to maintain 2 plants for 3-4 weeks.

The three soil layers which are separated by this technique in order to be compared by analysis represent a reproducible gradient of root influences. A basic requirement for the validity of conclusions drawn from such comparisons is undisturbed transport of water and solutes across the layers. Disturbance may occur either through shrinkage of soil by drying or due to the tendency of the roots to grow at the interface. This phenomenon is strengthened by soil compaction. It is therefore recommended to adjust the soil density to 1.1 to 1.2 g/cm^3 and the water content to 70% of the W.H.C.

The authors combined this technique with ^{14}C-labelling and microbial biomass determination in order to trace and study the turnover of plant derived carbon in soil zones of different proximity to the plant roots. Homogeneous labelling the plants with ^{14}C is achieved by long term (at least 2 weeks) application of $^{14}CO_2$ of constant specific activity (usually 35 μCi/g C) to the shoots. This requires a gas tight separation between shoots and roots. For this purpose, a rubber washer is fixed between the lid and the lip of the container. The plant shoots pass through openings drilled into the container lid and are sealed with silicone rubber. A circulating air stream carries the $^{14}CO_2$ to absorbing flasks containing 3% NaOH. The total amount of ^{14}C thus collected from the rhizosphere during the growth period is the sum of two components, namely root respiration and microbial root decomposition.

At the end of the growth period the shoots are cut, the individual soil layers separated by unscrewing the frame and the roots carefully removed from the central zone. Root damage during this separation can be kept small by adjusting the soil moisture content before harvest to about 50% of the water holding capacity. Microscopic examination helps in removing any visible root fragments. The ^{14}C-content in soil and plant samples is determined by liquid scintillation counting after dry combustion of the sample in a Woesthoff Carmograph. To measure plant derived carbon which is incorporated into the microbial biomass, soil samples are analysed by the chloroform fumigation technique of *Jenkinson and Powlson [1976]*.

An example of results obtained by the authors *(Helal and Sauerbeck [1986a])* is presented in Table 3. It shows that the root carbon remaining in the rhizosphere is mainly (60%) bound in microbial cells. This suggests a prevailing contribution of young easily decomposible root tissues to rhizosphere turnover. Furthermore the data in Table 3 indicate a considerable migration of labelled root carbon. 29% of the plant-derived ^{14}C in soil was found outside the immediate root zone. Similarly 20% of the microbial biomass ^{14}C in soil was located outside this central zone. This means that root-derived carbon is transported to a considerable distance away from the roots and available there for microbial utilization.

Table 3 Distribution of plant-derived labelled carbon in soil zones differing in proximity to roots of 30 d old maize plants

	total ^{14}C		microbial ^{14}C	
	mg/pot	relative	mg/pot	relative
root zone	57.6	71)	38.3	80)
intermediate zone	14.3	18)	6.2	13)
outer zone	9.1	11)	3.5	7)
sum	81.0	(100)	48.0	(100)
relative	(100)		(60)	

The important conclusion which can be drawn from this work is that the rhizosphere area is not restricted to the immediate root-soil interface but involves a much larger soil volume. *Helal and Sauerbeck [1986a]* suggested using the detection of root-derived carbon in the soil as an indicator for estimating the actual size of the rhizosphere.

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Techniques for Studying the Ionic Environment at the Soil/Root Interface

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Summary

The study of the ionic medium in the near rhizosphere encounters a problem of the solid phase which prevents access at the study site. This difficulty originates from the diversity of study techniques used and developed in this field: dye indicator and derivative techniques, the techniques of microprobing and of soil labelling, micromorphology and electronic microanalysis. It seems that a particular effort should be made, on the one hand, in the development and the utilisation of glass ion-sensitive microeletrodes which permit the direct measurement of ion activity in solution, on the other hand, in the utilisation of micromorphology and associated techniques which permit the study of the near rhizosphere in undisturbed soil.

1. Introduction

The absorption of mineral ions by the roots is accompanied by the exsorption of acid or basic equivalents, inducing strong pH and ionic gradients around the roots *(Nye [1981])*. This physiological process produces some important physico-chemical modifications in the near rhizosphere such as the displacement of ionic equilibrium on the soil exchange complex *(Kauffman and Bouldin [1967]; Farr et al. [1969]; Kuchenbuch and Jungk [1982])*, the reduction of metallic oxides and hydroxides *(Marschner et al. [1982])*, the mobilization of insoluble elements *(Aguilar and van Diest [1981]; Grinsted et al. [1982]; Hedley et al. [1982])*, even the alteration of soil mineral constitutents *(Spyridakis et al. [1967]; Malquori et al. [1975]; Jaillard [1984])*. Yet, if the various effects of the roots on the medium are today well known, their influence on the soil mineral phase are clearly less well known, because of the complexity of the reactions which take place, and technical and methodological difficulties encountered in the study of the ionic medium in the near rhizosphere.

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The problems are a result of the small dimension of relevant volumes, and of the dynamic aspect of the processes which take place, but especially of the presence of a structured solid phase which prevents access at the study site. Different methods and associated techniques have been developed and adapted to resolve this difficulty. Some, like micromorphology and electronic microanalysis, permit direct access in the undisturbed soil. But they are destructive. Others, like labelling and microprobing, are still often experimental. For, if they permit taking the solid phase into account, they are efficient only in disturbed soils. Finally, it is equally possible to dispose of the problem by eliminating the solid phase and by substituting for it a gel substrate which is more easily manipulated.

In this paper, we present the actual technics best adapted to an approach on an artificial medium, on disturbed soil or on undisturbed soil. In particular, we will insist on their respective advantages and disadvantages, and on the type of information that they permit us to obtain.

2. Study Techniques on an Artificial Medium

2.1 The pH indicator technique

Plant culture on an artificial gel substrate is a modification of culture on a nutrient solution. In effect, an agar-agar support is nothing but another stabilised solution, a solid-solution whose composition can easily be changed like a nutritive solution. From this principle, it becomes possible to examine the root activity along the root using an adequate indicator. This enabled, *Wiesenseel et al. [1979]* to propose the use of a dye indicator to reveal the variations of pH induced by the roots. The technique consists of embedding the roots of a plantlet in a film of agar-agar gel, in which has been incorporated a pH dye indicator (Figure 1a). Acidification zones are shown up by first raising the pH of the solid-solution to a value above that of the color change, alkalinization zones by reducing it.

Indicators that can be used are few because they must respond to several conditions. The indicator must not be lethal, nor toxic, for the roots, and it must not be too strongly absorbed. Its color change must take place within the range of soil pH, that is around neutrality. Finally, the color change must be sufficiently clear to be observed. But the color change range can be relatively large, a continuous variation of color favors the quantification of pH change induced *(Pilet et al. [1983]; Versel and Mayor [1985])*. Consequently, only three dye indicators are at present used: bromocresol green *(Haussling et al. [1985])*, which changes the color at pH 4.5 (yellow-blue), bromocresol purple *(Wiesenseel et al. [1979])*, the most commonly used indicator which changes color around pH 5.6 (yellow-purple), and phenol red *(O'Neil and Scott [1983])*, which has a color change near pH 7.5 (yellow-red).

This technique has several advantages which explain its success. It is simple to use and is cheap. The revelation is fast, in the order of a few minutes to an hour depending on the conditions. Above all, it permits in a single operation the visualisation of the functionning of the whole root system of a plantlet. Furthermore, it distinguishes the variation in function of the different roots of the same plantlet. However, except into the weak color change of the indicator, this technique is not quantitative. Moreover, the agar film is asphyxiating and so it is not adapted to long-lived cultures.

Since its introduction, the pH indicator technique has been improved and adapted to the study of the variations induced by the roots in the soil. Like a photosensitive film, the colored agar film is laid on a flat surface of soil along which the roots are grown. Two processes are used: either the film is formed directly on the soil surface at 35-40 C (Figure 1b), or films prefabricated in the laboratory are placed on the surface (Figure 1c) *(Haussling et al. [1985]).* The second process is interesting because the film can be taken off after revelation and the plate set in place again. So it becomes possible to observe change in root activity of the same plant with time. These improvements allow *in situ* study of the near rhizosphere of large plants such as trees.

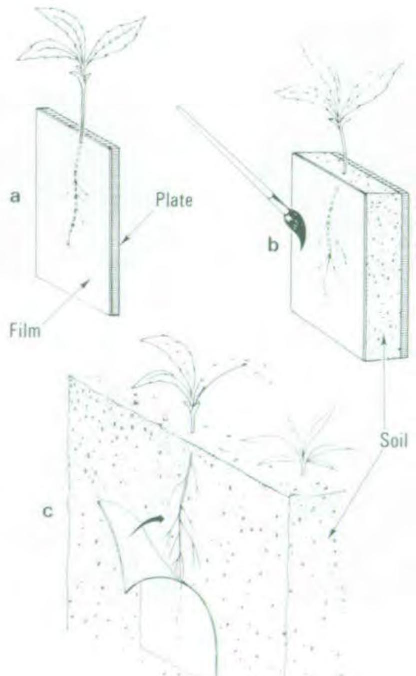

Fig. 1 Improvement of pH indicator technique: (a) The roots of a plantlet are embedded on a film of dye agar which is laid on a plate. (b) A flat surface of soil, along which roots are grown, is embedded with a dye film. (c) A prefabricated film is put onto a flat surface of soil.

The principal results obtained with this technique involve the localisation of zones of acidification/alkalinisation of the external medium along the roots. If the root hairs strongly acidify the medium at the tip *(Wiesenseel et al. [1979])*, it is because the growth of these cells is essentially apical, whereas the roots acidify preferentially the external medium in the zone of cell elongation *(Mulkey and Evans [1981]; Pilet et al. [1983])*. The intensity of this action varies NO3-/NH4+ ratio of the N-nutrient *(Marschner and Römheld [1983]; Moorby et al. [1985])*, the deficiency of iron *(Marschner et al. [1982])*, or the elongation rate of the roots *(Versel and Mayor [1985])*. These results show that action of the subapical zone on the soil is of high intensity.

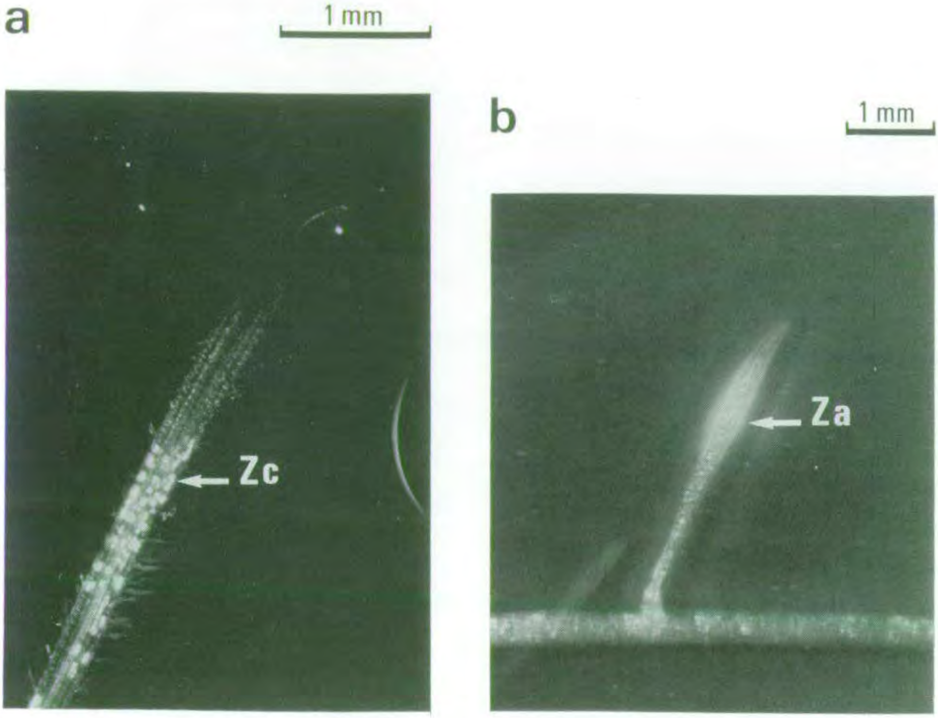

Fig. 2 Determination with the pH indicator technique of the life-status of calcified roots of rape developed in a solution of $Ca(HCO^3)^2$ at pH 8.15. The roots are placed in a dye solution of bromocresol purple (0.4 g/l) at pH 7.2, between two glass plates. Then, they can be observed with both (a) a microscope with polarised-analysed transmitted light to reveal the intraradicular calcite crystals and (b) an epimacroscope to reveal the acidification of the external medium. (Zc = zone of crystallization; Za = zone of acidification).

In a contrary sense, this root property can be used to establish the life-status of roots. Thus we have utilisated the dye indicator technique to examine rape roots which contain calcite crystals after one day of culture in alkaline calcic solution (Figure 2a) *(Jaillard and Davidian [unpublished data])*. The roots are placed in an alkaline dye solution between two glass plates. The color change of the pH indicator is observed, and the presence of calcite crystals in the roots is verified under the microscope. The rapid change of color of bromocresol purple in the crystallization zone which corresponds to the elongation zone (Figure 2b) shows that the calcified cells are alive. In these conditions the absorption of calcium is accompanied by its accumulation and crystallization as calcite in the cells of the elongation zone.

2.2 Derivative techniques

The root reducing activity can also be shown through reactions which accompany the color change. Thus, *Ambler et al. [1971]* used an oxidation-reduction reaction between a chelate of Fe III, (FeEDTA), and a chelatant of Fe II, which produced a colored complex. In the presence of both reagents, a red coloration appeared as a result of the fall in redox potential of the solution. Similarly, for manganese, a decoloration of the solution is observed when the manganese oxide, which is brown, is reduced. Following this principle, *Marschner et al. [1982]* incorporated the reagents into an agar film. Like the pH indicator technique, the position along the roots of the zones of reducing activity is shown by the colour changes of the substrate. The time of revelation is in the order of one hour for iron, and of one day for manganese under Fe-deficient conditions.

Beyond the results obtained, this work is especially interesting because of the principle which uses a chemical reaction and a phase change process. In effect, since the agar solid-solution plays no physico-chemical role, except an augmentation of buffer-capacity of the medium, it is possible not only to incorporate into it other chemical reagents, but also mineral particles. Moreover, if it is convenient to reveal and to observe the studied phenomena by a simple color change, other analysis techniques could be used: secondary chemical reactions, autoradiography, electronic microanalysis, fluorescence or polarized light. Though limited by its principle, excessively reductionist, this technique should be susceptible to new developments, especially with regard to the introduction of a mineral suspension into the agar film.

3. Study techniques in disturbed soil

Most studies on the solid phase have been on disturbed soil. Among the techniques used, two permit access to the near rhizosphere of a single root: microprobing and soil labelling.

3.1 Microprobing

This paper is limited to ion-sensitive electrodes the utilisation of which has become generalized in chemistry and in biology. At present, there are specific electrodes for most ions exchanged between soil and root: H^+, K^+, Na^+, NH_4^+, Ca^{2+} for the cations, and Cl^-, $NO3^-$ (and $HCO3^-$ with platinum electrode) for the anions. The electrodes permit direct and continuous measurement of the activity of the ions in solution. Their time of response is short, generally less than one minute. However, many applications require probes of a small dimension. Therefore, a special effort has been made in the direction of miniaturisation. Actually, the dimensions of commercial microelectrodes are in the order of one millimeter. This is not the lower limit. To measure the pH and the specific activities of plant and animal cells, electrophysiologists have built microelectrodes in which the diameter of the sensitive tip does not exceed one micrometer *(Thomas [1978])*. If the term microelectrode is appropriate for micrometric probes, then the term minielectrode might well be appropriate for millimetric probes.

Miniaturisation causes fragility of the tip, both at the sensitive membrane and the probe tip itself, this limits their application in soil science. Moreover, the use of electrodes in the soil poses a problem of contact between the soil solution and the ion-sensitive part of the probe. This problem becomes more difficult as soil moisture is decreased. These constraints induced *Schaller and Fischer [1981]*, then *Haussling et al. [1985]* to fabricate antimony minielectrodes. Built into reinforced Pasteur pipettes of 0.9 to 0.5 mm diameter, these probes have the advantage of being sufficiently strong to support, without damage, the mechanical constraints imposed by the presence of a solid phase. *Haussling et al. [1985]* even introduced them into compacted soils. Since they are less selective than the glass membrane electrodes *(Quehenberger [1977]; Schaller and Fischer [1981])* they have better contact with the soil solution, and consequently they are better suited to the study of the soil solution.

Schaller and Fischer [1985] and *Schaller [1987]* inserted them in a special experimental device in which there are about ten electrodes. But with this method, it is necessary to orient the root growth toward the probes. The problem is resolved by promoting the growth of the roots along the side wall of the sample by inclining the culture device. They show that the different pH profiles in the near rhizosphere are similar to the theoretical profile calculated by *Nye [1981]* and depend mainly on the buffer-power of the soil. The extension of the pH rhizosphere is inversely related to the buffer-power of the soil. A better relation is obtained with short term buffering, measured 5 minutes after the addition of HCl, a notion which includes a kinetic aspect in the reaction processes of the mineral phase.

In fact, despite these techniques being potentially among the most interesting, the microprobes are little used in the study of the ionic medium in the near rhizosphere. It seems that a particular effort should be made in this direction, because the techniques of microprobing are at present the only ones that permit a determination of specific ion activities in the near rhizosphere solution during its functioning. They should take into account both the diffusive and the kinetic aspects which are important as soon as there are chemical reactions with the soil.

3.2 The technique of soil labelling

A second method consists in introducing into the soil a specific label, most commonly a radioactive element *(Walker and Barber [1961]*. This method is solely experimental. Autoradiography shows the distribution of the radioactive label, either by exposing a sensitive film, or by direct analysis with a microintegrator or a microdensitometer. The technique is specific for the element introduced, and interference is unlikely. The natural background noise is negligible and the sensitivity of this technique depends at once on the texture of the soil used, which must be very fine, and on the initial homogenity of the label distribution. These conditions are general for all microanalytical techniques, like electronic microanalysis (see below). *Claassen et al. [1981]* show that the resolution is better with radioelements which emit radiation of low energy.

The realisation of a flat surface poses a problem. This can be achieved by the side wall of a culture pot. The advantage of this method is to permit the study of the evolution of the depletion profile along the roots (Figure 3a). This method, already mentioned under the techniques of pH indicator and of microprobing, is the most frequently used because it is the most convenient, but it favours some undesirable side-effects: first, the reduction by a half of the soil volume exploited by the roots, second, the preferential growth of root hairs along the sample wall, and finally, the creation of an anisotrophy of transfer properties of the medium. These edge-effects are removed by the culture device used by *Farr et al. [1969]* and *Kuchenbuch and Jungk [1982]* (Figure 3b). But this does not permit to study the rhizosphere of a single root. The flat surface can be made on a consolidated sample *(Sanders [1971])*, but embedding could possibly induce a secondary redistribution of the element under study. *Kraus et al. [1987]* propose consolidating the sample by quick freezing, which can then be sawn. Advantageously, consolidation makes the possible the study of a transverse section of the near rhizosphere (Figure 3c).

Unlike the techniques of dye indicating and of microprobing, autoradiography does not inform us directly about the ionic composition of the soil solution. It gives an image of the distribution of the fixed elements in the near rhizosphere. The concentrations are calculated from the absorption isotherms, assuming that we are at equilibrium. Moreover, unlike the techniques previously described, which give an instantaneous image of the ionic environment of the root, autoradiography reveals the cumulative root action on the diffusion of elements over a period.

Autoradiography has been used with most nutrient elements. In particular, it has shown that a soluble element which is not absorbed by the root as a sulfate is accumulated at the root surface *(Barber et al. [1963])*. This phenomenon is well known in the soil in the case of gypsum and lime. The artificial introduction of the radioelement permits selective labelling of certain reactive sites, for example the soil exchange complex. Using this property, *Jungk et al. [1982]* showed that the depletion of potassium is most marked to a distance of 0.7 mm, which corresponds to the zone explored by the root hair. Elsewhere, the distribution of potassium is characterised by steep gradients which extend a few millimeters from the root surface. This form of profile is similar to that of another immobilized element, phosphorus *(Bhat and Nye [1973]; Kraus et al. [1987])*. This technique originated from important results which justify in it, but it does not seem likely that it can be developed further.

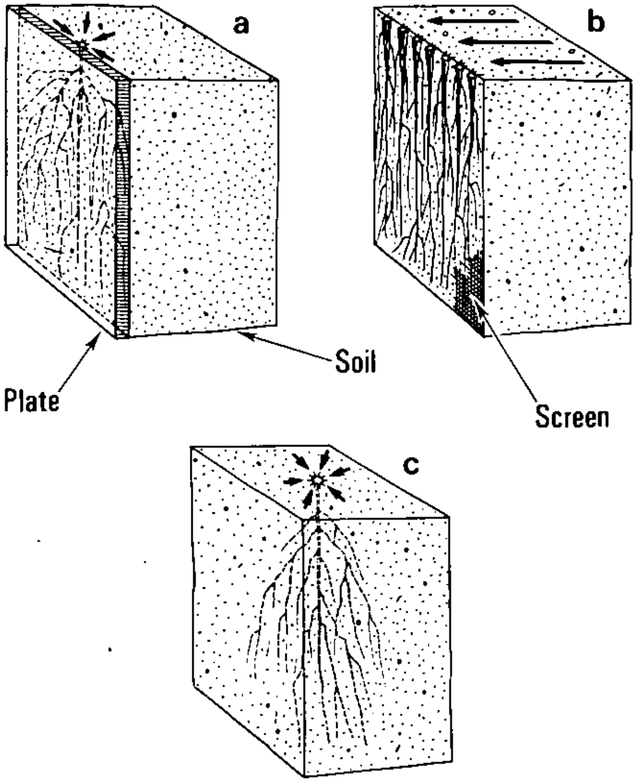

Fig. 3 Different dispositions of the roots for the study of the ionic medium in the near rhizosphere: (a) Realisation of a longitudinal section in orienting the root growth along the flat side wall of the soil sample (pH indicator, autoradiography and microprobing). (b) Growth of a root plane along the side of the soil sample (method of thin slicing rhizospheric soil). (c) Realisation of a transversal section in a consolidated soil sample (autoradiography, electronic microanalysis and micromorphology).

4. Study techniques in undisturbed soil:

A third group of methods for study of the ionic medium in the near rhizosphere includes micromorphology and electronic microanalysis. These permit the observation of undisturbed soil samples taken from the field, and further, they allow the study of modifications induced by the roots in nature. Developed by solid physics and used in soil science *(Bullok et al. [1985])*, they rely on the observation of polished surfaces and thin sections of soil samples under various light conditions. The soil samples are consolidated by embedding in synthetic resins, sawn and then polished. There are several methods of observation: optical microscope with natural or polarised transmitted light, with reflected or fluorescent emitted light. The choice depends on the type of information that one hopes to obtain. Actually, these techniques are extended by scanning or transmission electronic microscopy.

Micromorphology is most often associated with electronic microanalysis *(Wieder and Yaalon [1974]; Qureshi et al. [1978])*, the development of which is linked with the electronic microscope. In effect, a sample bombarded by an electron beam emits various signals of which certain can be transformed into a three dimensional image, while others can be used for analysis *(Maurice et al. [1978])*. The spatial resolution of electron microprobes is in the order of a cubic micrometer. That is the best spatial resolution among the analytical techniques that we have exposed. Multipurpose, these methods have found numerous applications in soil science, in fields as different as mineralogy, soil physics, soil biology and study of the rhizosphere *(Lund [1965]; Foster et al. [1983]; Tippkotter et al. [1986])*.

Micromorphology on soil thin sections provides much information on the structure and organisation of the near rhizosphere resulting from the ionic processes which take place. Phenomena such as the reorientation of clays in the near rhizosphere can be clearly observed with polarised-analysed light (Figure 4). The nature and distribution of the minerals can be determined both by observation under polarised light and microanalysis. Thus, the first ionic accumulation or depletion phenomena in the near rhizosphere have been identified by observation on crude samples *(Harley and Lindner [1945]; Greenland [1979])*, then soil thin sections *(Callot et al. [1983]; Jaillard [1985])*. Figure 5 shows a rhizostructure which is characterised by the segregation of soluble and insoluble fractions of soil. This rhizostructure is developed in a calcareous marl, density 1.55 to 1.80 g/cm^3 and lime content 0.76 g/g. Observation on soil thin section by polarised-analysed light reveals a well marked ring of calcite alteration. In this zone of depletion, the clays are oriented parallel to the root axis. Electron probe microanalytical study permits the quantification of element concentrations. The profiles of calcium (Figure 6a) and of phosphorus (data not presented) confirm the depletion of these elements in contact with the root, in zones only 150 to 250 μm in width. In this case, the high buffer capacity of lime considerably reduces the extension of the rhizosphere. Conversely, aluminium (Figure 6b) and potassium (data not presented) accumulate in the near rhizosphere. Both profiles are equally informative because they reflect the distribution of the soil clay fraction. From this fact, aluminium and potassium generally are equally distributed. We have shown *(Jaillard and Callot [1987])* that a such distribution of soluble and insoluble soil fractions must be interpreted as the result of the dissolution of soluble minerals by the root, while the insoluble fraction is displaced and concentrated around the growing root. As we have shown earlier, the accumulated calcium precipitates into the root, which enables it to grow in very compact carbonated soils.

These two examples show that the joint utilisation of micromorphology and of electronic microanalysis is efficient, in particular in the study of the reorganisation and of the alteration of the minerals. But these techniques are limited by the analysis of the total concentration of each element analysed. The depletion of the exchange complex cannot be shown by these methods. Presently, they remain the only study techniques of the near rhizosphere in the undisturbed soil.

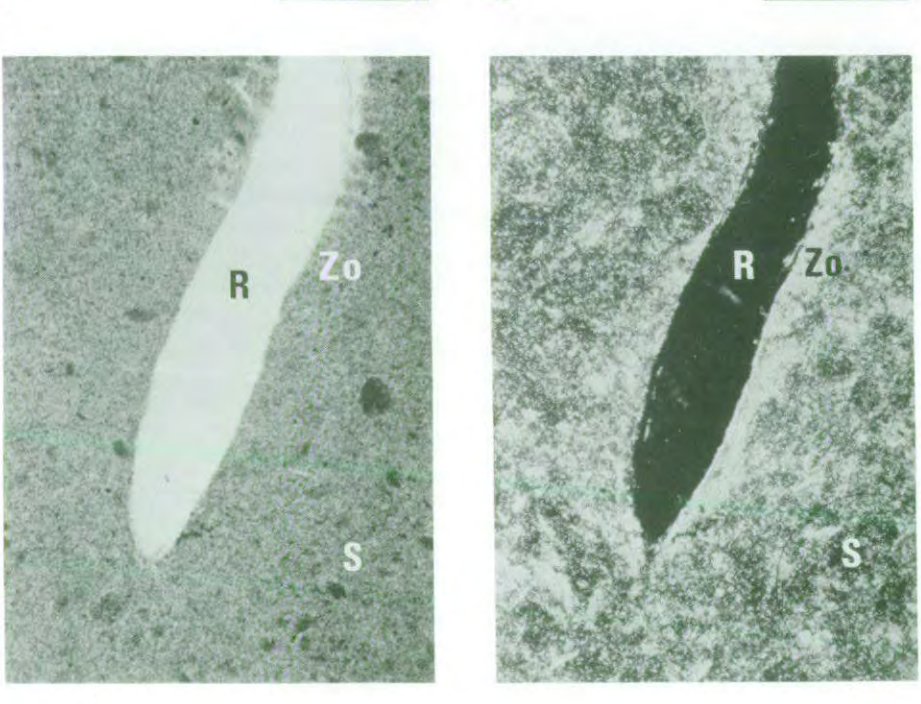

Fig. 4 Evidence of the reorganisation of the near rhizosphere by micromorphology. Longitudinal section of the near rhizosphere of rape root developed in a clay paste. Observation on soil thin section (a) with natural light and (b) with polarised-analysed light showing the reorientation of clay in the near rhizosphere (S = soil; R = root; Zo = zone of clay reorientation).

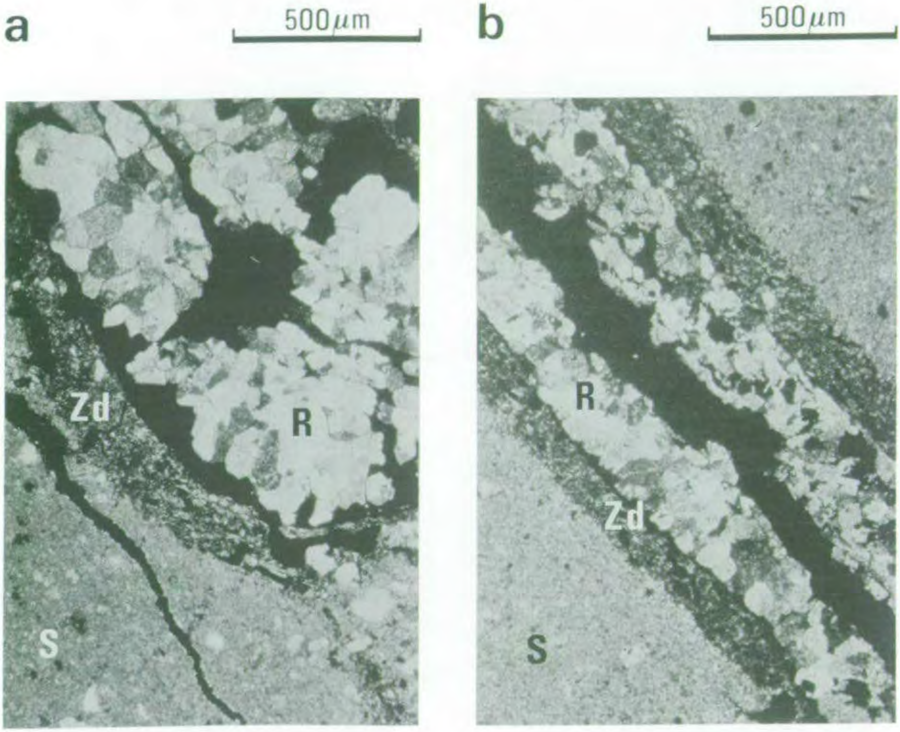

Fig. 5 Evidence of the alteration of mineral phase of the near rhizosphere by micromorphology. (a) Transverse section and (b) longitudinal section of a root developed in a calcareous soil (S = soil; R = calcified root; Zd = zone of calcium carbonate depletion).

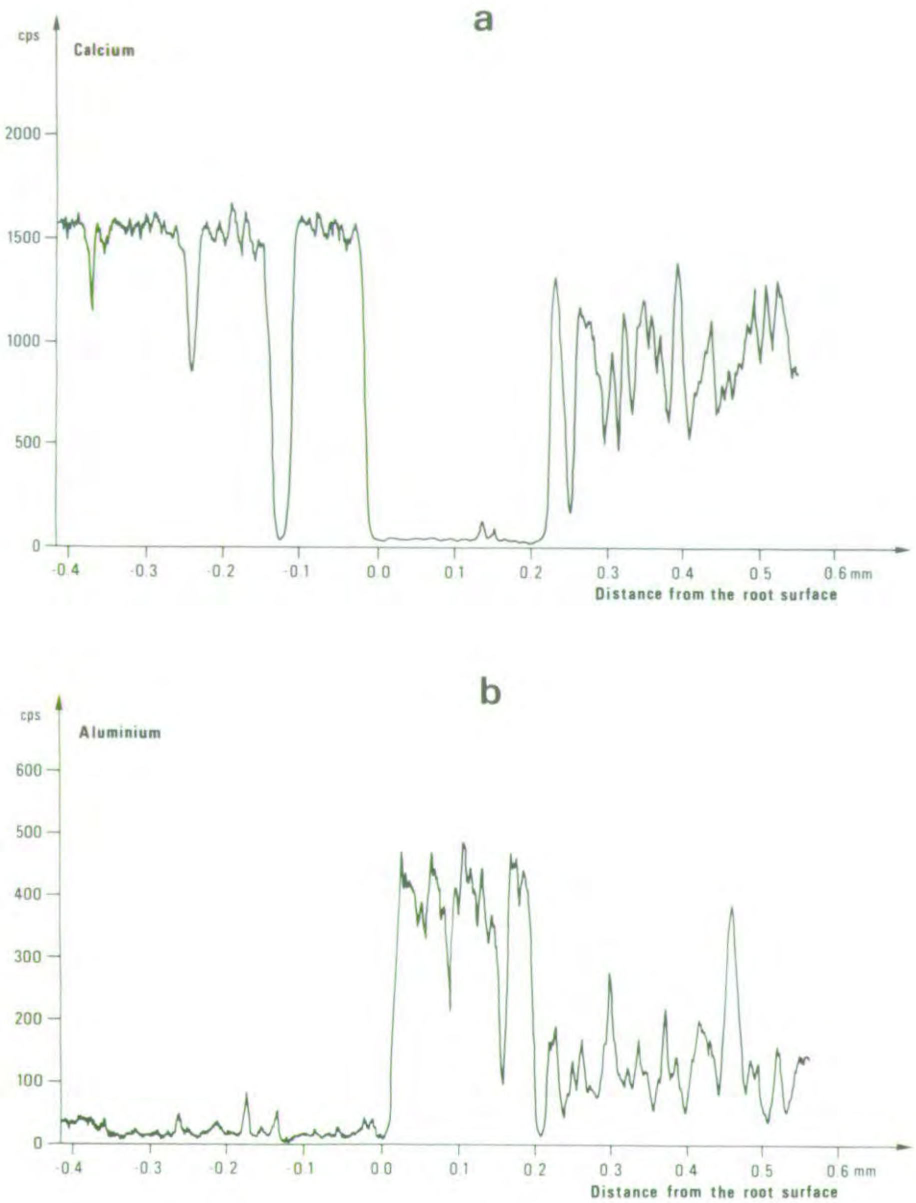

Fig. 6 Determination of the distribution of the elements in the near rhizosphere by electron probe microanalysis (cf fig 5) Distribution profiles across the zone of calcium carbonate depletion (a) of calcium and (b) of aluminium.

5. Conclusion

In discussing techniques for study of the ionic medium in the near rhizosphere, we have tried to show how the effect of the solid phase on root action and the effect of root activity on the soil mineral phase can be taken into account. Both the specificity and the complementarity of each of the methods used has been underlined.

While methods using an artificial medium enable one to show the effect of the root on the medium, their application is limited to the acidifying and the reducing activity of the roots. Labelling techniques and microprobing are well adapted to studies on disturbed soils. Microprobing methods should be developed, for these are the only techniques that permit direct determination of the activity of ions in solution, as well as the composition of the air in the near rhizosphere. However, they are poorly adapted to the study of undisturbed soil.

On the other hand, although not able to approach the functionning of the soil-root system, the techniques of micromorphology and of electronic microanalysis record the effect of root activity on the reorganisation and the alteration of different mineral constituents of soil. They can be used equally well in disturbed and undisturbed soils. Moreover, they permit study of the near rhizosphere of roots growing under difficult conditions, *e.g.* in the deep horizons of the soil. These techniques could be more frequently employed in this field.

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Methods for Quantification of Root Distribution Pattern and Root Dynamics in the Field

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Summary

For a functional evaluation of root systems in the field, two aspects deserve special interest and require separate methods for their study:

A. Spatial root distribution: heterogeneity of local root density in relation to planting pattern, soil structure, and heterogeneity of nutrient supply. Recently such heterogeneities have become the subject of research as such and are no longer treated as merely a nuisance in establishing effects of experimental treatments on average root densities. On a detailed level the degree of actual soil-root contact has become of interest.

B. Root dynamics in time: root growth and decay in the field can hardly be studied by destructive means, due to the large spatial heterogeneities. They have to be quantified by repeated observations of the same roots, under conditions which approach field conditions as much as possible.

For both types of information additions to and improvements of classical techniques are given: relations between basic root parameters, sampling schemes, quantification of root anisotropy, quantification of pattern in root distribution, quantification of soil-root contact and the mini-rhizotron technique for quantifying root dynamics.

1. Introduction

As the root system in its size, distribution and dynamical pattern forms an important link between plant and soil, the current trend of devising more efficient fertilisation techniques requires thorough knowledge of roots *(Van Noordwijk & De Willigen [1986])*. Classical techniques for excavation and study of roots have been described extensively *(Schuurman & Goedewaagen [1971]; Böhm [1978])*; in this paper new additions to the methods will be discussed.

Root studies in the field usually have one of the following three objectives:

- study of overall root pattern as indicator of soil conditions,
- quantification of roots for an interpretation of the relative availability of water and nutrients in various soil layers throughout the season, and
- quantification of input of organic matter through the root system to the soil ecosystem.

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Here we will concentrate on the last two, quantitative objectives. Root research in the past mainly quantified root dry weight, which is still of interest for the third research objective. For the second objective, root length and root surface area are more interesting parameters. We will first consider the relations between these root parameters.

2. Relations between basic root parameters

2.1 Geometry of roots

Generally roots can be assumed to be cylindrical in shape, *i.e.* increase of diameter along the length of a root and deviations from a circular shape in cross section are negligible. For such a cylinder simple relationships exist between length, surface area and volume:

$$V_r = \pi \cdot R_0^2 \cdot L_r = A_r \cdot R_0/2 \ [\mathrm{cm}^3] \tag{1}$$

where:
V_r = root volume [cm^3]
A_r = root surface area [cm^2]
L_r = root length [cm]
R_0 = root radius [cm]

Root volume is related to root fresh weight via the specific weight and root porosity; root dry weight is related to root fresh weight via the dry matter content:

$$D_r = M_{d,r} \cdot F_r = M_{d,r} \cdot (1\text{-}P_r) \cdot S_r \cdot V_r \ [\mathrm{g}] \tag{2}$$

where:
D_r = root dry weight [g]
F_r = root fresh weight [g]
$M_{d,r}$ = dry matter content of roots
P_r = air filled root porosity as fraction of V_r
S_r = specific weight of root tissue without air filled pores[g cm^{-3}]

A root system consists of a set of partly interconnected cylinders of various lengths and diameters. The relationships between root system values of basic dimensions such as length, surface area and volume are similar to those for single roots, except for the definition of the average root radius. If the root system consists of n classes of roots, each with root radius R_0 (i) and root length per class L_r (i), we may define two types of average root radius, a linear average $\bar{R}_0$ and a quadratic average $\tilde{R}_0$:

$$\bar{R}_0 = \Big(\sum_{i=1}^{n} L_r(i) \cdot R_0(i)\Big) \Big/ \sum_{i=1}^{n} L_r(i) \ [\mathrm{cm}] \tag{3}$$

$$\dot{R}_o = \sqrt{\sum_{i=1}^{n} L_r(i) \cdot R_o(i)^2 / \sum_{i=1}^{n} L_r(i)} \; [\mathrm{cm}] \tag{4}$$

For the root system as a whole we find:

$$V_{rp} = \sum_{i=1}^{n} \dot{V}_r(i) = \pi \cdot \dot{R}_o^2 \sum_{i=1}^{n} L_r(i) = \pi \cdot \dot{R}_o^2 \cdot L_{rp} \qquad [\mathrm{cm}^3] \tag{5}$$

$$A_{rp} = \sum_{i=1}^{n} A_r(i) = 2 \cdot \pi \cdot \dot{R}_o \sum_{i=1}^{n} L_r(i) = 2\pi \cdot \dot{R}_o \cdot L_{rp} \qquad [\mathrm{cm}^2] \tag{6}$$

and consequently

$$V_{rp} = A_{rp} \cdot (\dot{R}_o/\dot{R}_o)^2 \cdot \dot{R}_o/2 \qquad [\mathrm{cm}^3] \tag{7}$$

The term $\dot{R}_o/\dot{R}_o$ has been neglected by several authors when relating root volume to root length via average root diameters. This term reflects the variation in root diameters in the root system, being 1.0 for homogeneous root systems and >1 for heterogeneous root systems. If root porosity and dry matter content vary independently from root diameter, equation (2) holds for the root system, using (linear) average values for all parameters. Combining (2) and (7) we find for the specific root surface area, A_{rp}/D_{rp}:

$$A_{rp}/D_{rp} = 1/(M_{d,r}.\ (1\text{-}P_r) \cdot S_r \cdot (\dot{R}_o/2) \cdot (\dot{R}_o/\dot{R}_0)^2) \quad [\mathrm{cm}^2/\mathrm{g}] \tag{8}$$

For the specific root length, L_{rp}/D_{rp}, we find:

$$A_{rp}/D_{rp} = 1/(\pi \cdot M_{d,r}.\ (1\text{-}P_r) \cdot S_r \cdot (\dot{R}_o^2 \cdot (\dot{R}_o/\dot{R}_o)^2) \quad [\mathrm{cm}/\mathrm{g}] \tag{9}$$

Figure 1 shows commonly found values for the A_{rp}/D_{rp} and L_{rp}/D_{rp} ratio, as influenced by the parameters of equations (8) and (9). A plant apparently has four possibilities to obtain a larger surface area per unit dry weight: a low average root radius, a low dry matter content, a high root porosity and a homogeneous root system (in terms of root radius). The parameter S_r will not deviate much from 1.0.

Equation (9) shows that the average root radius alone does not give sufficient information to estimate the ratio of root length and root dry weight. Moreover, the condition used for deriving equation (9) that root porosity and dry matter content vary independently of root diameter will not usually be fulfilled. Root length and dry weight have to be measured on individual (sub)samples to get reliable results.

Specific root length for various crops and situations usually is in the range 100-300m/g, for roots with an average root diameter of 0.2-0.3mm.

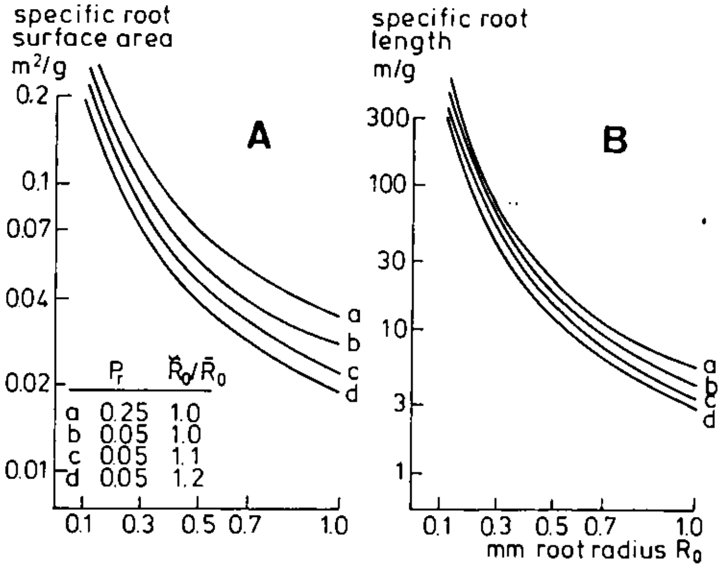

Fig. 1 Ratio of root dry weight and root surface area (A) or root length (B) as function of average root diameter (equations [8] and [9]); parameters used $M_{d,r} = 0.075$, $P_r = 0.05$ or 0.25, $S_r = 1.0$; the lines for $P_r = 0.25$ can also be interpreted as $M_{d,r} = 0.059$, $P_r = 0.05$.

2.2 Methods

Usually root length and diameters are determined on subsamples, using dry weight as a reference for calculating total root length and surface area. Root length is measured on a grid by counting root-line intersections following *Tennant [1975]*, choosing the grid size in such a way that about 400 intersections are found per subsample (this reduces the experimental error to less than 5%). Root diameter is measured on 20-30 randomly chosen roots per subsample. For calculations of average root diameter data of a number of subsamples have to be pooled, depending on the coefficient of variation; for a c.v. of 0.3, 40 readings are required to reduce this experimental error to less than 10%, for a c.v. of 0.5 100 readings and for a c.v. of 0.7 200 readings, in practice the c.v. of root diameters in root samples excluding tap and main roots is found somewhere in this range. By measuring root diameter at every 10th intersection of a root system with a line grid, both types of average root radius defined in (3) and (4) can be calculated:

$$\hat{R}_0 = \sum_{i=1}^{n} R_0/n \tag{10}$$

$$\hat{R}_0^2 = \sum_{n=1}^{n} R_0(i)^2/n = \mathrm{var}(R_0) + \hat{R}_0^2 \tag{11}$$

with Var(R_o) as the variance in the usual statistical definition. The latter equation implies that the factor $(\check{R}_o/\check{R}_o)^2$ in equations (8) and (9) is given by:

$$\left(\frac{\check{R}_o}{\check{R}_o}\right)^2 = CV(R_o)^2 + 1 \qquad (12)$$

with CV(R_o) as the coefficient of variation (standard deviation divided by the mean).

When data on specific root length (or surface area) of subsamples are to be used for calculation of total root length in a sample as a whole, losses of dry weight due to sample handling have to be known. Losses of dry weight of roots during washing and handling of roots have been evaluated recently *(Brouwer & van Noordwijk [1978]; Floris & van Noordwijk [1979]; Floris & De Jager [1981]; Grzebisz et al.*, in prep.). As Figure 2 shows a rapid loss of dry weight initially after sampling is followed by a stabilisation of root dry weight at 60-80% of the original value, depending on crop and washing procedure used; sodium-pyrophosphate for clay soils and HCl for seperating roots from rockwool result in relatively large losses. The first step in dry matter loss may be due to root respiration, although respiration inhibitors did not stop dry matter loss of cucumber roots.

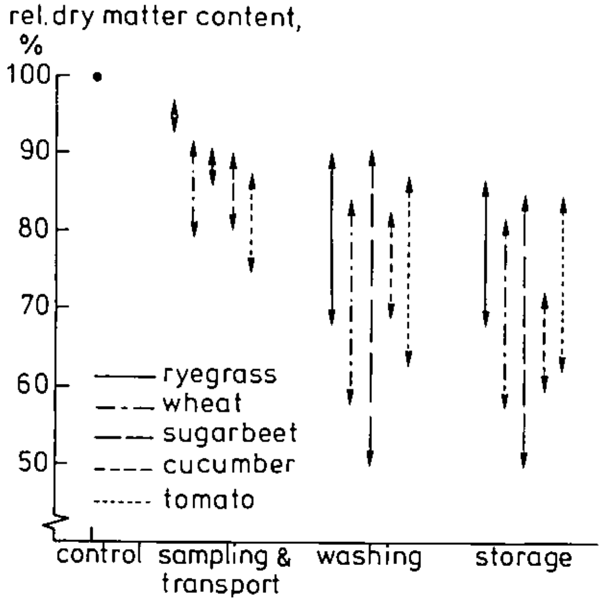

Fig. 2 Dry matter loss during washing and handling of root samples, simulating various standard procedures on roots obtained from a solution culture: ryegrass *(Floris & De Jager [1981])*, wheat *(Van Noordwijk & Floris [1979])*, tomato *(Brouwer & Van Noordwijk [1978])*, cucumber (unpublished, treatments include a respiration inhibitor (0.1 mM KCN + 25 mM salicyl-hydroxamate at pH 5)), and sugar beet *(Grzebis et al.*, in prep.).

Stabilisation of dry matter after the initial losses allows L_r/D_r ratios for subsamples to be used for the remaining part of the roots. Values for $M_{d,r}$ usually reported for field studies probably are 20-40% lower than those of intact roots.

An unsolved problem in root research is the establishment of a reliable criterion for distinguishing between live and dead roots. Conventionally visual and «manual» criteria (colour and elasticity) are used when cleansing roots. TTC (tetrazoliumchloride) can sometimes be used on rapidly washed roots, as its colour reaction depends on H-donation by metabolically active roots under anaerobic conditions *(Schuurman & Goedewaagen [1971])*. Other staining and microscopic techniques are also used *(Holden [1975]; McCully & Canny [1985]). Dyer & Brown [1983]* described a technique for observing fluorescence of roots in the cell-elongation stage. For a physiological interpretation of possibilities for uptake, the TTC method may give the most reliable criterion, despite problems of observing a colour change on dark-coloured older roots.

Root porosity can be measured by comparing the specific weight of roots as such and after grinding, when all pores may be expected to be water-filled *(Jensen et al. [1969])*. Results of this technique are in agreement with visual inspection of microscope slides *(Van Noordwijk & Brouwer*, in prep.). Root porosity is important for internal aeration of roots when the external oxygen supply is insufficient.

3. Spatial distribution of roots

3.1 Distribution patterns on various scales

Root parameters may be expressed per plant, per unit soil volume or per unit cropped soil area. The first way is most relevant for studying root/shoot relationships, the second for studying relative depletion of nutrients and water present in the soil and the third for studies on a crop level, for instance of dry matter input into the soil ecosystems by roots.

These three bases of comparison may be distinguished by a second subscript: L_{rp} [cm], L_{rv} [cm cm^{-3}] and L_{ra} [cm cm^{-2}], respectively (similarly for A_r etcetera). L_{rv} can be called «root (length) density». The dimensionless L_{aa} has previously been defined as *Root Area Index*, in analogy to the Leaf Area Index *(Barley [1970])*. A theoretical framework for a functional interpretation of L_{rv} values for depletion of N, K, P and water is now available *(Van Noordwijk [1983]; De Willigen & Van Noordwijk*, in prep.).

When considering root systems under closed crop canopies roots of neighbouring plants usually are intermingled and an individual plant may not be a convenient base for expressing root parameters. The size of the root system of an «average» plant corresponds to the amount of roots under a «unit soil area», U_a, as defined in Figure 3A.

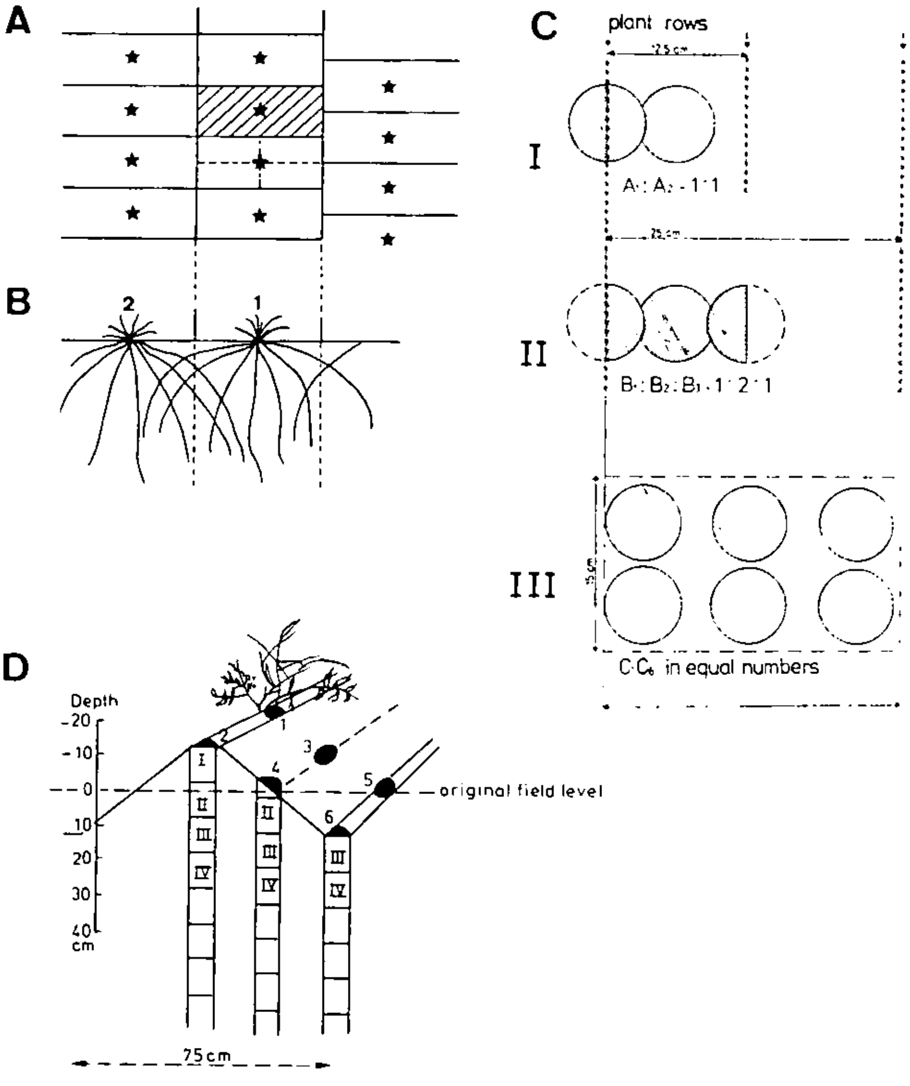

Fig. 3 A. Top view of the «unit soil area», Ua, for row crops; plants are indicated by an asterisk, Ua by the shaded area. B. Side view of the root system under the unit soil area. C. Sampling schemes for auger sampling: I. for row crops with narrow spacing (*e.g.* 12.5 cm), equal number of samples A1 and A2, II. for row crops with wide spacing (*e.g.* 25 cm), B1, B2 and B3 in 1:2:1 ratio, III. for crops with wider spacing in the row (*e.g.* sugar beet, C1, C2, C3, C4, C5, C6 in equal numbers), D. for ridged crops such as potato, D1, D2, D3, D4, D5, D6 in equal numbers *(Van Noordwijk et al. [1985a])*.

The unit soil area equals the reciprocal of plant density. Figure 3B shows that it may be expected that an equal number of roots of the central plant will be found outside the unit soil area, as roots of neighbouring plants enter this volume of soil. Relationships between the various bases of comparison are simple, *e.g.*

$$L_{ra} = L_{rp}/U_a \ [\mathrm{cm\ cm^{-2}}] \tag{13}$$

$$L_{ra} = \int_0^{Z_r} L_{rv}(h) \cdot dh \quad [\mathrm{cm\ cm^{-2}}] \tag{14}$$

where h = depth and Z_r = depth of rooted zone.

The unit soil area may be divided into four quarters of equal size, which form the smallest representative area of the field, except for different exposure of the soil surface to the sun.

Root density parameters vary in both vertical and horizontal direction. Part of this variation may be correlated with depth h or with radial distance r to the plant. L_{rv} (h, r, t) gives the average root length per unit volume of soil at depth h, at radial distance r from the plant and at time t.

Especially in the top layers of the soil a considerable part of the variation can be attributed to radial distance to the plant, r; this fact has practical consequences for sampling schemes. Depending on the adequacy of the L_{rv} (h, r) description used, a certain amount of variation around this average value will remain, which can be described as «pattern» in the root distribution (chapter 3.4)

3.2 Washed root samples

A careful consideration of sampling schemes to cover the unit soil area (Figure 3 C) may help to describe L_r (h, r) and may avoid the considerable bias in root weight which is inherent to the conventional scheme for row crops. The coefficient of variation in root weight in auger samples was found to be relatively constant with a value of 30-50% for different sampling occasions and depths *(Van Noordwijk et al. [1985a]).* Such a variation necessitates a large number of replicates, *e.g.* at least 10 to recognize 35% differences between two means and 25 for 20% differences, respectively.

Roots can be washed free from soil using samples either obtained by a soil auger (easily replicated, small samples) or obtained as soil monoliths, usually washed on pinboards (showing the complete shape of a root system). A monolith sampler which minimizes damage to experimental plots has been described by *Floris & Van Noordwijk [1984].* Washed roots have to be separated from debris and dead roots by hand, which still is the rate-limiting step in root research.

For measuring mycorrhizal hyphae and root hairs root samples have to be washed with greater care than otherwise. Small samples of soil are used from which roots are hand-picked and gently washed without trying to remove all soil particles. Mycorrhizal hyphae can be stained with trypan blue in lactophenol *(Philips & Hayman [1970])* and examined under a microscope. In addition to the conventional estimation of the percentage of root length which shows infection, hyphal length can be estimated from very gently washed samples. An intersection technique for recording both hyphal and root length in the sample is used, with root length as a basis for calculations for the root system.

3.3 Counts of roots intersecting a plane

An important aspect of variation in root distribution, related to root orientation, is described by the degree of anisotropy. An anisotropy factor A_n' can be defined, according to *Lang & Melhuish [1970]* from the number of roots N_a, N_b and N_c intersecting three mutually perpendicular planes A, B and C, respectively:

$$A_n' = \sqrt{(N_a - N_m)^2 + (N_b - N_m)^2 + (N_c - N_m)^2 / N_m^2} \qquad (15)$$

where

$$N_m = (N_a + N_b + N_c) / 3 \qquad (16)$$

and N_a, N_b and N_c are the number of roots seen per unit sample area. The definition given by *Lang & Melhuish* implies that A_n' falls in the range 0-2.45. For completely parallel root systems A_n' equals $\sqrt{6} = 2.45$. A normalized anisotropy factor A_n can be defined as:

$$A_n = A_n' / \sqrt{6} \qquad (17)$$

If root densities in two dimensions are equal, we may write $N_b = N_c = p \cdot N_a$ and consequently

$$A_n = (1 - p) / (2p + 1) \qquad (18)$$

Root-plane intersections can be counted in various ways. The two main sampling approaches used are: counts on auger samples which are broken for inspection *(Schuurman & Goedewaagen [1971])*, or counts on smoothed profile walls on which roots are made visible by removing some soil by spraying *(Böhm [1978])*. Roots can be counted in grids directly or after mapping on polythene sheets, either in a vertical or in the horizontal plane. The core-break method provides data of easily replicated, small samples, the profile wall method shows spatial arrangement of roots, for instance in relation to soil structure. As a third, less practicable method, blocks of soil hardened by resins can be inspected *(Melhuish [1968])*.

The number of roots seen per unit area of the sample can be related to the length of roots in a volume of soil by:

$$L_{rv} = 2 \cdot X \cdot N_m \tag{19}$$

where $X = 1$ for $A_n = 0$.

For root distributions which are not anisotropic equation (19) holds approximately when the average number of intersections for the three mutually perpendicular planes is used for N_m. *Marriot [1972]* has corrected earlier calculations by *Lang & Melhuish [1970]* on the effect of A_n on X in such a case. For two extreme types of root distribution a different relation is found, as shown in Figure 4A. As a curve-fit a quadratic relationship is adequate for both cases:

$$X = 0.5\ A_n^2 + 1 \tag{20}$$

$$X = 0.8\ A_n^2 + 1 \tag{21}$$

for the «linear» and the «planar» situation, respectively, with (1, 0, 0) and (1, 1, 0) roots in the three planes in the extreme case. In the usual application of the core-break method roots are counted only on a horizontal plane. Further correction is required as N_m may deviate from N_a. For roots with a preferential vertical orientation we may use $N_b = N_c < N_a$, *i.e.* $p < 1$. From (18), (19) and (20) it follows that

$$L_{rv} = N_a \cdot (3p^2 + 2p + 1)\ /\ (2p + 1) \tag{22}$$

and for roots with preferential horizontal orientation $N_b = N_c > N_a$, *i.e.* $p > 1$, from (18), (19) and (21):

$$L_{rv} = N_a \cdot (16p^2 + 8p + 6)\ /\ (10p + 5) \tag{23}$$

For $p = 1$ these equations reduce to $L_{rv} = 2\ N_a$; for $p = 0$ it follows that $L_{rv} = N_a$ and for large p (23) can be approximated by $L_{rv} = N_a\ (1.6p + 0.8)$. Figure 4B shows L_{rv}/N_a as a function of p.

When root counts are made in one plane only and no knowledge of p is available, as is usual in both the core-break method and the profile wall method, calibration is necessary by correlating N_a and L_{rv}. Values for L_{rv}/N_a found in this way may differ from theoretical values because of errors in counting all roots, for instance overlooking roots or counting dead remains of roots which are distinguished as such in washed samples.

Calibration factors L_{rv}/N_a usually vary with sample position, sample depth and time, as we may expect from the strong influence of factor p. Core-break methods thus can only give a rough indication of root distribution in the field. Theoretically A_n would not influence the relationship between N and L_{rv} when roots would be counted on half-spheres (De Wit, pers. comm.). This has not been practised yet.

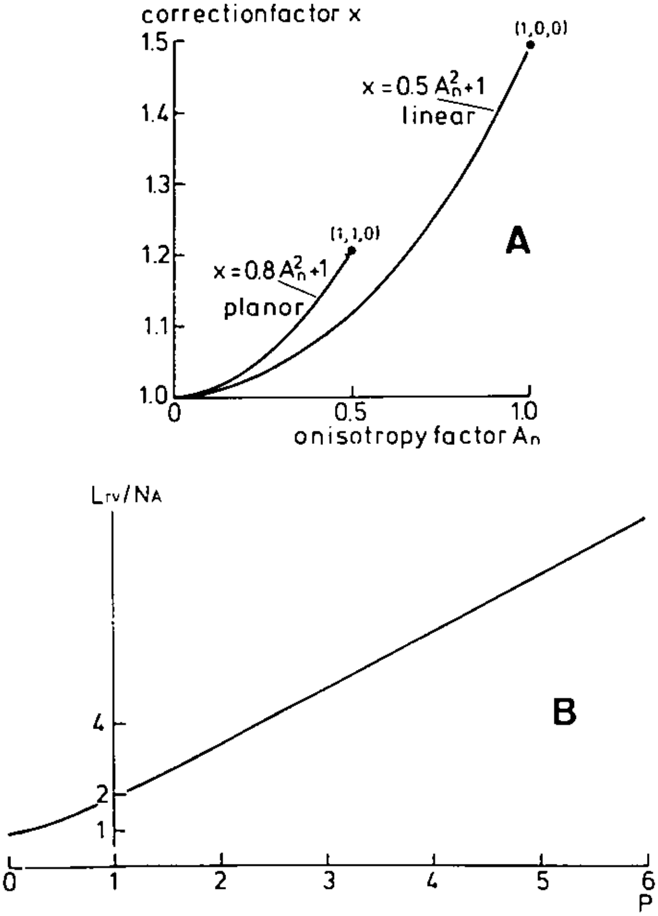

Fig. 4 A. Correction factor X in equation (19) as a function of anisotropy factor A_n, modified from calculations by *Marriot [1972]* for two extreme types of deviations from anisotropy («planar», roots in two dimensional orientation, «linear» roots in one dimensional orientation); B. L_r/N_a as a function of p according to equations (22) and (23).

3.4 Quantifying root pattern by nearest neighbour distances

When considering L_{rv} on a small scale (small volumes of soil) part of the variation is due to the fact that roots occur as discrete events, branch roots originating on main roots. Root distribution on this scale deviates from randomness either in the direction of regularity or in the direction of clustering. Definitions of such patterns are given in plant ecology *(Pielou [1969],* Figure 5A). The «pattern» can be quantified by measuring «nearest neighbour distances», *i.e.* by classifying all soil according to the distance to the nearest root (Figures 5B and 5C). Root distribution pattern can be influenced by soil factors (*e.g.* structure) as well as plant factors (*e.g.* branching).

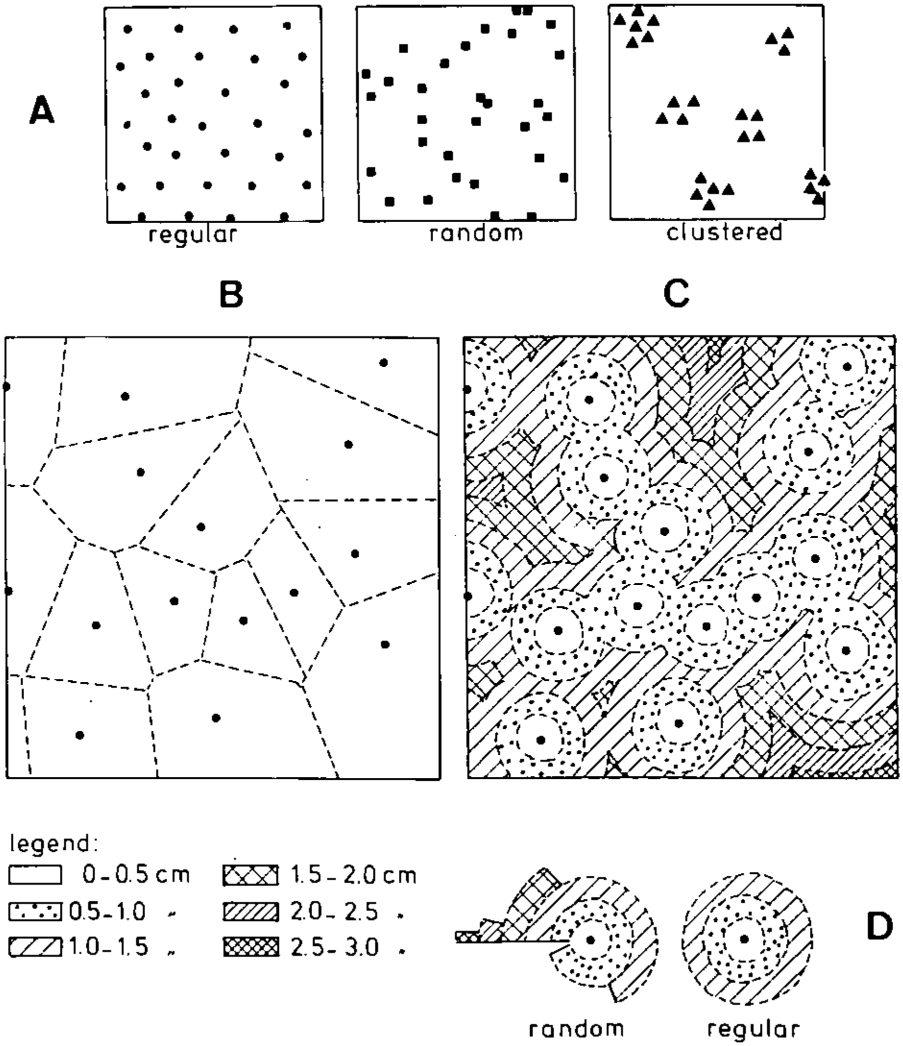

Fig. 5 A. Three basic types of spatial distribution: regular, random and contiguous (clustered); B. Division of area to nearest roots (Dirichlet tesselation); C. Classification of area on a root map according to the distance to the nearest root; D. Situation around an ‹average root›, for a regular and random root distribution.

On the basis of a comparison of point-root and root-root distances (Figure 6A), statistical tests of randomness are possible *(Diggle [1983])*.

The description of nearest neighbour distances on root maps is not only a technique for tests of randomness, it may also provide insight into the frequency distribution of real diffusion distances involved in nutrient and water depletion by a root system. In the three-dimensional reality, however, diffusion distances will be shorter than in our two-dimensional maps. The difference may be quantified as follows.

For the two-dimensional maps the frequency distribution of point-root distances in case of random distribution of roots, can be derived from a Poisson distribution as *(Pielou [1969]; Marriot [1972]*:

$$P\,[\delta < D_2] = 1 - \exp(-\lambda\, D_2^2) \tag{24}$$

where:

D_2 = two-dimensional distance

δ = distance of a point on the map to the nearest root

λ = number of roots per circle of unit radius.

For randomly oriented roots equation (19) shows:

$$L_{rv} = 2\,\lambda\,/\,\pi \tag{25}$$

For three-dimensional distances of points to randomly oriented and spaced lines *Ogston (1958)* and *Barley (1970)* derived that:

$$P\,[\delta < D_3] = 1 - \pi\, L_{rv}\, R_0^2 - \exp\,(-\pi L_{rv}\,(D_3^2 + 4/3 \cdot \psi \cdot D_3^3) \tag{26}$$

where:

D_3 = three-dimensional distance

ψ = number of root tips per unit root length

The second term in equation (26) is a correction for the volume occupied by the roots, which normally is negligible. As Figure 6B shows, ψ in equation (26) is of considerable importance. Its role follows from the possibilities of end-point contact for a half sphere around the root tip, added to the tangential contact for cylinders around the root.

For $\psi = 0$ we may compare equation (26) to equation (24) and relate D_2 to D_3:

$$D_3 = D_2\,/\,\sqrt{2} = 0.71 \cdot D_2 \tag{27}$$

This result strictly depends on random orientation of the roots with regard to the plane in which two-dimensional distances are measured. If D_2 is measured in a plane perpendicular to a parallel root system D_3 will equal D_2. In no case will D_3 be larger than D_2 measured in any plane.

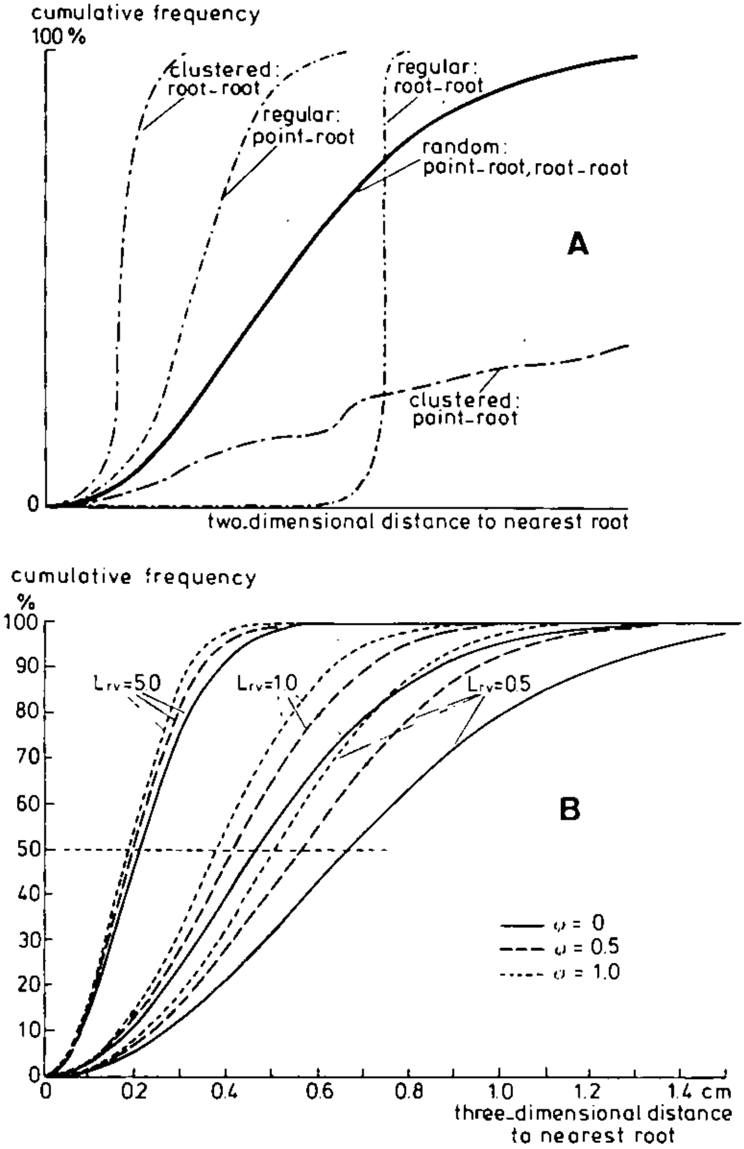

Fig. 6 A. Cumulative frequency of two-dimensional nearest neighbour distances for random points to roots (p — r) and roots to roots (r — r) for the three types of distribution shown in figure 5A; B. Cumulative frequency of three-dimensional distances of random points in the soil to the nearest root, for three root length densities and for three values of φ, the number of root tips per unit root length, according to equation (26).

Deviations from the regular root pattern usually assumed in theoretical models, have a considerable effect on relative depletion potential of a root system, especially for nutrients of lower mobility in the soil such as potassium and phosphate *(De Willigen & Van Noordwijk [1987])*.

3.5 Soil-root contact

Uptake of water and nutrients can only take place by direct contact between a root and the solid + water phase of the soil *(De Willigen [1984])*. The complement of soil-root contact is formed by root-air contact; for roots of low porosity the degree of root-air contact is important for aeration *(De Willigen & Van Noordwijk [1984])*. Root-soil contact can be quantified from thin sections of the soil, as used in soil micro-morphology, but no method for routine analysis is available as yet.

Root-soil contact will vary along the length of a single root and for a root system a frequency distribution of % contact has to be known.

For establishment of soil-root contact and for a direct role in uptake processes, root hairs can be relevant. The average length of root hairs L_h [cm], average radius R_h [cm] and root hair density per cm of root H_{rl} [cm^{-1}] may be necessary to describe root hairs in detail.

In some cases a «root hair cylinder» of radius $R_o + L_h$ is a useful concept.

4. Root dynamics

4.1 Dynamics of fine roots

A root may be expected to increase linearly in length of its main axis and exponentially when all branch roots are considered. When considering the increase of «root depth» in time linear functions will be adequate, while exponential functions may be required for describing root length density as a function of depth.

The root system of a plant is in a dynamic balance between root growth and root decay or root death. The total length of a root system is mainly determined by the length of fine branch roots. These fine branch roots may die after some time, while the main axis on which they are formed survives, at least to carry on its transport function.

Comparable to definitions for populations, a birth rate, death rate and average life expectancy can be defined for fine roots. If the potential for water or nutrient uptake is considered to be age-dependent, cohorts of roots of the same age can be described.

4.2 Sequential root observations of root dynamics

When destructive methods are used for frequent observations, the heterogeneity of root distribution leads to very high coefficients of variation for the estimates of relatively small differences in total root density between two observation dates. Several authors have neglected this variation and have attributed every positive difference between estimated root density at time T + 1 and that at time T to root growth, and every negative value to root decay. Especially for frequent sampling programmes true root dynamics can be vastly overestimated by this technique *(Singh et al. [1984])*. Another problem of this method is that simultaneous root growth and decay in the same soil layer – if it would occur – cannot be measured.

As alternatives for frequent destructive measurements, various techniques exist to observe root growth and decay on individual roots; such techniques suffer from the problem that the observations can only be made under non-natural conditions. Large-scale rhizotrons *(Huck & Taylor [1982])* are expensive and observations are limited to one soil type or artificially filled soil columns. As a less expensive and more flexible alternative the «mini-rhizotron» technique is now available for recording root growth along a glass or lexane wall under field conditions *(Sander & Brown [1978]; Vos & Groenwold [1983]; Van Noordwijk et al. [1985b])*. If observation tubes are introduced into the soil at sowing or planting time, root development and root decay can be observed for the whole growing period under conditions of little disturbance. Calibration of root lengths seen on the rhizotron wall (by evaluating photographic negatives on a grid for counting intersections) to L_{rv} from washed samples gives variable results (unpublished results, *J. Vos*, pers. comm.), necessitating calibration with washed samples if information on the exact root distribution is required.

By visual inspection of a series of photographs from the same mini-rhizotron at the same depth in soil, the length of new roots on each observation date can be quantified as well as the length of the roots which have disappeared since the previous observation. As root decay and root death may be gradual processes a visual criterion for presence or absence has to be set and observations preferably have to be made by one person. At any time t in the growing season the following equations holds:

$$R(t) = CTR(t) - CDR(t) \tag{28}$$

where:

R(t) = standing root intensity in the observation plane at time t [cm cm^{-2}]
CTR(t) = cumulative total of roots observed till time t [cm cm^{-2}]
CDR(t) = cumulative total of roots decayed till time t [cm cm^{-2}]

For annual roots CTR(t) is equal to CNR(t), the cumulative total of new roots observed till time t. By the end of the growing season at t = e we obtain data for CNR(e), CTR(e), CDR(e) and R(e). From these data we can define two ratios which may summarize the root dynamics during the growing season as a whole:

$$\mathrm{TRL} = \mathrm{CDR(e)} / \mathrm{CTR(e)} \tag{29}$$

and:

$$\mathrm{RRR} = \mathrm{CNR(e)} / \mathrm{R(e)} \tag{30}$$

where:

TRL = turnover of root length during a growing season [−]
RRR = root replacement ratio during a growing season [−].

The latter quantity is especially relevant for perennial crops as it gives information on the average longevity of individual roots. If RRR = 1 we may conclude that the average longevity of a root is 1 year, provided that R(e) is constant from year to year. The frequency distribution of individual root longevities cannot be estimated this way.

To avoid the comparatively large voids between the standard lexane rhizotron wall and the soil *(Van Noordwijk et al [1985b])* we also use metal frames in which an inflatable rubber tube (made from a motorcycle inner tyre) can be introduced and kept under constant pressure. The pressure used is such that roots grow unimpeded between the tube and the soil. At regular intervals the observation equipment (fibre-optics plus camera) are inserted in the lexane tubes and in the metal frame (after removing the deflated tyre) for photographing roots at every depth in the soil. For each photograph total root intensity is measured with the line-intersect method with due correction for the magnification factor. Individual roots are compared on subsequent photographs with a counting grid as overlay in exactly the same position by checking each intersection between a root and a line. In this way the length of new roots since the previous observation and the length of roots which had disappeared can be measured.

In future computer-aided image analysis may reduce the large amount of time involved now.

If the criterion of visibility used in analysing photographs is similar to that used in cleaning washed root samples, the results obtained can be used for estimating net root production for a whole growing season based on destructive sampling with an auger, monolith or pinboard method on one date and a series of photographs covering the whole growing season. Net root production over one growing season can be estimated from:

$$\mathrm{NRP} = \mathrm{DRP(m)} \times \mathrm{CDL} \times \mathrm{CTR(e)} / \mathrm{R(m)} \tag{31}$$

where:

NRP = net root production over the whole growing season [kg/ha]
DRP(m) = root dry weight per unit soil area at the time of maximum standing root mass [kg/ha]
CSS = correction factor for the sampling scheme used [−]
CDL = correction factor for losses of dry weight in sampling and washing procedures [−]

CTR(e) / R(m) = cumulative total of roots seen per growing season (cm cm^{-2}) divided by root intensity (cm cm^{-2}) at the time of the DRP(m) sampling [−].

The correction factor CSS equals 1.0 if an appropriate sampling scheme is used. For data obtained by other schemes correction factors can sometimes be estimated *(Van Noordwijk et al [1985a])*. The correction factor CDL can be estimated from seperate experiments (Figure 3). If relative root dynamics are different for various layers in the soil a correction may be required as the ratio between root intensity seen per cm^2 of observation wall and root length density measured in washed samples is not necessarily constant for crops, seasons and soil layers. A point of concern is whether or not estimates of root turnover are based on unbiased samples as regards root diameter, as we may expect that fine branch roots have a different (probably higher) turnover than thicker main roots.

5. Conclusion

A recent trend in root research is to try to understand root functions on a more detailed level by studying the synchronisation of root activity and the presence of mobile soil resources and the ‹synlocalisation› of active roots, micro-sites of oxygen supply, less mobile nutrient sources and soil organisms. To solve such research problems, root research using methods as outlined here, has to be coordinated with small-scale studies of soil chemistry, soil physics and soil biology.

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Rhizosphere Organisms – Potassium Interactions with Emphasis on Methodology

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Summary

There are multiple interrelationships between the rhizosphere microflora and plant nutrition involving *inter alia* the potassium nutritional status of plants and potassium availability. To elucidate some of these interactions plants have to be grown under axenic conditions. Exclusion of microorganisms is important *e.g.* for distinguishing between the activity of roots *sensu stricto* and their microbial associates as well as for collecting root exudates. The methods for axenic cultures of plants are briefly outlined. The selected substrate is a major problem in growth studies of sterile and nonsterile plants, as sterilization of soil either by heat or by γ-irradiation produces toxic compounds. Experiments have to be restricted to more or less artificial media like nutrient solution or sand. Using nutrient solution culture it was found that the K nutritional status influences microbial activity on roots via its effect on plant metabolism and root exudation. Low K supply increases the quantity of readily decomposable organic compounds released from roots.

Enumeration of microorganisms is done either directly by microscopical counting or indirectly by plate counting involving incubation on nutrient media. Both techniques showed increasing numbers of bacteria with decreasing K supply, indicating that K availability is not a limiting factor for microbial growth in the rhizosphere. Moreover, rhizosphere bacteria seem to compete successfully with plants for potassium.

Potassium nutrition affects the quantity and quality of low molecular compounds in roots and root exudates, and the composition of the rhizosphere microflora and microbial transformations in the root vicinity. Denitrification in general and certain processes in the rhizosphere of rice like those associated with iron toxicity and N_2 fixation are discussed with a brief description of the methods applied.

Weathering mediated by free living rhizosphere organisms and mycorrhizal fungi is another line of research. The results indicate that potassium release from minerals is insufficient to support optimal growth of crops.

Attempts to enhance K availability by inoculation of seeds with «silicate» bacteria are mentioned. A recent review is sceptical about the significance of these inoculants.

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1. Introduction

Since the discovery of greater abundance of microorganisms around roots compared to bulk soil, a number of scientists have been interested in the question: «are rhizosphere organisms opportunists, scavenging simply the waste products from roots, are they bandits being detrimental to the plants, or even benefactors having beneficial effects on plant growth and health?» *(Brown [1975]). Hiltner* who introduced the term «rhizosphere» as early as 1904 suggested that *«von der Zusammensetzung der Bodenflora in der Rhizosphäre die Ernährung der Pflanzen nicht unwesentlich abhängt»* (the nutrition of plants certainly depends upon the composition of the soil flora in the rhizosphere). Observing the dense bacterial flora on the root surface, he noted that «certain bacteria do not only form a cover but even penetrate into the upper cell layers of the roots and – analogous to the ectotrophic mycorrhiza – form a bacteriorrhiza». He tried to estimate bacterial numbers per mm^2 of root surface.

The term «bacteriorrhiza» did not succeed, and others are used nowadays to characterize the different habitats in the root-soil interface. Today the rhizosphere *sensu stricto* is also called the outer rhizosphere, while the rhizoplane is identical with the root surface *(Clark [1949])* and the endo- or inner rhizosphere describes the cortex *(Dommergues [1978]).* In older root regions the cortical layer is often densely colonized by saprophytic microorganisms. The different zones cannot be strictly seperated from each other, but are interrelated and overlapping. The increase in microbial numbers and activities as well as the greater abundance of representatives of the micro- and mesofauna due to the root environment is called the rhizosphere effect *(Katznelson [1946]).* Many workers have shown that the microbial population of the rhizosphere differs both quantitatively and qualitatively from that in the soil remote from the roots.

2. Abundance of microorganisms on roots as affected by plant nutrition and environmental factors

Many techniques have been applied to quantify the rhizosphere effect.

2.1 Plate count technique

Detailed descriptions are available *(e.g. Kaunat [1965]; Parkinson et al. [1971]).* Sampled parts of a root system are gently shaken to remove loosely attached soil. A distinct amount of roots with adhering soil, representing the rhizosphere soil sample, is placed in bottles with sterile water or a dispersing solution of 0.2% Na-pyrophosphate and shaken for a certain time (30 min) in order to detach microorganisms from soil particles and roots and to disintegrate bacterial microcolonies. The soil suspension is serially diluted in water and aliquots (0.1 or 1 ml) of the appropriate final dilution are mixed in Petri dishes with a molten agar medium according to the traditional plate count technique after *Koch*. Based on the number of microbial colonies grown after incubation the number of propagules or cell forming units per gram of soil can be calculated. Numerous modifications of the plate count technique have been described. Limitations of the procedure and difficulties in comparing R/S ratios (number of rhizosphere organisms divided by number of nonrhizosphere organisms) are discussed by *Rovira and Davey [1974] and Curl* and *Truelove [1986]*.

Among the nutrient media simple, low-concentrated nutrient broth solidified by agar *(Trolldenier [1971a])* has been confirmed as giving the highest number of «total» bacteria *(van Vuurde and Lange [1978])*.

To separate microorganisms of the outer rhizosphere from those of the rhizoplane and inner rhizosphere, the roots with adhering soil are gently shaken in water, placed in another flask, and then shaken with glass beads *(Louw and Webly [1959])* or macerated shortly in a blender *(Katznelson [1961]; Trolldenier and von Rheinbaben [1981a])*. Root washings were also used to isolate fungi from roots *(Harley and Waid [1955]; Parkinson et al. [1963])*. Specific groups of bacteria like nitrifiers, denitrifiers or nitrogen fixers are counted by using the most-probable-number procedure *(e.g. Trolldenier [1971b])* discussed by *Alexander [1982]*.

The root zone represents a microbial gradient in which microbial activity decreases with increasing distance from the roots. The decline of numbers in the counts of bacteria, streptomyces and fungi with increasing distance from the roots was shown by *Papavizas and Davy [1961]* using a multiple-tube device for sampling 3 mm cores from the root surface up to 22 mm apart. The steepest decline of numbers was found in the first 3 mm from the root surface.

A newer concept of understanding the dynamics of root colonization is the study of the generation or doubling time of bacteria on roots. Large differences were found between species of *Pseudomonas (Rovira [1979])*. The doubling time of an organism in colonizing the rhizosphere is *e.g.* an important parameter in estimating its efficiency as an inoculant.

2.2 Direct microscope techniques

These techniques have been used for studying the distribution of microorganisms on roots as well as for calculating R/S ratios. Classical contact slides after *Cholodny [1930]* and *Rossi [1936]* may be used for examination of microorganisms colonizing root hairs. Fluorescence microscopy has proved to be highly suitable in observing the colonization of root hairs attached to contact slides and of thin sections of the root surface *(Trolldenier [1965a, b])*. With a slide incubation chamber *Polonenko and Mayfield [1979]* were able to study microbial colonization of living roots. Direct observation revealed root tips to be nearly devoid of microorganisms, while older parts are often densely colonized *(Rovira [1956])*. The rate of root colonization seems to depend on environmental conditions. It was demonstrated by transmission electron microscopy that – in contrast to well aerated roots – the mucilage of the root caps of roots suffering from oxygen deficiency is already colonized by many bacteria and that on older root parts the cortex is heavily invaded by microorganisms *(Trolldenier and Hecht-Buchholz [1985];* Figure 1).

The most extensive study of the rhizosphere by electron microscopy has been published by *Foster et al. [1983].*

When bacteria are counted by the indirect plate count technique and by direct microscopy in the rhizosphere and in the bulk soil, characteristic differences between both zones become manifest. Soil plate counts as compared with microscopic counts yield considerably lower numbers in the non rhizosphere soil (1-4%) than in the rhizosphere soil (11-51%) (Table 1). This discrepancy indicates qualitative differences in the bacterial population of the two zones. Obviously roots stimulate zymogeneous organisms – those relying on easily decomposable substances and growing on cultural media – while in the non rhizosphere soil autochthonous organisms *(Winogradsky [1925]),* having more complex nutrient requirements, predominate. From the increase of zymogeneous organisms in the presence of plant roots it may be deduced that the greater availability of easily decomposable compounds is the actual cause of the rhizosphere effect. The growth of bacteria with simple nutrient requirements in the rhizosphere is further enhanced by low potassium nutrition (Table 2) for the reasons discussed in the next section.

Table 1 Bacterial numbers ($10^6 \cdot g^{-1}$) in the rhizosphere of different plants and in nonrhizosphere soil obtained by fluorescence microscopy and plate count *(Trolldenier [1967])*

Age of plants	Nonrhizosphere soil		Rhizosphere soil of							
			Triticum sativum				*Vicia faba*			
(Weeks)	Microscopy	Plate	Microscopy	R/S ratio	Plate	R/S ratio	Microscopy	R/S ratio	Plate	R/S ratio
5	483.3	10.8	1.145.7	2.4	153.8	14.2	556.8	1.2	60.0	5.6
7	324.6	13.4	684.6	2.1	221.5	16.5	300.7	0.9	154.6	11.5
10	681.6	7.8	922.9	1.4	172.6	22.1	853.9	1.3	262.6	33.7

Table 2 Total bacteria on roots estimated by plate counts and relative proportions of bacteria having different nutritional requirements in relation to potassium application to wheat *(Trolldenier [1971c])*

Plant nutrient ratio K_2O:N (N = 1)	Total bacteria $10^9 \cdot g^{-1}$ root dry matter	Bacterial incidence (%)		
		Group I	Group II requiring	Group III
		Glucose	Glucose + amino acids	Pepton
0.5	32.6	69.0	20.5	10.5
1	27.8	42.9	26.0	31.1
2	20.9	46.9	17.5	35.6
3	21.2	26.6	15.2	58.2

Fig. 1 Outer root cortex of the lateral root zone of a wheat root grown in unaerated nutrient solution showing abundant microbial colonization in the rhizoplane. The cortex cells have been invaded by bacteria (b) *(Trolldenier and Hecht-Buchholz [1984])*

3. Methods of growing plants in axenic culture

Organic material released from roots is rapidly metabolized by microorganisms as indicated by the higher root respiration of nonsterile roots compared with sterile roots *(Trolldenier [1972])*. Therefore it is necessary to exclude microbial contamination when studying the nature of root exudates. Limitations in adapting the results obtained with plants grown in axeni culture to natural conditions have been discussed by *Tinker [1984]*. It is furthermore necessary to exclude microorganisms in the control treatment when the effect of rhizosphere microflora on plant growth is examined. Hence, axenic plant culture starts with seed sterilization.

A variety of procedures has been applied, often including treatment of seeds with sodium hypochlorite solution. We obtained reliable results by shaking the seeds for 30 min. in 30% hydrogen peroxide solution followed by the usual washing with sterile water. Unlike some other sterilizing agents, hydrogen peroxide does not affect germination. By germination on nutrient agar seeds still contaminated can be identified and discarded. Definitely sterile seedlings are transfered to flasks or tubes containing sterile nutrient mineral solution as described elsewhere *(Trolldenier [1972]; Figure 2).* Selected methods of growing plants under axenic conditions have recently been compiled by *Curl and Truelove [1986].*

Detailed analysis has been made only from watersoluble nonvolatile root exudates *(Rovira et al. [1974]).* Data on the effect of plant nutrition and other factors on root exudation are very limited *(Hale and Moore [1979]).* With regard to potassium it was demonstrated with $^{14}CO_2$ treated bush beans that plants low in K released more labeled organic substances per unit root weight than plants which had been supplied with higher rates of potassium *(Trolldenier [1972]).* In a more detailed study with maize grown at different K levels increased release of sugars, organic acids and amino acids per gram of root dry matter was found at low K supply *(Kraffczyk et al. [1984];* Table 3).

Table 3 Organic compounds (mg · g^{-1} root dry matter) found in sterile nutrient solutions with different K levels after 23 days of maize growth *(Kraffczyk et al. [1984])*

Treatment	Sugars	Organic acids	Amino acids
K_1	7.68	15.87	0.17a
K_2	4.73a[1]	3.42a	0.13ab
K_3	5.39a	4.72a	0.11b

[1] In a column, means not followed by a common letter are significantly different at the 5% level

The higher root exudation at insufficient K supply may be associated with accumulation of soluble carbohydrates and amino acids in the plant due to impaired synthesis of starch, cellulose and proteins.

The comparative uptake of nutrients by sterile and nonsterile plants has rarely been studied because of methodological difficulties. In an experiment with red clover, uptake and translocation of ^{86}Rb as a tracer for potassium and of ^{45}Ca was compared by *Trolldenier and Marckwordt [1962]* in sterile and nonsterile plants grown in nutrient solution. Shoots and roots of sterile plants had higher contents of Rb and Ca while total translocation into the shoots was similar. The lower concentration of Rb in the tops of nonsterile plants was probably a dilution due to more rapid growth in the presence of microorganisms. In contrast, *Williamson and Wyn Jones [1972]* found higher Rb accumulations in nonsterile grown plants. They suggested that the specific inoculum employed is of great importance. This is concomitant with earlier findings by *Welte and Trolldenier [1963].* The attempts to study plant-rhizosphere organism interreactions in soil failed so far, because toxic compounds, *inter alia* ethylene, are produced during sterilization by heat and γ-irradiation *(Rovira and Bowen [1966]; Rovira and Vendell [1972]).*

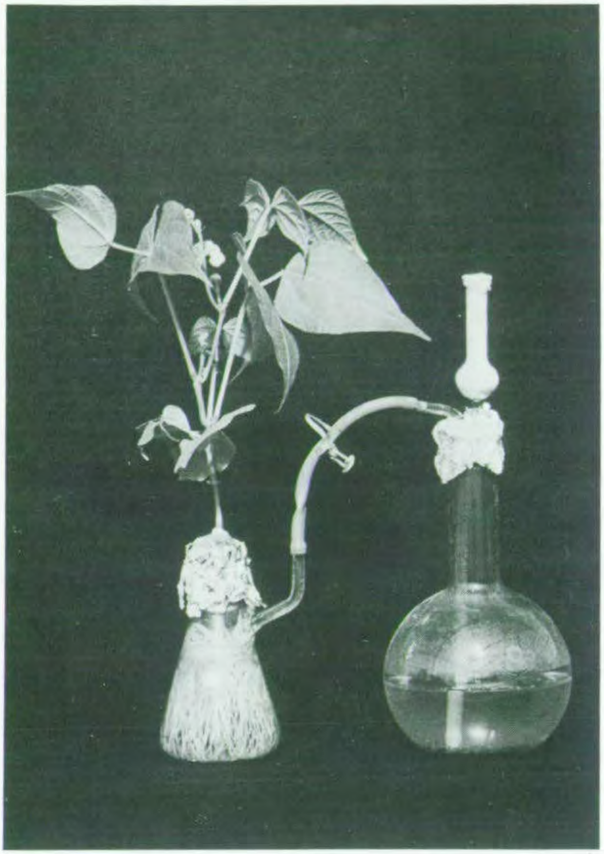

Fig. 2 Axenic nutrient solution culture of bush beans. The flask is connected with a water reservoir. *(Trolldenier [1972a])*

4. Change of nutrient availability by rhizosphere organisms

4.1 Mineralization and immobilization

A major function of microorganisms is mineralization of organic residues thus supplying plants with essential nutrients. Soil respiration was found to be a general indicator of microbial activity.

Due to the contribution of roots and microorganisms respiration is higher in the rhizosphere than in the soil remote from roots. *Stille [1938]* was probably the first to notice that nonsterile roots have higher respiration than sterile roots. Using a Warburg respirometer *Trolldenier [1972]* found that roots of bush beans colonized by microorganisms consumed more than twice as much oxygen as sterile control roots. Concomitant with their higher bacterial population respiration was highest with roots of plants low in potassium (Table 4).

Table 4 Respiration of sterile and nonsterile roots, bacterial numbers on roots and dry matter of bush beans in relation to K nutrition *(Trolldenier [1972a])*

Treatment	O_2 consumption $\mu l\ O_2 \cdot (100$ mg root fresh weight $\cdot h)^{-1}$	Bacteria $10^6 \cdot g^{-1}$ root fresh weight	Dry matter $mg \cdot plant^{-1}$ Shoots	Roots
K_1 sterile	94.2	–	864	201
nonsterile	273.6	1124	844	172
K_2 sterile	102.0	–	1320	373
nonsterile	235.2	710	1302	315

It is well established that part of the stable humic fraction will be mineralized when readily decomposable compounds are added to the soil. The «priming effect» is ascribed to a stimulation of microbial activity *(Harmsen and Kolenbrander [1965])*. Root exudates exert a similar effect as already suggested very early by *Löhnis [1910]*. He stated: *«Die Wurzeltätigkeit der Kulturgewächse und anderer Pflanzen ist ebenfalls ein an der Humuszersetzung mitwirkender Faktor»* (Root activity of crop and other plants is also a factor affecting humus degradation). This was confirmed by recent experiments with ^{14}C-labeled plants *(Helal and Sauerbeck [1984])*. Studying carbon turnover in the rhizosphere *Helal and Sauerbeck [1986]* suggest that mineral nutrients rather than carbon supply limit microbial growth. Indirect evidence is available for nitrogen often being a limiting nutrient. Several papers report on increasing bacterial numbers and respiration of nonsterile roots with higher N application *(Macura [1961]; Trolldenier [1971]; Trolldenier and von Rheinbaben [1981a])*. It is, however, still uncertain whether increasing N nutrition will also enhance root exudation thus stimulating microbial growth. Increased mineralization in the rhizosphere need not necessarily be accompanied by higher availability of plant nutrients. Though N mineralization in cropped soil is much greater than in fallow soil, total immobilization – obviously due to rhizosphere microflora – can be considerable *(Bartholomew and Clark [1950])*.

Unlike nitrogen, potassium probably does not limit microbial proliferation in the rhizosphere, otherwise potassium deficiency would not have the opposite effect of nitrogen deficiency on bacterial numbers. No effect on the density of root colonization by bacteria was found with different phosphorus levels *(Trolldenier and von Rheinbaben [1981b])*.

The amount of plant nutrients contained in the microbial biomass of several soils has been calculated by *Anderson and Domsch [1980]* assuming C:N, C:P, C:K and C:Ca ratios found in the biomass of pure cultures. The estimates of the upper soil layer (12.5 cm) for N, P, K and Ca are on the average 108, 83, 70 and 11 kg ha^{-1}, respectively. It can be expected that these amounts will increase during vegetation with the build-up of a rhizosphere population.

4.2 Microbial weathering

The participation of plant roots in association with their rhizosphere inhabitants in soil genesis is well documented. A recent review by *Robert and Berthelin [1986]* describes degradation and transformation of primary and secondary minerals, formation of deposits and synthesis of minerals. First observations were made by *Düggeli [1930]* concerning the solubilization of carbonate rocks by pure cultures of microorganisms. The solubilizing action of plant roots can easily be demonstrated by allowing roots to grow along a polished marble plate. After removal of the roots the course of root growth can be followed by the etched traces they have left *(Trolldenier [1971];* Figure 3).

A powerful tool for examining the weathering process is scanning electron microscopy. An interesting approach to study the effect of vegetation is to bury porous bags with minerals in the root zone of the plants and to analyse the loss of elements *(Robert and Berthelin [1986]).* Table 5 shows that, under spruce, weathering proceeds more rapidly than under other forest trees. The transformation of mica into vermiculite is promoted when K is absorbed from the solution by fungi, whereby the K equilibrium is shifted *(Weed et al. [1969]).* Uptake of K by roots may have a similar effect. An important role in biological weathering is ascribed to organic acids and chelating agents like siderophores. Both are also produced by roots and microorganisms. In the literature, cited by *Robert and Berthelin [1986],* it is reported that nutrient deficiency in culture media supports the formation of these compounds.

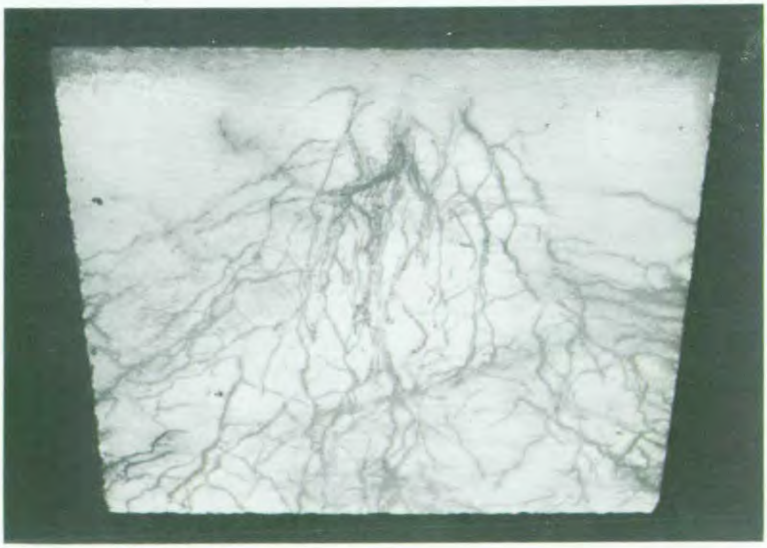

Fig. 3 Marble plate showing etched traces of root growth. *(Trolldenier [1971a])*

One may speculate that the greater exudation of organic acids and the stimulation of bacterial growth in the case of K deficiency may help the plant to overcome its stress situation. Indeed, it has been shown by *Berthelin and Leyal [1982]* that the rhizosphere microflora and to some degree VA mycorrhiza are able to improve K uptake from biotite and plant growth. However, the solubilizing action is obviously not sufficient to meet the requirements of normally growing plants (Table 6).

Table 5 Effect of different forest plants on the weathering of a mica (biotite) buried for 4 years in the A_1 horizon *(Sadio [1982]*, after *Robert and Berthelin [1986])*

Plant	K_2O	Fe_2O_3	MgO % loss	Al_2O_3
Picea	35	32	10	8
Vaccinium	19	7	7	7
Abies	26	1	1	0
Fagus	22	2	3	0
Festuca	5	4	3	4

Table 6 Effect of the rhizosphere microflora of maize and VA mycorrhiza on cation uptake, K being supplied as biotite, Ca as $Ca(NO_3)_2$, and Mg as $MgSO_4$ *(Berthelin and Leyal [1982])*

Treatment	Shoots mg	K	Ca mg · plant^{-1}	Mg
Sterile	456 ± 180	1.5 ± 0.1	1.8 ± 0.3	2.1 ± 0.8
Rhizosphere microflora	979 ± 46	2.6 ± 0.1	4.8 ± 0.6	4.9 ± 0.3
VA mycrorhiza	1050 ± 60	1.9 ± 0.1	3.2 ± 0.3	3.4 ± 0.2
VA mycorrhiza + rhizosphere	1170 ± 334	2.8 ± 0.5	3.7 ± 0.8	4.8 ± 1.2

5. Effect of mycorrhiza on K nutrition of plants

Brief mention of mycorrhiza should be made because of its significance in mediating nutrient uptake by plants. An excellent publication is available on «Methods and principles of mycorrhizal research» *(Schenck [1982])*. However, the majority of publications in this field concerns phosphorus nutrition and only a few deal with the effect on potassium uptake.

With ectomycorrhiza of trees *Hatch [1937]* has already shown improved N, P and K uptake by mycorrhizal plants as compared with plants without their microsymbionts. Further references to the beneficial role of ectomycorrhiza in improving K uptake are given by *Harley [1969]* and *Edmonds et al. [1976]*.

The stimulatory effects of symbiosis on plant growth or yield level generally decrease with higher K nutritional status of the plant. This also applies to VA mycorrhiza of herbaceous plants.

Little is known about VA mycorrhiza effects on K uptake *(Powell [1975])*. Results of *Smith et al. [1981]* indicate that mycorrhizal infection can improve K nutrition of *Trifolium subterraneum* when internal K concentrations are low. The authors conclude that increased K uptake may be an indirect result of improved P nutrition and *Yost and Fox [1982]* come to a similar conclusion. Slightly higher K concentrations in VA mycorrhizal plants compared to non-mycorrhizal plants were also found by *Sieverding [1983]*.

6. Bacterial fertilizers to improve K availability

Efforts to improve plant nutrition and growth by seed bacterization are countless. So called silicate bacteria were recommended and used for seed inoculation as a means of increasing potassium nutrition in plants. Citing earlier literature *Saber and El-Sherif [1975a, b]* studied the effect of silicate-dissolving bacteria on potassium uptake by *Sorghum helepensis* (Sudangrass). Unfortunately no accounts are given either of exchangeable K contents of the used soils or of the K nutritional status of the plants. In soil with Nile silt addition K uptake was higher than in soil mixed with sand. In the soil mixed with Nile silt inoculation did not improve K uptake, whereas in the sand/soil mixture seed inoculation with silicate bacteria, an unidentified Bacillus strain, increased K uptake by about 20% independent of the calcium content of the soils. Whether the inoculant itself supplied additional potassium is questionable. *Saber and El-Sherif [1975a]* deal with the enumeration procedure for silicate-solubilizing bacteria in detail.

In a critical review *Mishustin et al. [1981]* stated that «although potassium is released from silicates by microorganisms, the process is not active enough for complete provision of the plants with this element. The positive effect of treatment of seeds with silicate bacteria is determined largely by the biologically active substances that they produce». Analogous conclusions have often been drawn to explain effects after inoculation of nitrogen-fixing and P-solubilizing bacteria.

7. Microbial processes as influenced by K nutrition of plants

This aspect has been reviewed earlier *(Trolldenier [1981])*. Several processes are altered in magnitude by variations in potassium nutrition of plants. In K deficiency the increased root exudation accompanied by accelerated microbial proliferation and respiration may lead to oxygen depletion in the rhizosphere thus favouring denitrification specifically *(Trolldenier [1981]; von Rheinbaben and Trolldenier [1983])*. Denitrification is furthermore supported nonspecifically by longer preservation of higher soil moisture due to more restricted growth of K deficient plants. The relation between K deficiency and iron toxicity in rice plants seems also to be linked with more rapid O_2 depletion in the rhizosphere and the decrease of oxidizing power of rice roots *(Trolldenier [1977])*.

In a long term experiment with rice we found appropriate K nutrition to enhance associative nitrogen fixation. At moderate mineral nitrogen fertilization about one quarter of plant nitrogen was derived from N_2 fixation *(Trolldenier [1986])*. Possible mechanisms involved are: more rapid uptake of soil-N due to better plant growth (thus minimizing the repression of nitrogenase), greater availability of organic acids which are sources of carbon for important nitrogen fixers, and provision of suitable redox conditions around the roots.

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Coordinator's report on the 3rd working session

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Physical and biological methodology of the behaviour of nutrients and microbial activity near the root surface were discussed.

Calculations and actual measurements of K concentration at various distances from an active absorbing root surface were presented elegantly by *Kuchenbuch.* He showed that the distribution profile of K in proximity of an absorbing root surface depends on two kinds of parameters: *Soil parameters* like initial K concentration, buffer capacity of the soil, moisture content. *Plant parameter:* the ability of the root to extract K.

According to his calculations the plant is extracting in the root hair region K ions that are not exchangeable by ammonium acetate extraction. Two problems need further studies: 1) the development of an independent method to measure the uptake efficiency of the root (Km - *Michaelis-Manten* constant). 2) A more reliable determination of the amount of K taken up from the interlayer positions.

Jaillard has reviewed the method employed in studying the chemical changes induced by the living root on the immediate soil environment. To study root excretions during growth, the agar with dissolved pH-indicator method is used. It is possible by that method to monitor the active regions of the root that are releasing acid or basic substances to the growth medium.

Using the polarized light microscope at the end of the growing stage one can monitor the cumulative effects of the root on the soil around it. It was demonstrated by the use of the Electron Dispersive System that the growing root compresses the clay around the root and reorients it. Calcium carbonate was also demonstrated to concentrate around the root.

Van Noordwijk has discussed the amount of labour involved in root study under actual field conditions. He emphasized the dynamic nature of the root system. There is a dynamic balance between root growth and root decay.

To observe actual root growth in the field, the use of fiber optics with a video camera enables the research worker to observe actual growth and decay of a single root, as well as the changes in the root density around the lucid tubes inserted in the field. There are tremendous variations in the method used to study root density in the field which is an indicator of the early stage of this scientific field. The complex reactions near the growing root need a joint effort from several disciplines to synchronize the reactions around the root under field conditions.

Helal and *Trolldenier* have dealt with the methods to study the biological activity around the root.

A new root cage to study the rhizosphere was presented by *Helal*. It allows a better and more accurate sampling of biological activity at predetermined distances from the root surface. He has found that up to 20% of the photosynthetic carbon is released from the root to the soil. If this method proves accurate it is expected that it will spread to other disciplines of plant research.

Trolldenier has surveyed the methods used to study the activity of bacteria around the root. He demonstrated that the C/N ratio, as affected by N application and the levels of available K have an influence on the number and composition of the bacteria in the rhizosphere. The lower the K level the higher the root excretions, hinting to the possibility that the root membrane integrity is damaged in the case of deficient K in the soil.

Chairman of the 4th Session

Prof. Dr. *H. Beringer,* Director, Büntehof Agricultural Research Station, Hannover/Fed. Republic of Germany

4th Session

Field Studies on Potassium Availability

The Influence of Soil Structure on Rooting, Nutrient Uptake and Yield Formation

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Summary

Water supply to the plant, soil aeration and through-rooting are important aspects of soil structure. Together with particle size distribution packing density (degree of soil compaction) is a decisive factor. Bulk density alone is not a good indicator of this; particle size distribution must also be taken into account. Measurement of compaction by penetrometer is not altogether reliable because resistance to penetration depends not alone on packing density reliability but on water content, particle size distribution and other soil properties.

After stoniness, root penetration is hindered or limited mostly by soil aeration or drying out of the soil. Resistance to penetration often gives only indirect information of the reasons for differences in root exploration.

The yield potential of a soil is determined by its rooting capacity – especially in the subsoil – and by the supply of plant available water in the root-room.

Root penetration and available water capacity of the soil are of decisive importance for nutrient uptake. Under present-day conditions in central Europe, soil structure is a more important factor in determining crop yield and stability of yield than is nutrient supply.

1. Soil structure

Investigation of soil chemical factors (nutrient supply, pH) which affect plant growth is well-developed but the investigation of soil physical factors (soil water, soil aeration) is not so well developed. Causes of yield differences are nowadays less likely to be found in nutrient supply and are more likely attributable to soil structure.

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By soil structure, we understand the spatial arrangement of solid components and the resulting system of pores. Pore arrangement is largely determined by texture. Inter-particle spaces are designated primary pores. Secondary pores are formed in the development of the structural units (peds) (by frost, biological activity, cultivations etc.).

The most important structural properties are:

- Pore volume
- Pore size distribution
- Continuity of macro pores
- Stability of soil structure.

These can be investigated by physical methods *(Hartge [1971]; Hartge [1978]; Hillel [1982])* and, quite reliably, by field methods *(Bodenkundliche Kartieranleitung [1982]; Harrach [1984])*. More detailed and very important information on structural units can be obtained using microscopy (micromorphology, morphometry) *(Altemüller [1974]; Maier-Kühne [1986])*.

Table 1 summarises important functions and soil physical parameters of the structural units.

Table 1. Functions of soil structure and decisive physical properties of soils

Storage of plant available water
Available water capacity (A.W.C.) of individual soil layers
A.W.C. of soil penetrated by roots
A.W.C. of effective root-room
Hydraulic conductivity
Saturated permeability
Unsaturated permeability
Aeration
Air capacity
Permeability to air
Diffusion rate of oxygen
Redox potential
Thermal regime
Heat capacity
Thermal conductivity
Consistence
Shear strength
Aggregate stability
Plasticity
Root penetration
Soil strength (shear strength, resistance to penetration)
Aeration
Chemical factors (pH, toxic material)

2. Packing density of soils and compaction

The structural units can undergo change. The plough-layer of arable soils is altered by natural processes and by cultivations through periodical loosening and compaction. There may also be compaction below the depth of cultivation – plough pan – and this is only rectified very slowly, if at all, by natural means. Further, there may be compaction of geological or pedogenic origin in the deeper layers.

Soil compaction is variously defined by soil scientists. From the point of view of crop production we mean such compact arrangement of crumbs, *so close packing of the solid soil material that through-rooting and yield potential are adversely affected.*

With change in packing density, properties and functions of the structural units alter. Increasing density results in:

- Reduction in pore volume,
- Increase in bulk density (solid material per unit volume),
- Change in pore size distribution (large decrease in macro and slight increase in fine pores),
- Decrease in satured hydraulic conductivity and permeability to air,
- Increase in mechanical strength *(e.g.* resistance to penetration).

Figure 1 after *Dumbeck and Harrach [1985]* gives an example of *pore size distribution* in a loess soil. Pore size distribution in the surface layer is shown for different packing densities and the correlation between density and pore size range is given. The regression lines are so arranged that their separation indicates change from the original pore size distribution. In the loosest packing, density is less than 1.35 g/cm^3 and the pore volume over 50% (vol/vol). In the closest, the corresponding values were 1.50g/cm^3 and less than 44%. Pores < 3 µm equivalent diameter increased with increasing compaction, pores > 3 µm decreased sharply. This value for the transition point does not apply to all soils. *Dumbeck [1986],* working with a range of soils, found a definite decrease in pores as a result of compaction; this was mainly in the 3 µm size but also to some extent in those of 10, 30 or even 50 µm equivalent diameter. Particle size distribution played a part in this *[ibid.* p. 191].

All the above named structural parameters from pore volume to resistance to penetration are relevant in describing compaction. These parameters depend not only on packing density but also on other soil properties – mainly texture, organic matter content. ..

Thus, for instance, *bulk density,* a relatively easily measured parameter, can only be used as a measure of packing density in comparing closely similar soils. Soils richer in clay at the same packing density have lower bulk density (Table 2). Content of heavy minerals and organic matter content also affect density. For comparison of soils of different clay content, the so-called effective packing density *(Bodenk. Kartieranleitung* [1982]) can be used:

Effective packing density = Bulk density + 0.009. clay content

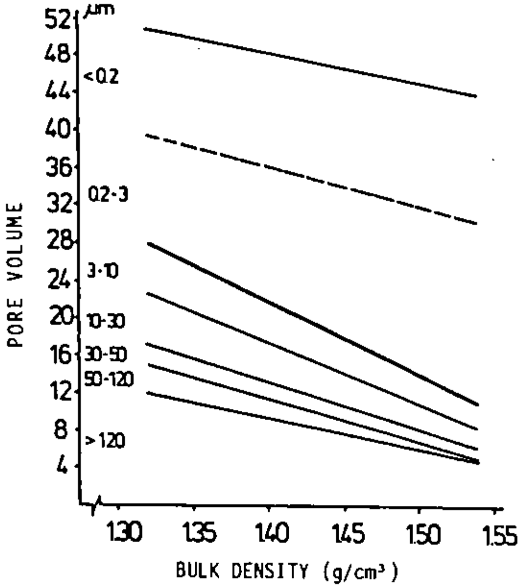

Fig. 1. Pore size distribution as a function of bulk density (additive plot of the regression) *(Dumbeck and Harrach [1985])*

It is still simpler to measure *resistance to penetration*. Various types of penetrometer are available for these measurements down to 70 or 100 cm depth. Small needle probes can be used both in profile pits in the field and in the laboratory. Interpretation of such measurements must be done in the knowledge that their magnitude depends upon a number of soil properties. According to *Dumbeck [1986]* and *Horn [1984]*, the most important are:

- Substrate properties which determine ped stability (clay content, cation composition, sesquioxide content etc.).
- Water content – most important,
- Packing density,
- Likely content of skeletal material,
- Weight of overlying soil horizons.

Therefore, packing densities should only be measured by penetrometer for comparison of essentially similar soils (identical substrate) at the same water content. It is, of course, difficult to arrange for the same water content in field investigations! In effect, therefore, the use of the penetrometer for this purpose raises problems and, so far as concerns farming practice and advisory work, macroscopic examination in the field (using the spade) is more fruitful. For scientific work, investigation of pore size distribution is likely to result in the most useful information.

Table 2. Bulk density and pore size distribution of the most important textures as a function of packing density (org. subst. < 2%) (suggested by *Harrach* and *Wourtsakis)*

Texture	Packing density*	Bulk density g/cm^3	finepores (< 0.2 µm)	micropores (0.2-10 µm)	macropores		total porosity
					fine (10-50µm)	large (> 50µm)	
			Vol. %	Vol. %	Vol. %	Vol. %	Vol. %
Sand	high	1.70-1.80	2- 6	5-10	2- 8	10-16	30-36
	medium	1.55-1.72	2- 6	4- 9	2-10	13-22	35-41
	low	1.35-1.57	2- 6	3- 8	5-20	16-28	40-50
Silty sand	high	1.70-1.80	3- 8	9-14	4- 8	10-15	32-36
	medium	1.55-1.70	3- 7	8-13	5-10	12-20	35-41
	low	1.20-1.55	2- 7	7-12	7-20	14-25	40-52
Loamy sand	high	1.66-1.80	7-12	9-14	3- 8	4-14	32-38
	medium	1.50-1.68	6-11	8-13	4-12	7-17	37-43
	low	1.35-1.52	5-10	7-12	5-20	10-20	42-50
Sandy loam	high	1.70-1.80	15-18	10-15	2- 4	2- 6	32-36
	medium	1.55-1.70	14-17	10-15	3- 5	4-10	36-41
	low	1.30-1.55	12-15	10-15	4- 6	8-18	41-51
Silt to loamy silt	high	1.45-1.65	11-15	19-25	2- 5	0- 4	38-42
	medium	1.40-1.55	10-14	18-25	2- 6	4- 8	42-48
	low	1.20-1.50	9-13	17-23	3- 8	8-20	44-55
Silty loam	high	1.50-1.68	15-20	15-20	2- 4	0- 4	38-43
	medium	1.45-1.60	14-18	15-20	3- 5	4- 8	40-48
	low	1.25-1.55	13-16	14-19	3- 7	8-18	44-52
Clay loam	high	1.35-1.60	21-28	12-16	1- 4	0- 4	40-48
	medium	1.30-1.54	20-27	11-16	2- 5	4- 8	43-50
	low	1.20-1.45	19-26	11-15	3- 6	8-16	46-55
Loamy clay	high	1.30-1.50	30-38	7-12	1- 2	0- 4	43-50
	medium	1.26-1.40	29-37	9-14	1- 3	4- 8	46-53
	low	1.20-1.35	28-36	12-17	2- 4	8-14	49-56

* Can be estimated by using the spade

3. Through rooting of soils

Taylor and Klepper's [1978] survey of the literature lists 24 factors which influence root growth, saying that this list is still incomplete. After soil chemical factors they list those connected with soil structure (soil strength, permeability to air, water content and temperature). These factors will be examined in turn.

In discussing structure the various requirements of different plants will be kept in mind. For example *Lehfeldt [1986]* says that plough pan is not so serious a constraint for spring rape as it is for winter wheat. Spring barley is even more sensitive. In considering effects of structure in practical terms the discussion should be based on the most demanding crops (sugar beet or barley).

3.1. Resistance to penetration

The root system can explore only a part of the soil. Large pores (> 10 μm) are absolutely necessary for root hairs and roots. By exerting pressure, the roots shift soil particles and so can further penetrate the cavity space, provided the mechanical resistance of the soil does not prevent it.

There is a copious literature on the effects of mechanical resistance on root growth and the intensity of through-rooting. The main aim of this work has been to establish limiting values for through-rooting. Three principal methods can be distinguished.

- Measurement of the radial or axial pressure exerted by the root,
- Measurement of the pressure which brings about reduction in root growth, by applying external pressure.
- Measurement of root growth in relation to the soil's resistance to penetration.

Axial and radial root pressure have been found to be in the range 0.3-2.6 MPa *(Misra et al [1978]; Whitley [1981])* (see also Table 3). The plant's requirements in relation to packing density can be found by making such measurements on seedling roots.

Root growth can be reduced by up to 50% by a soil pressure of 20 KPa. In some plants a reduction of 20% results under certain conditions from a pressure of 50 KPa *(Abdallah et al [1969]; Taylor and Ratcliff [1969]; Russel [1977])*.

Values measured by penetrometer for the restriction of root growth lie somewhere between 0.8 and 5.0 MPa *(Cannel [1977]; Goodeham [1977])* or sometimes higher (see Figure 2). According to *Ehler's [1983]* literature survey critical values for prevention of root growth are between 2.0 and 2.5 MPa. However, in field experiments, he found values between 3.6 and 5.1 MPa.

Critical values measured by penetrometer are sometimes much higher than those derived from model experiments measuring maximum radial and axial root pressures. The reason for this discrepancy is that the roots can grow around barriers in the soil *(Bandara and Fritton [1986])* and, to a large extent, because of earthworm activity and the presence of old root-channels in compacted zones *(Ehlers et al [1983])*. Further, constrictions in pores can be penetrated by slimming of the roots *(Altemüller and Haag [1983])*. Such possibilities are not apparent to the penetrometer.

A further cause of discrepancy is methodological. A critical analysis by *Gooderham [1977]* pointed out that different workers used different types of probe and often worked with only one soil type or plant species. Further the role of gas permeability was often insufficiently taken into account. Not least it must be pointed out that resistance to penetration is much affected by soil water content. On account of these difficulties, the use of penetrometers to determine critical values is perhaps of limited value.

Table 3. Maximum axial and radial root growth pressures available from the published literature (from MISRA et al. 1978)

Authors and year of publication	Plant species used	Axial/ radial pressure	No. of obser- vations	Mean pressure (kPa)	Range of values (kPa)
Pfeffer [1893]	*Faba vulgaris*	axial	6	1082	704-1936
Gill and Bolt [1955]	*Faba vulgaris*	radial	6	509	390- 611
	Zea mays	axial	4	1451	953-2494
	Zea mays	radial	1	659	—
	Vicia sativa	axial	2	1080	826-1333
Taylor and Ratliff [1969]	*Pisum sativum* (*cv.* Brunswick)	axial	63	1300	600-2600
	Gossypium hirsutim (*cv.* Coker 413-68)	axial	64	940	600-1600
	Arachis hypogaea (*cv.* Virginia Bunch)	axial	71	1150	500-2000
Eavis et al [1969]	*Pisum sativum* (*cv.* Alaska)	axial	290	1150	700-1600
	Gossypium hirsutum (*cv.* Coker 413-68)	axial	242	888	400-1300
Agarwal and Prihar [1975]	*Cicer arietinum*	axial	10	450	120 (SE)[a]
	Zea mays	axial	10	1090	187 (SE)

[a] SE indicates standard errors of the mean

In compact sandy soils, it is recognised that it is not gas permeability but mechanical resistance of the soil that limits root growth. The same holds for compacted layers *(e.g.* humic layers, hardpan, limonite). In such cases mechanical resistance of the soil must be taken into account. But, more usually, it is not enough to base conclusions as to gas per permeability merely on penetrometer readings. Better methods are needed.

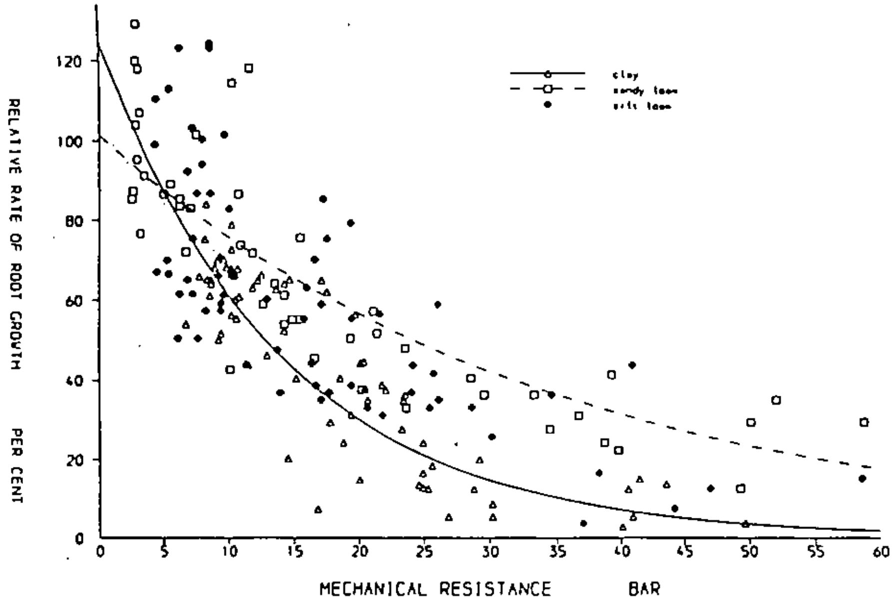

Fig. 2. Effect of resistance on root growth rate for three soils *(Gooderham [1977])*

3.2. Soil atmosphere

Soil air capacity is important. This is related to the proportion of air-permeable pores at field capacity, *i.e.* 2-3 days after copious watering. Air capacity means the minimum of air filled pores in the soil in critical times following heavy rain *(e.g.* in the spring). In well drained soils at field capacity, depending on the unsaturated hydraulic conductivity of the whole profile, macro pores > 10 μm or > 30 μm or > 50 μm equivalent diameter are available for penetration by air *(Hartge [1978]* p. 212).

The oft-quoted limiting value for optimum gas exchange of 10% air filled pores *(Grable [1971])* is viewed as being over-simplified by *Hamblin [1985]. PLA* [cited by *Hamblin]* found adequate O_2 diffusion when macro pores (> 30 μm) amounted to 8% so that root penetration was not hindered. *Ehlers* [1983] arrived by calculation at values of 6 and 11% (vol) according to continuity of macro pores. *Czeratzki [1972]* calculated a figure of 3 vol. %.

Gas exchange with the atmosphere is predominantly by diffusion. Thus the measurement of air permeability is only an indirect method of characterising soil ventilation *(Bowen et al [1983])*; it is suitable for the determination of pore continuity *(Groonevelt et al [1984])*. The connection between air permeability and root growth was investigated by *Dumbeck [1986]* and *Gättke [1984]*.

Dumbeck [1986] worked with a mollic luvisol with gleyed subsoil derived from loess. This soil had been subject to spoliation by mining machinery. Due to differing degrees of damage there was compaction to varying degrees reaching up to a depth of 100 cm. Compaction was measured by soil physical methods and rooting pattern of winter barley examined by using the profile wall method. Figure 3 shows how density along the roots in individual horizons varied with the proportion of macro pores and Figure 4 the air permeability in the relevant horizons. From the figures it can be seen that rooting decreased from the surface downwards though there was no compaction, uninfluenced variant. With increasing compaction rooting density decreased differently as between depths. It was particularly marked in the surface soil.

Soil structure is often described in terms of bulk density which under certain conditions is closely connected with the proportion of large pores (see Figure 1). But this connection – as already mentioned – holds only for soils of the same substrate and of the same texture. Critical values of bulk density in relation to through-rooting given in the literature can be extrapolated only with reservation *(Czertazki [1972]; Cannel [1977]; Eavis [1972]; Bowen [1981])*. Criteria for the evaluation of bulk density as indicating permeability to roots are given in Table 2; inhibition of root growth can be expected when bulk density indicates close packing. The reverse applies for bulk densities indicating loose packing.

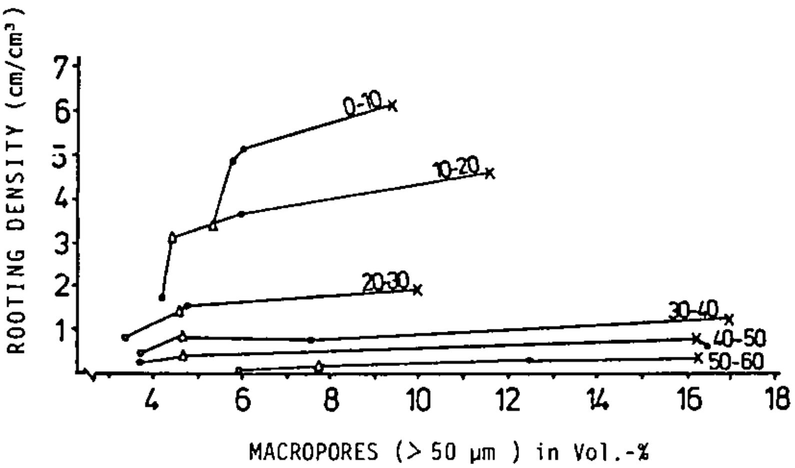

Fig. 3. Rooting density as a function of macropores (> 50 µm) in different depths *(Dumbeck [1986], p. 116)*

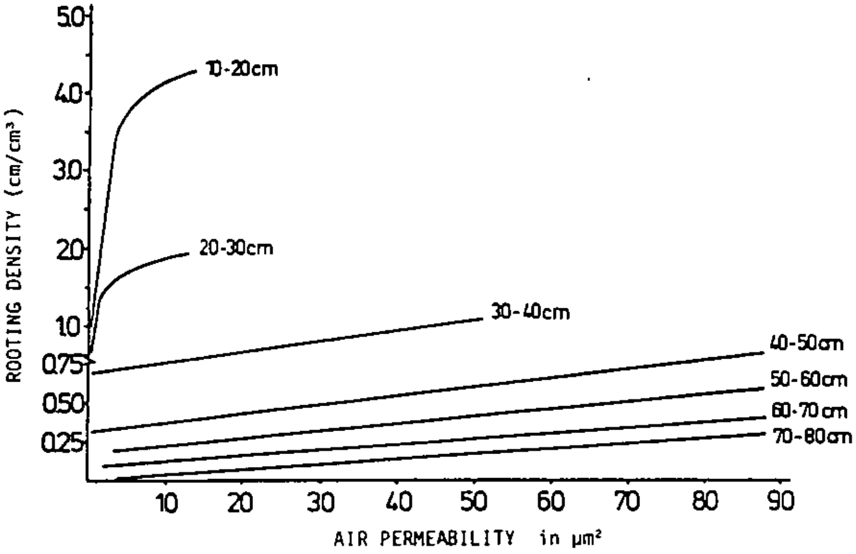

Fig. 4. Rooting density as a function of air permeability in different depths *(Dumbeck [1986], p. 118)*

3.3. Temperature

So far as concerns growth, branching and physiological functioning of the roots, different plant species have different temperature requirements. The effect of soil temperature on root growth is illustrated in Figure 5. *Voorhees et al [1981]* give the following optimum temperatures (to 30 cm depth): for wheat 20 deg C, for barley 18 deg C and for sugar beet 20-24 deg. In the field, diurnal variation has also to be reckoned with.

3.4. Multifactorial approach

No generally applicable critical values for each of the various physical parameters limiting root growth can be given as these parameters are mutually interdependent. The parameters describing structure change with change in packing density or water content. It is not therefore easy to decide which parameters closely affect root ecology and which only give indirect information on the causal connection. An example or two will make this clear.

In an experiment with samples of a loamy sand in which moisture content at a bulk density of 1.60 g/cm^3 was varied, *Lehfeldt [1986]* found reduction in root growth at 40% of field capacity but no such reduction at 80%. In this example, the cause was increased mechanical resistance.

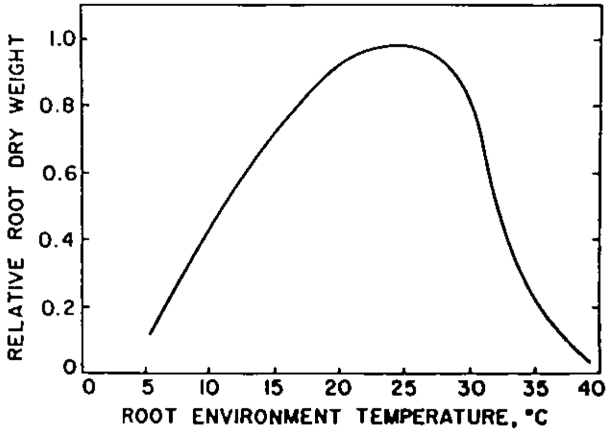

Fig. 5. Relative root dry weight as a function of temperature (generalized from data by *Brouwer [1962]*). (cited by *Voorhees et al [1981]*)

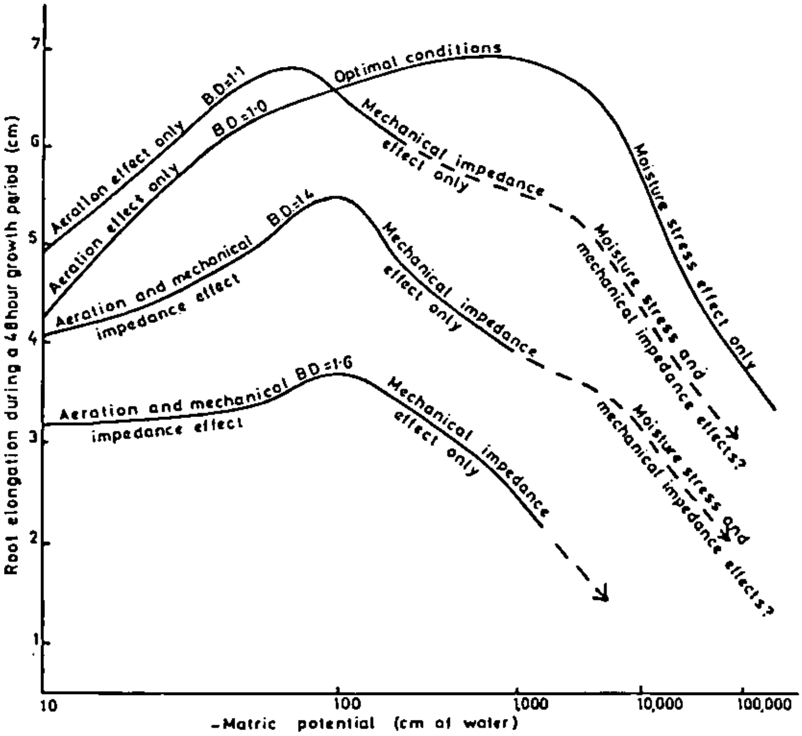

Fig. 6. Summary of role of mechanical impedance, aeration and moisture stress on pea seedling root elongation in a sandy loam held at different matric potentials and bulk densities *(Eavis [1972], p. 621)*

Figure 6 after *Eavis [1972]* shows how root growth was influenced by permeability to air, mechanical resistance and lack of water when packing density and water content were both varied.

Lehfeldt et al [1986] found a reduction in root growth in tiped sandy loam at a lower bulk density (1.70 g/cm^3) than in unaltered soil (1.77 g/cm^3). In this case, the cause was destruction of pore continuity in the sieved soil.

4. Effect of root development on yield

The yield potential of a site depends on a number of factors. These may or may not be subject to modification by cultural treatment. Nutrient supply can be corrected by fertilizer; structure of the surface layer can be improved by appropriate cultivation. But root penetration in the subsoil can at best be only slightly improved. Even more difficult to contend with are unfavourable climatic or weather conditions. Temperature and rainfall affect atmospheric humidity. According to *Renger and Strebel [1980]* there is a close connection between yield and the ratio transpiration/relative humidity deficit. The less the deficit the more effectively is water used by the plant and the higher the yield.

Kneib and Schroeder [1984] found in Schleswig Holstein that variation in cereal yield was due among other things to changes in relative humidity (sum of mean values for May and June). According to them, a decrease of 1 mm Hg is associated with a yield increase by about 5% of the maximum.

Those yield-limiting environmental factors which cannot be altered or compensated by feasible cultural means determine the value and potential yield of a site. Site potential can be defined as the average potential of the site at an economically justifiable level of input.

The yield potential of a soil is determined by its capacity for through-rooting – especially into the subsoil, and upon the availability of water in the rooting zone.

The effect of root penetration on yield has been discussed by *Brown and Scott [1984], Canarache [1984], Dumbeck [1986]* and *Gattke and Rex [1984].* Figure 7 shows the significance of rooting into the subsoil for sugar beet yield *(Dumbeck [1986]).* The results stem from an experiment with 5 cultivation treatments which produced contrasting compaction of the surface soil. These resulted in differential penetration of the subsoil and were closely correlated with yield.

Rex and Harrach [1984] did experiments with different cereals in four localities. At each place two or three different soils were compared under the same management. A deep loamy soil from loess was compared with a poorly drained, physiologically stagnant soil. Figure 8 shows yield in relation to total root-lenght in the subsoil. The comparisons are between identical crops and identical cultivation. In all four cases the same tendency is seen: the more intensively the subsoil is explored by roots, the higher is the yield. On sites where rooting in the subsoil was weak, rooting was more intensive in the topsoil. Consequently, there was negative correlation between intensity of topsoil and yield *(Rex [1984]).*

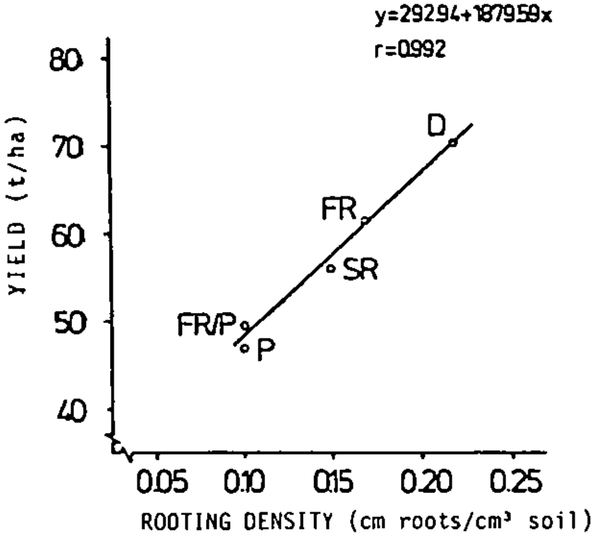

Fig. 7. Correlation between yield of sugarbeet and average rooting density in the subsoil (30-100 cm) of an Eutric Fluvisol *(Dumbeck [1986], p. 50)*

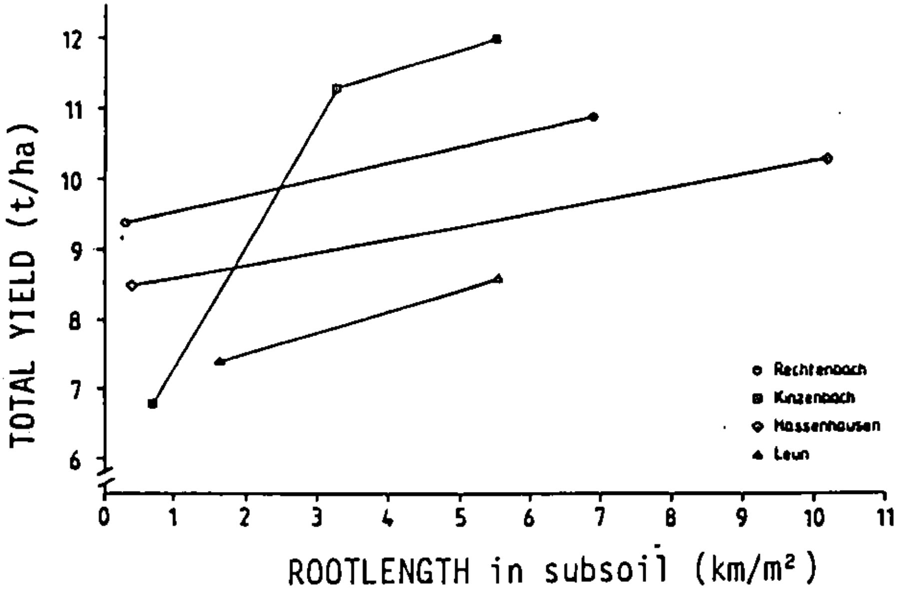

Fig. 8. Correlation between total yield of winter wheat respectively oats and the root length (km/m²) in the subsoil (30-100 cm) *(Rex [1984], p. 184)*

Potential yield is determined not only by root penetration but also by availability of water in the root-room *(Ritchie [1986])*. To illustrate this point, yields on the sites referred to in Figure 8 are plotted against available water capacity of the through-rooted soil after *Rex et al. [1984]* in Figure 9.

If water supply to the roots is insufficient, the soil soon dries out to the extent that root growth is inhibited. Thus, as the topsoil dries out, the subsoil assumes greater significance *(Taylor and Klepper [1978]; Ehlers et al. [1983])*. Here it is not only the absolute depth of rooting that is significant but, even more, early unrestricted root penetration to depth *(Taylor et al. [1972])*.

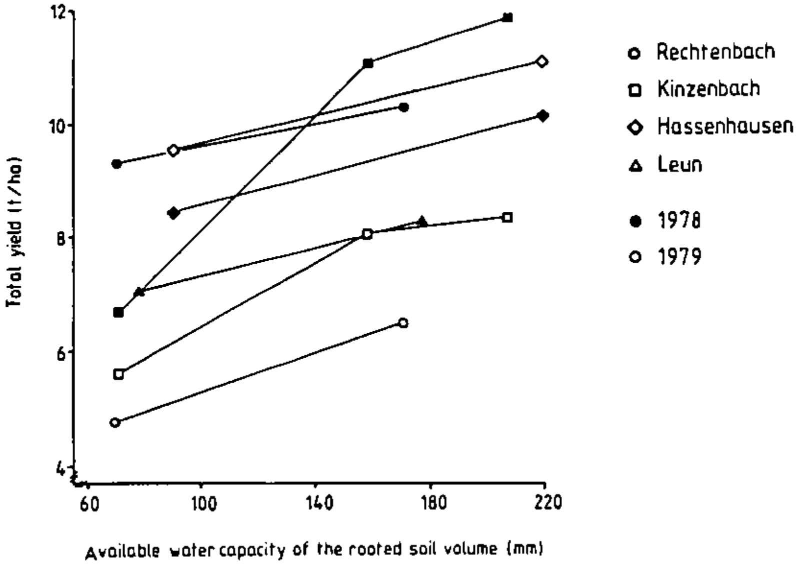

Fig. 9. Total yield of cereals as a function of available water capacity of the rooted soil volume *(Rex, Németh and Harrach [1985])*

5. Effect of through rooting on nutrient availability

Rex [1984] determined uptake of N, P and K by cereals (grain plus straw) in the above-mentioned experiments and found this was correlated with the extent of rooting. Figure 10 shows K uptake plotted against available water capacity of the rooting zone. The scatter of the data is due to the fact that climate was not exactly the same on the four sites. Further there was differences between the types of cereals and between varieties planted. *Rex* could find no definite connexion between K content of topsoil and K removal and concluded that the latter depended more on the extent of rooting in the subsoil. Better water supply led to better conditions for K uptake in soils with higher AWC in the zone penetrated by roots. *Grimme et al. [1981]* also found a significant contribution to K supply to the plant from the subsoil (sometimes over 50%) and this was significantly affected by soil moisture as determined by weather conditions in the growing season.

Rex [1984] illustrated the importance of soil K supply in a multifactorial diagram (Figure 11) taking account of both AWC and plant available (EUF) K. Through rooting of the subsoil was affected by both AWC and available K. Clearly, the exploitation of plant nutrients is largely influenced by through rooting of the profile.

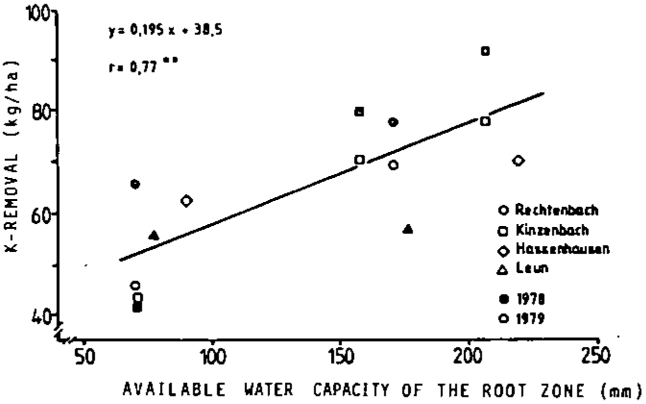

Fig. 10. K-removal of cereals as a function of the readily available water capacity of the root zone *(Rex and Harrach [1984])*

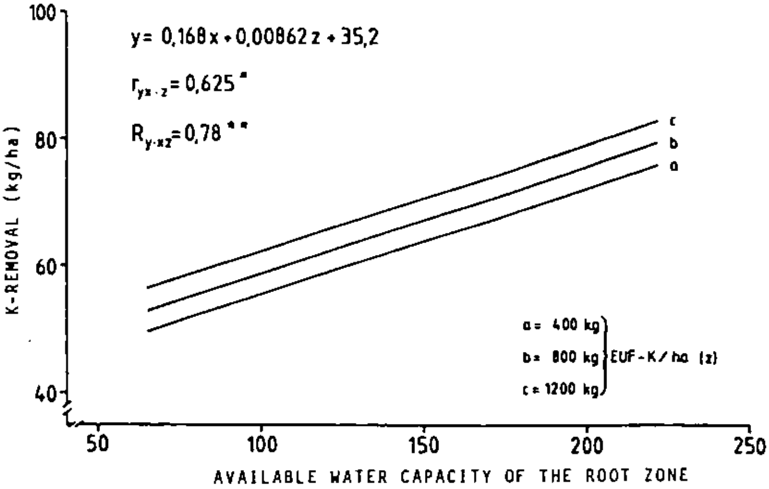

Fig. 11. Regression lines between K-removal by cereals as a function of available water capacity and K-content of the soil *(Rex [1984], p. 203)*

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Field Methods for the Evaluation of Soil Factors Affecting Potassium Response

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Summary

Apart from water soluble K content in the soil K availability and total K content depend on a number of soil properties and site factors which can readily be assessed directly in the field with simple methods and without the use of expensive equipment. They allow the estimation of parent material, soil texture, humus content, cation exchange capacity, structural type, pH value, bulk density, root depth, and available water capacity.

The recorded soil properties result in the designation of a soil type. Different soil types of a whole landscape together form a soil association which can be shown in a soil map. Respective maps can be provided showing the distribution of soil properties with regard to K response.

Permanent field installations like soil solution samplers, tensiometers or even weather stations allow a continuous monitoring of soil nutrient status and climatic site parameters.

1. Introduction

The effect of the potassium on crop growth, especially with regard to the optimization of yield and quality depends on a number of environmental factors. Besides the main soil properties, both climatic conditions and management practices, such as rate and time of fertilizer application affect K response (Figure 1). As the skills and the objectives of the farmers vary, their decisions also vary, so that the influence of farm management practices on K response is difficult to assess. Climatic and soil factors, on the contrary, can often be assessed in qualitative and semi-quantitative terms by using relatively simple field methods. Because of the paramount importance of the soil in agricultural production systems quantification of relevant soil properties (Figure 2) is of primary interest in land suitability evaluation.

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Fig. 1

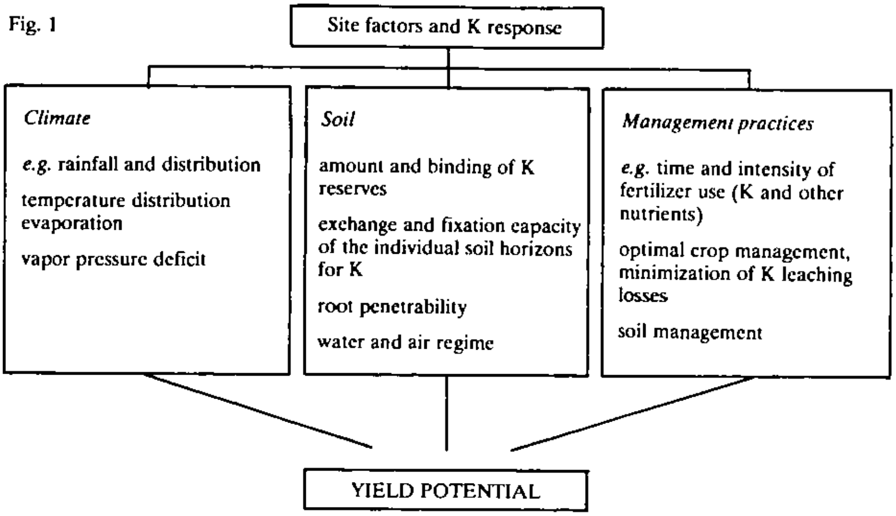
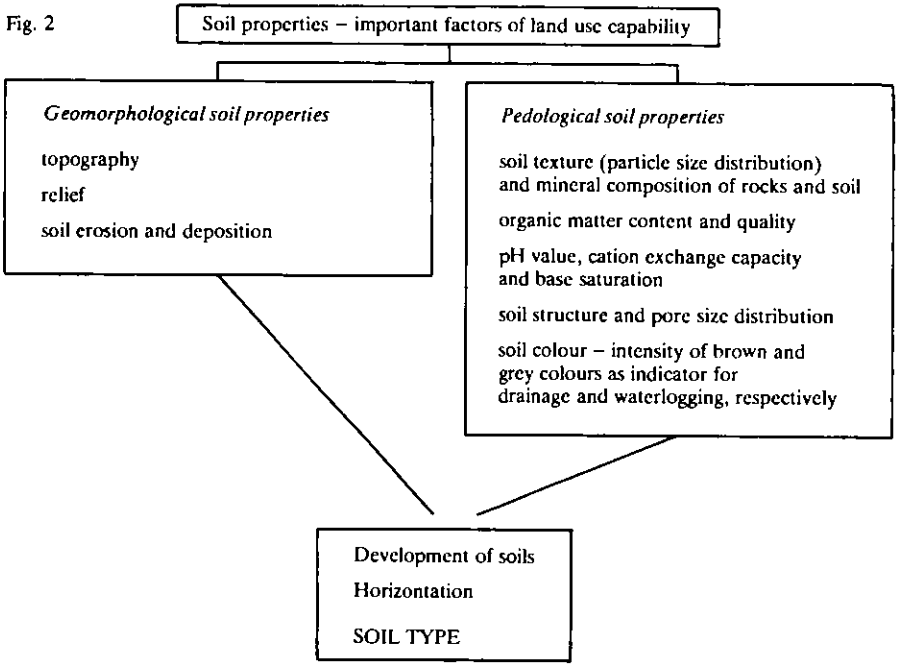

Site factors and K response
Climate
e.g. rainfall and distribution
temperature distribution
evaporation
vapor pressure deficit
Soil
amount and binding of K reserves
exchange and fixation capacity of the individual soil horizons for K
root penetrability
water and air regime
Management practices
e.g. time and intensity of fertilizer use (K and other nutrients)
optimal crop management, minimization of K leaching losses
soil management
YIELD POTENTIAL

Fig. 2


Soil properties – important factors of land use capability
Geomorphological soil properties
topography
relief
soil erosion and deposition
Pedological soil properties
soil texture (particle size distribution) and mineral composition of rocks and soil
organic matter content and quality
pH value, cation exchange capacity and base saturation
soil structure and pore size distribution
soil colour – intensity of brown and grey colours as indicator for drainage and waterlogging, respectively
Development of soils
Horizontation
SOIL TYPE

2. Field methods for the identification and assessment of soil characteristics as related to K behaviour in soils

2.1 Preliminary studies

Before attempting soil and site description, valuable information can be gathered from the study of topographic, geological and soil maps of the area under consideration. These maps may be obtained from the geological survey agencies. Geological maps provide information on the parent material and therewith often on the mineralogy and the K reserves of the soils. Topographic maps allow conclusions to be drawn on past or present erosion processes and erosion hazards. The consultation of soil maps and – if available – of aerial maps should be a matter of course in the preparatory stage of field work.

Good farmers keep records *(Schlagkarteien)* of crop yields and inputs on each field. These data give information on the variability of past crop yields in relation to local weather conditions, fertilizer inputs and phytosanitary measures. The change of soil K status with time as related to crop yield and fertilizer rates gives some insight into the behaviour of K in the soil. The farmer should also be interviewed before starting field studies because nobody knows his fields better than he does with respect to yield potential and the year to year variability in yield and also with respect to the effect of soil and crop management on crop performance.

2.2 Simple tests in the field

Simple tests can be made in the field which aid survey work for mapping of soil types and ecological features. Some of these tests are also a convenient source of information on the effect of potassium on plant growth.

Choice, presentation and interpretation of the field methods are based on handbooks and other publications by *Schumann [1975], Scheffer & Schachtschabel [1982], Schlichting & Blume [1966], Blume & Lamp [1985], Schroeder [1984], Böhm [1976], Fiedler [1973], Hodgson [1978], Clarke [1961], Renger [1971]* and *AG Bodenkunde [1982].*

Identification of parent rock and its mineralogical composition

When the rocks from which the soils are formed by pedogenic processes are considered together with climatic factors, conclusions may often be drawn on possible chronosequences of soil types. Moreover, a rough classification of the rock material as the source of K in the soil can already give some information with regard to K release and K fixation (Table 1). The ability of rocks to supply K depends on their contents of K bearing minerals like K feldspars, phyllosilicates and clay minerals, *e.g.* mica schist > granite > quartzite. It also depends on the texture of the parent rock and hence on the reactive surface of the minerals. At comparable contents of

K bearing minerals, for instance, the release of K from the unconsolidated sediment loess is considerably greater than from the consolidated sediment siltstone.

In the course of soil development K release from both substrates may become similar due to physical weathering of the consolidated rock minerals. The release of K is also affected by the clay mineral composition. A marine silt, for instance, contains a high proportion of K-saturated illites, whereas vermiculites with high charge density and K depletion at the edges often predominate in alluvial river deposits. Although they can still release sufficient K from their non-exchangeable pool, they may give rise to K fixation, when K fertilizers are applied.

Table 1 Rough classification of some important parent materials as a source of K with regard to K release from the non-exchangeable pool and K fixation

		low	
Quartzite	Siltstone	Mica schist	possibility K fixation
Sandstone	(Limestone)	Claystone	
Fluvial sand	Mica granite	Marine silt	
Quartz granite	Mica gneiss	Loess, glacial till	
Quartz gneiss	Basalt	Alluvial river deposit	

low ——— [1] ———→ high

[1] Mica resp. clay mineral content

- Total K content, K release from the non-exchangeable pool (amount, intensity)
- Number of cropping periods without K fertilization, not resulting in yield depressions
- Risk of secondary K fixation after longterm cropping without K fertilization

A classification of rocks *in situ* is given in Table 2. The rocks can be broadly described in terms of degree of hardness and consolidation, content of coarse clastic components, texture, colour as well as presence of fossils, stratification and foliate or slaty structure.*

Direct field determination of many of the minerals, with the exception of carbonates, is only possible in coarse-textured rocks. In fine-textured rocks the minerals in unconsolidated material can be determined indirectly from the texture and in consolidated material according to light and dark colours *(e.g.* biotite content: basalt > quartz porphyrite). Important in diagnosis are pedogenic iron oxides which give mainly intense colours and show a characteristics distribution in the soil horizons, so that they are very useful in soil classification. Diagnostic features of the pedologically most important minerals or mineral groups are given in Table 3.

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* Stratification is the layered arrangement of many aquatic and aeolian sediments, whereas foliate or slaty structure results from the parallel arrangement of mica through metamorphism.

Table 2 Characteristic features of the most important rocks

Unconsolidated (= Sediment)		
– gravelly and stony:		bench gravel, glacial sand, glacial till
– non-gravelly and non-stony:		blowing sand, river sand, loess, marine silt, alluvial deposits, alluvial clay
Consolidated		
Stratified and/or containing fossils (= Sediment)		
– gravelly and stony:		conglomerate, breccia
– slightly gravelly and slightly stony to non-gravelly and non-stony:		limestone, sand-, silt-, clay marlstone, sand-, silt-, claystone
Slaty (= Metamorphite)		
– coarse-textured and multi-coloured:		gneiss
– fine-textured:	light:	quartzite
	dark:	mica schist, slate
Non-stratified, non-slaty and fossil free (= Magmatite)		
– coarse-textured	grey:	gabbro
(= Plutonite rock)	multi-coloured:	granite
– fine-textured	grey-black:	basalt
(= Vulcanite rock)	light pink:	quartz porphyry

Table 3 Diagnostic feature of important minerals or mineral groups in soil samples

Plastic, no single grains visible	Clay Minerals
Effervescence in 10% HCl	Carbonates
– weak	— 2%
– distinct, not persistent	— 2-10%
– strong, persistent	— 10-25%
Colourless mineral particles, harder than glass, shelly faces	Quartz
Coloured mineral particles	Silicates
– white, often reddish-yellow	– K feldspar
– whitish grey	– Na, Ca feldspar
– white, soft, translucent, platy	– muscovite
– dark brown to black	– biotite
– black	– hornblende

Mineral particles as coloured coating or as concretion	Fe, Mn Oxides
– rusty brown	– ferrihydrite, geothite
– orange to reddish brown	– lepidocrocite
– bright red	– hematite
– grey to greenish-bluish	– mixed Fe compounds (Fe II/III-hydroxides, – carbonates, -phosphates)
– bluish black (with HCl: smell of H_2S)	– Fe sulphite
– brownish black	– manganite

Determination of soil textural classes by «feel»

The feel of the soil with the hand when worked between fingers and thumb is one of the oldest and even now a very important method for a broad classification of the textural class in the field. Sandy, silty, loamy and clay soils can be approximately described by «feel». A sample of fine earth (< 2 mm dia.) is moistened and submitted to various tests (Table 4).

The main criteria which enable the field worker to estimate the textural class for the particular sample are its cohesion and plasticity. The textural class into which the soil sample is placed allows conclusions, to be drawn on the particle size distribution, *i.e.* on the relative proportions of sand, silt and clay in the soil sample (Figure 3). Due to the relatively close correlation between mineral composition and particle size, some conclusions may be drawn on the ability of a soil to supply K to growing plants. The clay fraction is predominantly composed of clay minerals which may contain considerable amounts of potassium and which are often characterized by a particularly high cation exchange capacity, whereas quartz which is not a K bearing mineral and which has only a low adsorption capacity is mainly present in the sand fractions of soil derived from sedimentary deposits. These properties have always to be considered in relation to the parent material and the degree of soil development. It is for instance quite possible that the sand fraction of a physically weathered gneiss may contain a large proportion of mica which means a good natural source of K which can be released from the non-exchangeable pool.

Determination of soil colour by means of the Munsell Soil Colour System

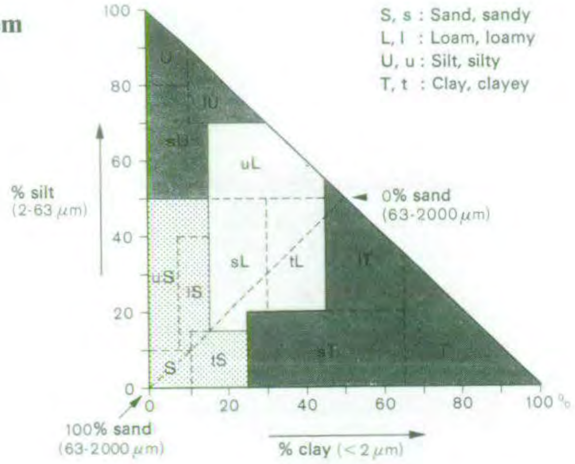
The soil colour is not directly related to potential K availability and K response. However, it is well known that low soil moisture decreases K availability, whereas K release and K response are greatly enhanced under moist conditions. The presence of a horizon with impeded drainage under otherwise comparable conditions may therefore already have a positive influence on K response. The occurence and intensity of colours and especially their distribution in the soil profile give information as to whether a site is influenced by surface water or by groundwater. Pseudogleying in a soil with stagnant water conditions and alternation of temporary

Table 4 Determination of soil textural class* by «feel»

Granularity detectable by feel and sight	Cohesion	Plasticity	Soil Textural Class (German system)
single grains predominant			Sands (S)
many single grains, gritty harsh feel	non cohesive non adhesive	non plastic	S sand
single grains, some fine material	non cohesive, traces of fine material left in the lines of the hand	non plastic	uS silty sand
single grains, much fine material	slightly cohesive, adheres to the finger	very slightly plastic tears and breaks	lS loamy sand
single grains, very much fine material	weakly cohesive, adheres to the finger	slightly plastic tears	tS clayey sand
smooth powdery feel			Silts (U)
no single grains	non cohesive, adhesive but non sticky	moderately plastic, breaks	U silt
few single grains, velvety	non cohesive, adhesive but non sticky	moderately plastic, breaks	sU sandy silt
no single grains, powdery	weakly cohesive, adhesive and slightly sticky	plastic tears and breaks easily	lU loamy silt
		can be rolled into pencil-thick «worms»	Loams (L)
few single grains, much fine material	weakly cohesive, adhesive and sticky	plastic, can be rolled pencil-thick, but breaks easily	sL sandy loam
very few single grains, much fine material	cohesive, adhesive and sticky	conveniently plastic, slightly brittle	uL silty loam
very few single grains, much fine material	cohesive, adhesive and sticky	conveniently plastic, very slightly brittle, dull surface	tL clayey loam
		shiny surface when friction is applied	Clays (T)
very few single grains, much fine material	cohesive, adhesive and sticky	conveniently plastic, slightly shiny surface	sT sandy clay
very few single grains, much fine material	very cohesive, adhesive and sticky	very plastic, slightly shiny surface	lT loamy clay
no single grains, only fine material	very cohesive, adhesive and sticky	very plastic, shiny surface	T clay

* Statements about the soil textural class are confined to the inorganic component of the fine earth (< 2 mm dia). As the organic matter has an influence on cohesion and plasticity, the humus content has to be taken into account and the soil textural classified accordingly.

German system



British system

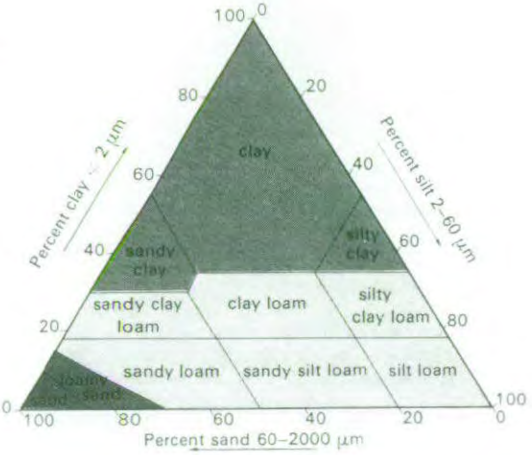


Fig. 3 Soil textural classes and particle size fractions *(Schroeder [1984])*

waterlogging and dryness leads to redistribution of iron and manganese through redox processes which gives rise to the so-called «mottling» where pale zones depleted of Fe and Mn oxides adjoin orange-brown patches of Fe and Mn oxide enriched zones (see also Table 3). Sometimes the accumulation of oxides may have become so concentrated that spots of brown Fe and brownish black Mn oxide concretions are observed. The influence of groundwater-gleying – in comparison with pseudogleying is characterized by a brown-coloured, Fe and Mn oxide-enriched, well aerated horizon overlying a bleached, often grey-coloured, Fe and Mn depleted and permanently waterlogged horizon.

For objective and reproducible description of the soil colour a moist soil fragment is compared with the *Munsell Soil Colour Chart.* According to the system of notation each colour may be considered as a resultant of three variables: hue indicating its relationship to the spectral colours yellow, red or blue; value indicating its lightness or darkness, and chroma indicating the strength or departure from a neutral colour of the same value. The area covered by contrasting colours (mottles, bands, veins) and by the matrix colour is estimated and thus permits conclusions on intensity and duration of the processes that have led to the colour differentation.

Soil colour as indicator of soil organic matter content

In soils the colours of oxides are often masked by coloured humic substances. Due to its fundamental role in soil fertility and its function as cation exchanger, soil humus influences potassium response. For this reason the estimation of humus content from soil colour could be useful. Up to a certain level and depending on soil texture the organic matter content correlates with the extent of black and white and thus the colour value read from *Munsell Charts.* Practical experience has shown that the values given in Table 5 can be readily used for humus content estimates.

Table 5 Estimation of humus content (%) according to Value (Munsell) and soil textural class

Colour	Value (Munsell)	Sand	Loam, Clay
light grey	7		< 0.2
grey	6	< 0.2	0.2-0.6
	5	0.2-0.4	0.2-0.9
dark grey	4.5	0.4-0.7	0.9-1.2
	4	0.7-1.5	1.2-4
black grey	3.5	1.5-3	4 - 6
grey	3	3 -5	6 - 8
	2.5	5 9	8 -12
black	2	>9	>12

Determination of pH value and estimation of cation exchange capacity and exchangeable cations

For measurement of pH directly in the field, distilled water is added to the soil sample at a soil: water ratio of 1:2.5. After stirring the suspension is left to stand for 10 minutes. The pH value is determined in the supernatant soil solution with indicator paper or portable pH meter. Subsequently KCl is added with a spatula by repeatedly stirring the suspension. Then it is allowed to stand for another 10 minutes and the pH value in the solution is recorded again. The difference between the actual (H_2O) and the effective (KCl) pH value depends on the acid species present in the soil. The commonly used pH ratings are given in Table 6.

Table 6 Soil description according to pH values in the soil solution

pH	3.5	4.5	5.5	6.5	7.2	8.5	>
	extremely acid	strongly acid	acid	weakly acid	neutral	alka-line	strongly alkaline

The cation exchange capacity (CEC) characterizes the ability of a soil to hold nutrient cations by adsorption in such a way as to prevent them from leaching on the one hand and to keep them readily available for plant uptake on the other. It depends primarily on clay content and the content of organic matter in the soil horizons.

In temperate latitudes the CEC of the clay fraction of many illite-smectitic soils ranges between 0.4 and 0.5 me/g clay, whereas values of 0.8 me/g clay (smectitic Vertisols) or even as low as 0.05-0.2 me/g clay (kaolinitic Ultisols, Oxisols) may occur in tropical or subtropical zones *(Scheffer & Schachtschabel [1982])*. Our considerations will only refer to soils of temperate climates. The cation exchange capacity of a soil can be roughly estimated by adding up the CEC values given in Table 7 for different soil textural classes and humus contents.

Table 7 Estimation of cation exchange capacity (CEC) according to soil textural class for soils of temperate climatic regions (a) and according to their humus content (b)

a) Soil textural class	S	lS,uS	tS	U	sU,lU	sL,uL	tL	lT	T*
CEC (me/100 g)	2	3	5	6	8	11	15	20	25
b) Humus content %	1-2		2-4	4-8	8-15	15-30 (an-moor)	30 (peat)		
CEC (me/100 g)	3		6	12	25	25-30	50-100		

* S = Sand, U = Silt, L = Loam, T = Clay
small letters = corresponding adjectives

At a given cation exchange capacity the sum of the exchangeable basic cations (Ca, Mg, K, Na) is an important indicator of soil fertility and normally closely correlated with soil pH. Although the sum of exchangeable basic cations is not necessarily correlated with the K saturations of a soil it is well established that K saturation is generally higher in neutral to alkaline soils (with the exception of saline soils) than in acid soils. Multiplication of the CEC values in Table 7 by the pH-dependent factors in Table 8 yields the approximate content of exchangeable basic cations. For sand, for instance, with 1% humus and pH 3.5 the calculated value for the content of exchangeable basic cations is 1 me/100 g, whereas about 45 me/100 g is characteristic of a loamy clay soil with 15% humus and a pH of 7.5.

Table 8 pH-dependent factors for the calculation of the sum of exchangeable cations

pH		< 3		4		5		6		7 >	
Factor	0.1		0.2		0.5		0.7		0.9		1.0

Soil structure and bulk density

The spatial arrangement of the soil particles and the degree of aggregation – the soil structure – is an important factor determining soil fertility. The structure is primarily related to pore size distribution and hence soil moisture retention and soil aeration as well as root penetration. Soil water and soil air regime in relation to potassium response have been described earlier in the text. As plants take up considerable amounts of water and nutrients from the subsoil, the effect of soil structure in the subsoil on rooting depth and rooting pattern is also of great significance in nutrient availability and crop response (Figure 4).

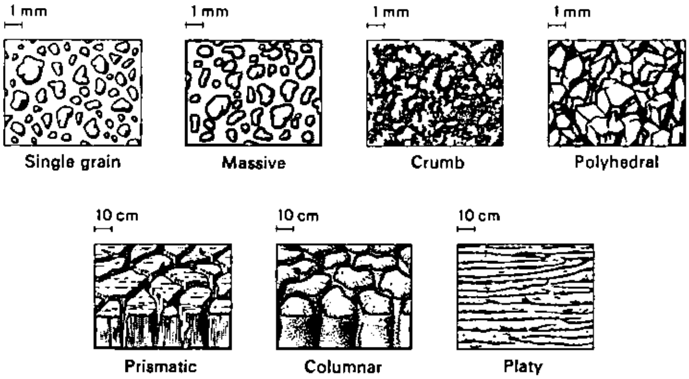


Fig. 4 Forms of spatial arrangement of solid particles (structural types) *(Schroeder [1984])*

The single grain type of structure is found in sandy soils and in silty soils low in clay and organic matter. In such soils the individual mineral particles are not combined into stable units or aggregates. In the massive type, which is unfavourable for root growth, the mineral particles are densely packed and cemented together by clay, carbonates and/or Al/Fe-oxides. This type is found, for instance, in compacted glacial till or in the iron pan of podsols. The optimal substrate for plant growth is characterized by a crumb structure in which the particles are aglomerated by organic matter and cementing agents resulting in round porous aggregates. Earth worm casts belong to this group. A narrow C/N ratio of organic matter as well as high Ca saturation on the exchange complex encourage formation and stability of crumb structure.

Clay and loam soils with low humus content or quality and low pH, or rather low Ca saturation are characterized by their high capacity for swelling and shrinkage when subjected to repeated cycles of wetting and drying. This may result in different forms of structured aggregates. These aggregates are often so densely compacted that their interior resembles the massive state and is resistent to penetration by roots. The polyhedral structure is characterized by weakly porous aggregates of different size with many surfaces and sharp edges. Increasing intensity of swelling and shrinkage with vertical cleavage gives rise to prismatic configuration (vertical > horizontal). Under the influence of high Na saturation the sharp edges become rounded due to peripheral dispersion resulting in a columnar structure. Plates are formed by swelling and shrinkage with cleavage in the horizontal plane (horizontal > vertical) as occurs in mechanically stressed soil horizons, *e.g.* in the plough pan area.

Many structural types are not only recognized visually, but also by their «bulk density» (volume weight). As the bulk density correlates with the soil consistence, field estimates can be made by a «penetrability test» in which the reactions to force delivered by hand are assessed (Table 9).

Table 9 Field estimates of bulk density with penetrability test by applying force with a pin on the profile wall

Penetrability	Bulk density (g/cm^3)	Constitution
Pin will enter easily and neatly, soil disintegrates and crumbles	1.0	very loose
Pin will enter neatly when applying slight force	1.2	loose
About half of the pin will enter	1.4	moderately compact
Pin will only enter a little	1.6	compact
Pin will not enter at well	1.8	very compact

Rough estimates of bulk density can also be obtained by assessing the reactions to augering. If the auger can be pushed easily into the soil by hand bulk density is < 1.2 g/cm^3. At a bulk density of about 1.4 g/cm^3 a hammer has to be used. Each blow would drive the auger 5-10 cm into the soil.

The stability of massive and aggredated structural forms can be determined in the field by means of the «swivel test». To make the test the sample considering of soil crushed to 2-5 mm is placed in a porcelain dish and well wetted so that water stands on the surface. Then the mixture is swirled for about half a minute. The structural stability is described according to criteria given in Table 10.

Table 10 Determination of structural stability by means of the «swivel test»

Criteria	Stability
Conspicuous disintehration, very turbid	very weak
Predominantly small aggregates, visibly turbid	weak
Large and small aggregates in almost equal proportions	moderately weak
Predominantly large aggregates	strong
No distintegration	very strong

Estimation of rooting depth in soil horizons

Plants utilize water and nutrients not only from the A horizon but also from horizons deeper down the profile. The proportion of nutrient uptake from the subsoil changes with crop and site and depends above all on the plant's genetic characteristics as well as on environmental soil properties encouraging the roots to grow into the subsoil. The actual rooting depth can be confined by solid rocks, compacted horizons and persistent waterlogging. Under non-limiting conditions the effective rooting depth is mainly determined by the soil textural class and plant type. The roots of annual agricultural crops grow down to 5-8 dm depth in sandy soils and 10-11 dm in silty, loamy and clay soils.

A rough estimate of the root distribution can be obtained by counting the roots exposed on the surface of the walls of a soil pit (Table 11). More reliable and precise is the method of *Böhm [1979]*, in which a few millimeters of the soil are washed from the profile face with water. Relatively good results are obtained by taking soil cores and separating soil and roots by washing with water *(Fiedler [1973])*.

Table 11 Estimation of root penetration in soil horizons

Fine roots (No./dm^2)	Root penetration
1 – 2	very weak
3 – 5	weak
6 – 10	moderate
11 – 20	strong
21 – 50	very strong
50	root mat

Characterization of the soil-water status

The capability of a soil to retain water in a plant-available form – the available water capacity (AWC) – depends on soil texture, humus content, structural form (bulk density) and root penetrability. The AWC for different textural classes of medium packing density is given in Table 12. In loams, silts and clays lower densities increase the AWC by 1-3%, whereas it correspondingly decreases at higher densities. The contribution of organic matter to AWC is shown in Table 13. When the values of Tables 12 and 13 are added up, multiplied by the depth of horizons (dm) and summed for the soil volume through which the roots can spread, this will yield the maximum storage capacity of plant available water. Values of < 100 mm are considered as low and of > 200 mm as very high.

Table 12 Available water capacity (AWC, Vol. %) for different soil textural classes of medium bulk density*

Soil textural class	gS	mS	fS	uS	lS	tS	U	sU	lU	sL	uL	tL	lT	T
AWC (Vol. %)	6	9	12	18	16	15	25	22	24	17	19	15	14	13

* high density: −(1-3) Vol. %; low density: +(1-3) Vol. %

Table 13 Increase of available water capacity (AWC) with organic matter (OM)

OM (%)	1 — 2	— 4	— 8	— 15	— 30	30
Sand:	+2	4	7	14	20	60-200 Vol. %
Loam, Silt, Clay:	+1	2	4	7	20	60-200

Table 14 Assessment of actual moisture in soil samples

Crusching	Moulding (forming a ball)	Wetting	Rubbing (in warm hand)	pF	Actual moisture
dusty	not binding	much darker	not lighter	4.0	very dry
dusty	not binding	visibly darker	weakly lighter	4.0 −2.7	dry
not dusty	formable (exception: sand)	not darker	visibly lighter	2.7 −2.1	moderately moist
sticky	some free water or weakly shiny	not darker	visibly lighter	2.1 −1.4	moist
free water	melting or dripping	not darker	visibly lighter	1.4	wet

The presence of a water table can play an important role as a source of water to plants during longer dry periods. The capillary rise of water from the water table to the rooting zone depends on pore size distribution – and hence on particle size – on the prevailing water potential and on the distance of the water table from the maximum depth of the rooting zone.

At a water potential corresponding to 50% of AWC and 1 m distance of the rooting zone from the water table, the amount of water that becomes accessible to the roots by capillary rise is e.g. 2-3 mm/day in a loamy silt (*e.g.* loess) and < 0.2 mm/day in a sandy soil or clay.

When comparing different localities and also in planning irrigation schemes it has proved expedient to observe the changes of water potential in the soil and hence soil moisture status during the period of vegetation. An assessment of actual moisture, i.e. the degree of saturation with water, can be made in the field by studying the changes in consistence and colour when the soil samples are wetted or dried (Table 14).

Description and classification of soils and soil associations

The visible and measurable characteristics of the different soil layers recorded in the field allow a horizontal differentation of the soil profile according to a formal system of soil horizon designations. In natural, uncultivated soils the sequence of horizons from top to bottom is: a litter layer (L) an organic horizon (O), a surface mineral horizon with humified organic matter (A), an eluvial (E or Ae) horizon and an illuvial (B), and the parent material or the C horizon. The system includes a further G horizon which occurs in hydromorphic soils under the influence of groundwater. Through cultivation L and O horizons are mixed with the underlying mineral (A) horizons. For a more detailed description and in order to take account of special features subscripts and affixes are added to the main symbols *(Schroeder [1984]).*

The symbols attached to each horizon and the vertical extent of each horizon describe the present stage of soil development. This description which should be as precise as possible makes possible conclusions on the history of the soil under consideration, on the predominant past soil formation processes and on the ensuing present soil properties. All this results then in the designation of a soil type.

The soils in a landscape are seldom homogeneous. Even if they have the same parent material and constant macroclimatic factors, different soil types may occur in association. Soil maps show the regional distribution of soils in a landscape or soilscape (Figure 5). The extent of lateral heterogeneity *i.e.* the variability of soil types and hence also the criteria of soil fertility per unit area, varies with geomorphological type of landscape, *e.g.* Mittelgebirge > Moränenlandschaft > Lösslandschaft (low mountain range > morainal landscape > loess landscape). The type of relief influences the extent and rate of lateral translocation processes and thereby generates a characteristic distribution pattern of soil types in a landscape. The lenght of a topographic sequence from hill top to valley floor determines the area covered by individual soil types within a landscape unit, whereas differences in elevation within a relief sequence (catena) contribute to the magnitude of differences in soil characteristics.

The Young Pleistocene, gently to moderately rolling morainal landscape in Schleswig-Holstein (Northern Germany) is for instance characterized by toposequences of about 150-250 m length and a height difference of 8-15 m. In these small landscapes which are comparable in size with agricultural fields the following soil types occur in association: Cambisols, Luvisols, Pseudogleys, Gleys and, to some extent also Low Moors. Figure 5 shows the topographic map of such a small landscape together with the soil map based on soil survey of the respective area. Similar maps can be provided showing the distribution of soil properties with regard to K response, *e.g.* available water capacity or cation exchange capacity.

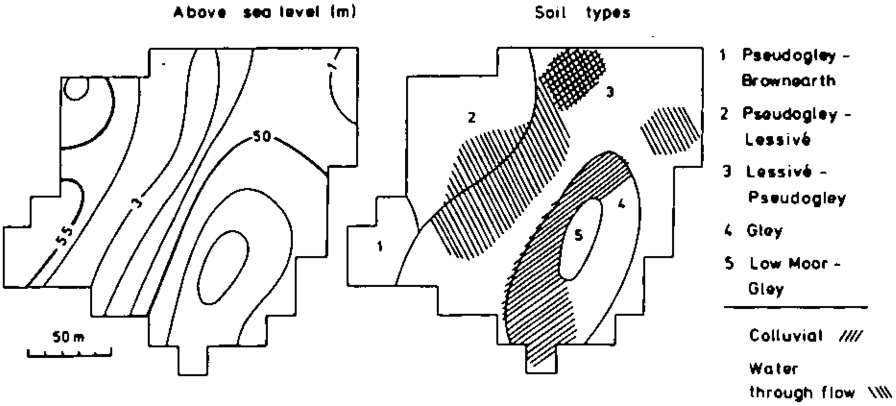


Fig. 5 Topographical map of a small landscape of the Young Pleistocene in Northern Germany (Schleswig-Holstein in the North of Selenter See) and respective soil map showing the distribution of soil types (German system)

2.3 Measurements with field installations

Measurement of potassium uptake from different soil depths

The quantities of K fertilizer that have to be applied to a crop are commonly based on the content of exchangeable K in the topsoil (0-30 cm). However, it has already been shown in the preceding sections that plants take up appreciable amounts of water and nutrients from the lower soil horizons depending on K content, rooting depth and other factors. Field experiments in which the percentage of K uptake from the subsoil was investigated revealed that *e.g.* 30-60% of the K requirements of spring wheat were taken up from the subsoil *(Grimme et al. [1981]; Kuhlmann et al. [1985])*.

Moreover, *Fleige et al. [1983]* were able to show that by far the greatest proportion of potassium – 90% – is transported to the plant roots by diffusion rather than mass flow. In the experiment (see *Strebel et al. [1980]* for details) the soil solution was sampled at 17 depths of a Luvisol (Udalf) by means of suction probes with small porous cups made of sintered Ni powder. At the same time soil water content and soil water suction were determined as a function of soil depth by means of a neutron probe and tensiometers, respectively. In a neighbouring profile the relation between water potential and hydraulic conductivity was determined. These data allow to quantify the contribution of the different horizons to nutrient supply and of diffusion to total nutrient flux.

Another method of determining the potassium uptake from the subsoil – the Rb tracer technique – is described by *Kuhlmann et al. [1985]*. The plants are pregrown in pots containing topsoil (0-30 cm) fertilized with small amounts of non-radioactive Rb as a tracer for K. Thus uptake from the subsoil can be distinguished from that from the topsoil. Two weeks after germination the bottoms of some pots are removed and the bottomless pots are sunk into the topsoil of a field allowing the roots to grow into the undisturbed and unlabelled subsoil. The K/Rb ratio in plants growing with or without contact to the subsoil enables the calculation of K uptake from the subsoil.

Automatic measurements of climatic-dependent site parameters

The importance of water for optimal plant growth and in particular the role played by water in K response has been pointed out in various parts of this paper. Especially, in highly intensive agricultural production systems water as a plant nutrient seems to become increasingly a yield limiting factor. Besides the soil factors influencing the water relationships, climatic factors, not only the macro-climate but also regional climatic influences, and presumably even relief-dependent microclimatic criteria, play an important role.

In recent years fully automatic monitoring systems have been developed which can be installed in the field in order to record microclimatic data and transmit them directly to a central computer *(e.g. ARAX,* Automatic Reporting Weather System). These observations include:

- air and soil temperature
- relative air humidity
- atmospheric pressure
- amount of rain
- solar radiation
- wind speed and direction
- snow conditions
- soil pH
- soil moisture

A comprehensive description of land with respect to land-use capability and crop productivity must include monitoring and evaluation of those continually changing environmental parameters as listed above. This is an essential prerequisite for optimal crop management and control of irrigation, crop protection, fertilization and tillage operations.

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Effect of Soil-Water Status as Affected by Irrigation on Potassium Transport in Soils

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Summary

Effects of varying soil-water content on K distribution and transport in soil were analysed, and the factors limiting K availability to plants are discussed. Restricted soil-root volumes require continuous monitoring of K concentration in the soil solution (C_K). Ceramic vacuum cups inserted in a sandy soil at depth of 20 and 40 cm below a tomato crop provided acceptable C_K values that could be used to improve K fertilization of the crop during the growing period.

1. Introduction

The introduction of sophisticated irrigation and fertilization systems to arid zones all over the world poses new questions regarding the effect of irrigation and water status in soils on nutrient transport and availability to plants. The objective of the present work was to analyse effects of soil water content and K application via the water on K movement in soils, and to discuss factors which may limit K uptake by plants. Since K concentration in the soil solution and water content in the soil determine K absorption by plants, means of monitoring these factors under field conditions are described, and data for a specific study case are presented.

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2. Theoretical Considerations

The flux of K in soils (F_K, mol cm^{-2} sec^{-1}) is equal to:

$$F_K = -[D_p(\theta)+D_{hd}(v)]\delta C_K/\delta x + v \cdot C_K \quad (1)$$

Here D_p and D_{hd} are the thermal and hydrodynamic dispersion coefficient of K (cm^2/sec), C_k is the K concentration in the soil solution (mol cm^{-3} solution), x is distance (cm), v is the pores water velocity (cm/sec), and θ is the volumetric water content of the soil.

According to *Olsen and Kemper [1968]*, D_p depends on the diffusion coefficient of K in water (D_o, cm^2 sec^{-1}) and on θ, as follows:

$$D_p = D_o \cdot a \cdot \exp(b \cdot \theta) \quad (2)$$

The empirical constants a and b account for soil tortuosity and cross section area of the soil available for ion movement. For most soils b is about 10 and a decreases from 0.005 to 0.001 as the specific surface area of the soil increases. According to *Nye and Tinker [1977]*, the term $a \cdot \exp(b \cdot \theta)$ may decrease by two orders of magnitude as field moisture decreases from —0.1 to —10 bars.

D_{hd} is a function of the solution velocity in the soil. *Olsen and Kemper [1968]* provide data on this relationship for flow velocities ranging between 0.01 and 1000 cm/day. For flow rates less than 0.2 cm/day, characteristic of water flow towards roots, the contribution of D_{hd} to the combined diffusion coefficient *[eq. (2)]* is small.

The flux of water in the soil depends on the hydraulic conductivity ($K_h(\theta)$, cm/sec) and the water head gradient in the soil (h, cm) (Darcy's law).

Expected variations in K_h, D_p and D_{hd} due to fluctuations in θ can be obtained from Figure 1, eq. (2), and the data of *Olsen and Kemper [1968]*, respectively. Examples of such variations, for a clay and for a sandy soil, are given in Table 1. The relationship between h and θ for the two soils is given in Figure 2.

Total K in the soil (Q, mol/cm^3 soil) is partitioned between the solution and solid phases of the soil. The solid-phase K is devided into readily exchangeable K (A_{ex}), fixed-K (A_f) and structural-K (A_s) (mol/cm^3 soil):

$$Q = A_{ex} + A_f + A_s + \theta \cdot C_k \quad (3)$$

Applying the continuity equation $-\delta F/\delta X = \delta Q/\delta t$ and including a sink term U *(e.g.* uptake by roots), eqs. (4) and (5) are obtained:

$$\delta Q/\delta t = \delta A_{ex}/\delta t + \delta A_f/\delta t + \delta A_s/\delta t + \delta\theta/\delta t \cdot C_K + \theta \cdot \delta C_K/\delta t - U \quad (4)$$

$$-\delta F/\delta x = \delta[D \cdot \delta C_K/\delta x]/\delta x - (\delta v/\delta x) \cdot C_K - v \cdot (\delta C_K/\delta x) \quad (5)$$

where $D = D_p + D_{hd}$

Table 1. Estimated effect of θ on soil-hydraulic conductivity (K_h), K-diffusion coefficient+ (D_p) and K-hydrodynamic dispersion coefficient* (D_{hd}) in two soils (0–20 cm)

θ cm^3/cm^3	K_h cm/sec	D_p cm^2/sec	D_{hd} cm^2/sec
Bet Dagan clay soil			
0.35	$2.5 \cdot 10^{-5}$	$6.6 \cdot 10^{-7}$	$3.0 \cdot 10^{-5}$
0.26	$2.8 \cdot 10^{-6}$	$2.7 \cdot 10^{-7}$	$1.2 \cdot 10^{-5}$
0.17	$1.7 \cdot 10^{-10}$	$1.1 \cdot 10^{-7}$	0
0.09	$1.0 \cdot 10^{-12}$	$4.9 \cdot 10^{-8}$	0
Besor sandy soil			
0.40	$1.7 \cdot 10^{-3}$	$2.0 \cdot 10^{-6}$	$2.2 \cdot 10^{-4}$
0.30	$3.5 \cdot 10^{-4}$	$9.0 \cdot 10^{-7}$	$1.3 \cdot 10^{-4}$
0.20	$8.0 \cdot 10^{-5}$	$4.5 \cdot 10^{-7}$	$9.0 \cdot 10^{-5}$
0.10	$2.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-7}$	$3.0 \cdot 10^{-5}$

+ D_p was estimated from eq. [2]. a and b for Bet Dagan soil were assumed to be 0.001 and 10, and for the Besor soil 0.005 and 10, respectively.

* D_{hd} was estimated from data by *Olsen and Kampar [1968]* relating D_{hd} to v (water flow rate). v was estimated to be equal to K_h (θ).

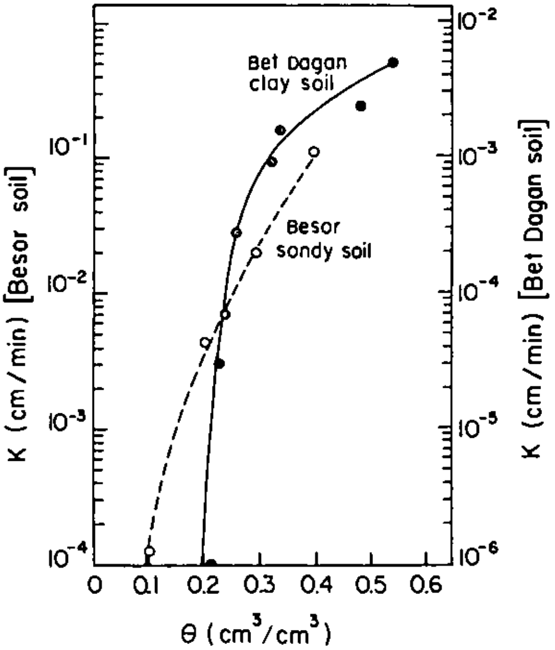


Fig. 1. Hydraulic conductivity (cm/sec) as a function of volumetric water content for Bet Dagan and Besor soils. Note the different ordinate scales.

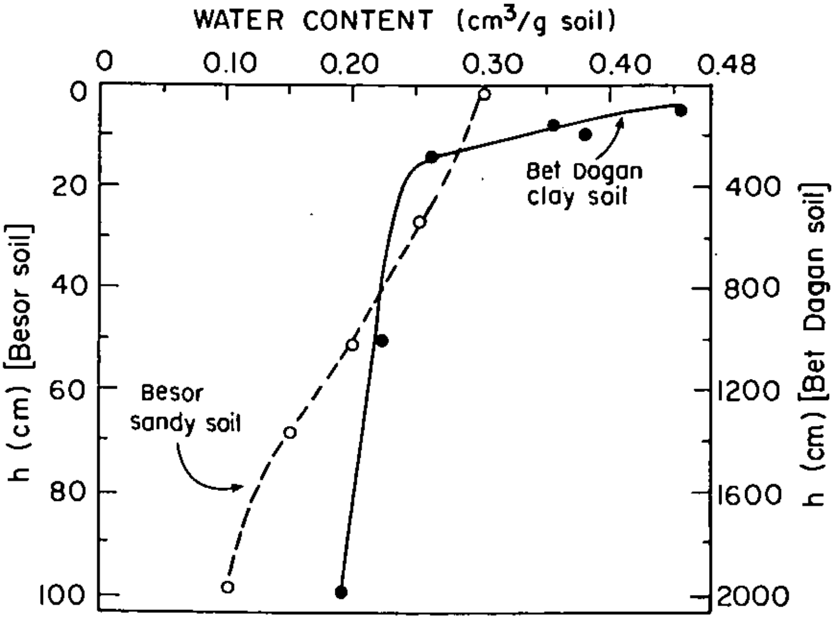


Fig. 2. Water retention curves for Bet Dagan and Besor soils. Note the different ordinate scales. For conversion to volumetric soil water content, use soil densities of 1.20 and 1.55 g/cm^3 for the two soils, respectively.

For the current analysis of effects of θ on K transport in soil, a single pool of solid phase K (S, mole/cm^3 soil) was assumed. Potassium in this pool was assumed to reach equilibrium with C_K very rapidly relative to its flow rate in the soil. Incorporating those simplifying assumptions into eq. (4), inserting $\delta S/\delta t = (dS/dC) \cdot \delta c/\delta t$ and $U = 0$, and assuming that θ and v are constants, eq. (6) was obtained:

$$(dS/dC_K + \theta) \cdot \delta C_K/\delta t = \delta[D \cdot \delta C_K/\delta x]/\delta x - v \cdot \delta C_K/\delta x \qquad (6)$$

Equation (6) can be solved analytically subject to appropriate boundary conditions, known initial uniform C_K in the soil, and known constant $(dS/dC_K+\theta)$ and v.

3. Materials and Methods

The field experiment reported herein was carried out in a greenhouse on a sandy soil (4-5% clay, CEC 50 mmol(+)/kg soil, 5% $CaCO_3$) in the Besor region of southern Israel. The test crop was tomato (local variety) planted in double rows in late October. The center-to-center distance between double-rows was 160 cm. The distance between rows in the double-row, and between plants along the row, was 40 cm. The tricklers were placed midway between plants in each double-row. The distance between tricklers along the tube was 40 cm; their discharge rate was 2L/hour.

The treatments differed in their time-averaged matric suction head in the soil-root volume and in the total application rates of water and K (Table 2). The N:P:K weight ratio in the irrigation water was constant with time (5:0.9:5.9) and equal in the two treatments. The concentration varied with time, as will be shwon below. Tensiometers (for description, see *Cassell and Klute [1986]*) and ceramic vacuum cups (Figure 3) were inserted in each plot midway between the trickler and plant at depths of 20 and 40 cm. Each treatment was replicated 4 times. Tensiometers were read daily at 0800 before irrigation. Soil solutions were collected after 24 hours of suction (50-70 cbar) beginning 5 hours after fertigation was terminated. Soil samples were taken on 25/11, 28/12, 8/2 and 19/4 between plant and trickler. The soil samples were dried at 40 °C, and analysed for $NaHCO_3$-soluble K *(Bar-Yosef and Akiri [1978])* and saturated-paste K.

The soil-water retention curve and $K_h(\theta)$ function for the Bet Dagan soil were taken from published results by *Bar-Yosef and Sheikholslami [1976]*. The data for the Besor soil were obtained by using the same procedures.

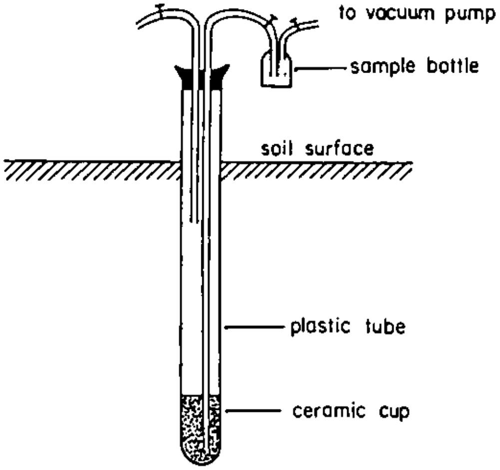


Fig. 3. Schematic description of a vacuum cup. The conductivity of the cup used in the experiment was 0.5 mL $hour^{-1}$ $cbar^{-1}$; the suction head applied was 50-70 cbar.

4. Results and Discussion

4.1 Predicted effects of soil moisture on K transport in soils.

Variations in D_p, D_{hd} and K_h due to changes in θ in the two studied soils are given in Table 1. The buffer capacity for K (dS/dC_K) was estimated from a study of Ca-K exchange in the two soils *(Feigenbaum and Levi,* unpublished data). Due to a lime content of 10 and 5% in the Bet Dagan and Besor soils, respectively, Ca concentration in the solution phase (C_{Ca}) of both soils was nearly constant despite the addition of K or Ca to the system. Under such conditions, A_K in the Gapon equation (7) can be partially differentiated with respect to C_K to yield eq. (8):

$$A_k/A_{Ca} = G \cdot C_K \cdot C_{Ca}^{-1/2} \tag{7}$$

$$\delta A_K/\delta C_K = A_{Ca} \cdot G \cdot C_{Ca}^{-1/2} \tag{8}$$

Here G is the Gapon constant of the soil and C_{Ca} is a constant. When the cation exchange capacity (CEC) of the soil consists mainly of A_K and A_{Ca}, and assuming that $A_{Ca} >> A_K$, A_{Ca} in [8] may be replaced by CEC. To use the same terminology as in (6), $S = A_K$.

Study case a: K application via the water on top of the soil.

The boundary and initial conditions for this case are given in eqs (9), (10) and (11) *(van Genuchten and Wierenga [1986]):*

$$C_K(x,0) = C_O \tag{9}$$

$$[-D(\delta C_K/\delta x) + v \cdot C_K]_{x=0} = v \cdot C_{in} \tag{10}$$

$$(\delta C_K/\delta x)\,(\infty,t) = 0 \tag{11}$$

The solution of (6), (9), (10) and (11) is *(van Genuchten and Wierenga [1986]):*

$$\begin{gathered}[C_K\,(x,t) - C_O]/[C_i - C_O] = 0.5 \cdot \mathrm{erfc}\,\{(R \cdot x - v \cdot t)/[2 \cdot (D \cdot R \cdot t)^{1/2}]\} \\ + [v^2 \cdot t/(3.14 \cdot D \cdot R)]^{1/2} \cdot \exp[-(R \cdot x - v \cdot t)^2/(4 \cdot D \cdot R \cdot t)] \\ -0.5 \cdot [1 + v \cdot x/D + v^2 \cdot t/(D \cdot R)] \cdot \exp(v \cdot x/D) \cdot \mathrm{erfc}[(R \cdot x + v \cdot t) \\ /2 \cdot (D \cdot R \cdot t)^{1/2}]\end{gathered}$$

Here erfc and exp are the complimentary error function and exponent, respectively.

Results of $C_K(x,t)$ for various values of θ in the soil are presented for Bet Dagan and Besor soils in Figure 4 and 5, respectively. The distribution in Bet Dagan soil after 20 days of continuous K application via the water under assumed constant field capacity conditions is described by line 2 (Figure 4). The cumulative amount of water supplied at the prescribed v (inset table) was 43.2 cm, far more than the depth to which K moved (~ 8 cm). The restricted movement is due to the large buffer capacity ($R = dS/dC_K + \theta$) of the system for K. When decreasing R tenfold, the C_K profile is far more extended than in line 2, even though t was only 5 days. When decreasing θ to 75% of field capacity ($\theta = 0.26$, line 5), v and D were estimated to decrease 9- and 2.5-fold, respectively (Table 1). This resulted in a very meaningful reduction in the C_K profile. The reduction stemmed mainly from the decrease in v, since when maintaining v as in line 2 and varying only D, the concentration profile (line 6) was similar to that of line 2. In addition to its effect on convection, v also determines the amount of K added to the soil via the water. When increasing t under the conditions of run 5, such as to accommodate the same volume of solution as in case 2, a steeper K-profile was obtained, and the ion moved deeper into the soil than in line 2 (line 7). The steeper curve stemmed from the enhanced dispersion which took place for 180 days, as compared with 20 days in run 2. The penetration depth (19 cm) agrees with the diffusion distance estimated from the equation $x=(2. \cdot D \cdot T)^{1/2}$, where D and t are as in run 7.

In order to add equal total K quantities at θ=field capacity and at $\theta=0.26$, it is possible to increase K concentration in the water in the lower-θ case. According to the current assumptions, this will not increase the depth of K penetration into the soil, which will still be <4 cm. However, C_K in the upper 4 cm will increase, and it will equal the C_K values obtained in case 2.

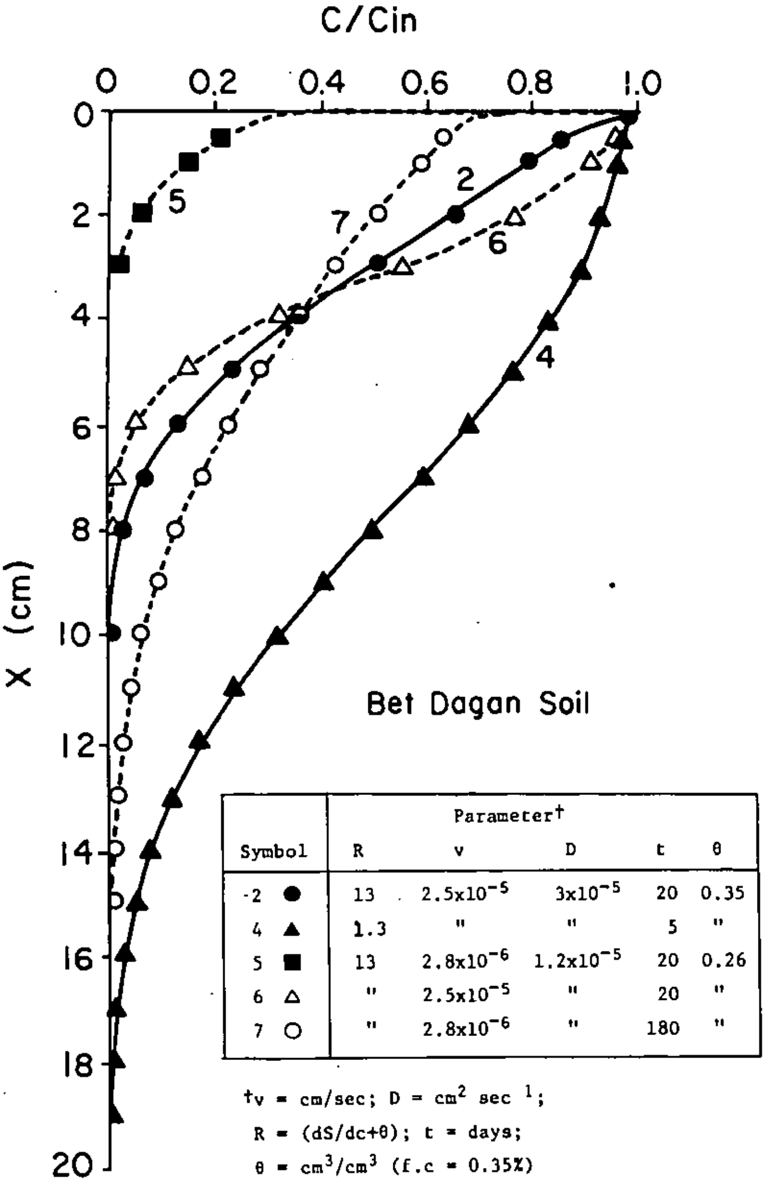
Similar effects of θ on C_K distribution in the soil were obtained in the sandy Besor soil (Figure 5). Due to the greater v and D and smaller R relative to Bet Dagan soil, K movement into this soil was much faster and K in the reference line No 1 reached a depth of ~ 20 cm in 1.2 hours. The expected diffusion distance in this case is less than 2 cm.

When reducing v five fold, corresponding to a decrease in θ from 85% of soil-water saturation ($\theta=0.40$) to $\theta=0.30$, and assuming that D was unchanged (line 2), a pronounced reduction in K transport occured, with no K found below 9 cm. When taking into account the expected decrease in D (from 0.00022 to 0.00013 cm^2/sec) as well (line 3), a C/Cin distribution not much different from line 2 was obtained. When extending the K application period to 5.8 hours to account for the reduced v and thus supply the same total K rate as in run 1 (run 8), a small difference in the C/Cin distribution relative to case 1 was obtained.

A further decline in θ to 0.20 v/v causes v and D to decrease to $8.\times10^{-5}$ cm/sec and $9.\times10^{-5}$ cm^2/sec, respectively. In this case K did not move below a depth of 4 cm (line 4). When increasing t to 25.5 hours to account for the reduced K application (line 9), K moved down to a depth > 25 cm, and the distribution with depth differed, due to the extended dispersion period, from those of either runs 1 or 8. The effect of a ten-fold smaller R (= 0.043) at $\theta = 0.20$ on the C distribution is presented in line 6. This may represent conditions where the buffer capacity factor consists mainly of θ ($dS/dC_K \rightarrow 0$).

Table 2. Irrigation treatments in the field experiment (four replicates).

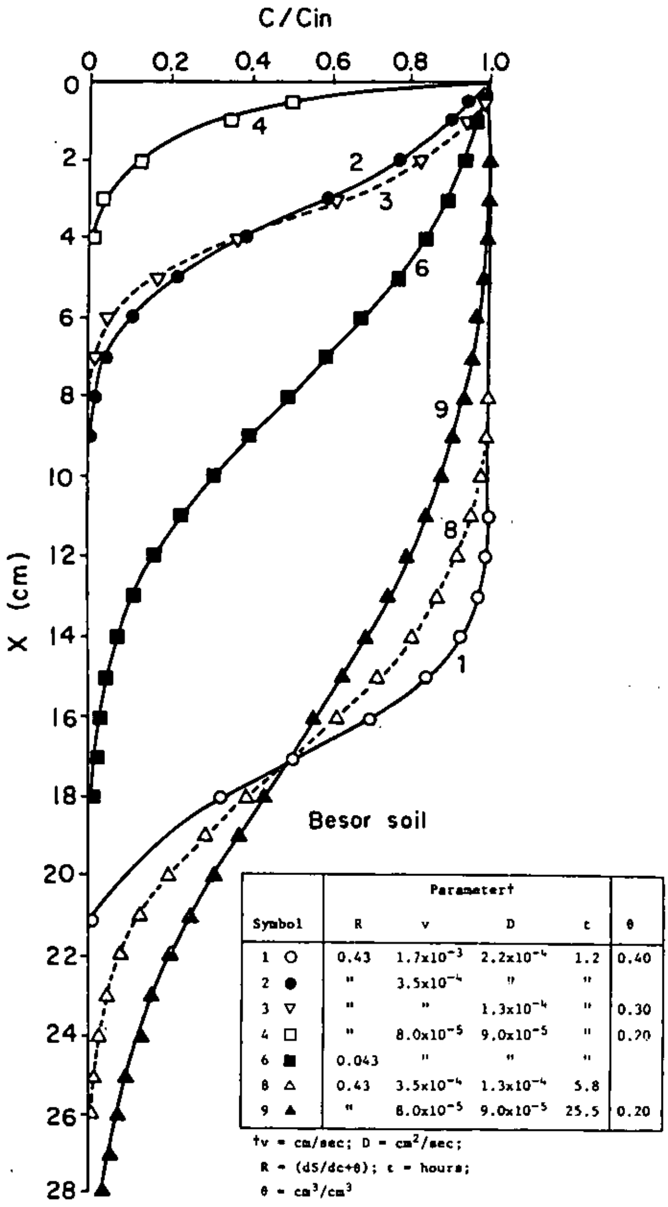
	Treatments	
	4	5
Planned suction head (cbar)	25	8
Total water applied (mm)	297	468
Days between irrigations	4-6	1-2



Symbol	Parameter† R	v	D	t	θ
2 ●	13	$2.5x10^{-5}$	$3x10^{-5}$	20	0.35
4 ▲	1.3	"	"	5	"
5 ■	13	$2.8x10^{-6}$	$1.2x10^{-5}$	20	0.26
6 △	"	$2.5x10^{-5}$	"	20	"
7 ○	"	$2.8x10^{-6}$	"	180	"

†v = cm/sec; D = cm^2 sec ^{1};
R = (dS/dc+θ); t = days;
θ = cm^3/cm^3 (f.c = 0.35%)

Fig. 4. Reduced K concentration in the soil solution (C/C_{in}, C_{in} being the concentration of K in the inflowing solution) as a function of soil depth under various conditions in the soil. Parameters and times used for the presented lines are given in the inset Table. Calculation according to eq (12). Bet Dagan clay soil.



Symbol	Parameter†				θ
	R	v	D	t	
1 ○	0.43	1.7×10^{-3}	2.2×10^{-4}	1.2	0.40
2 ●	"	3.5×10^{-4}	"	"	
3 ▽	"	"	1.3×10^{-4}	"	0.30
4 □	"	8.0×10^{-5}	9.0×10^{-5}	"	0.20
6 ■	0.043	"	"	"	
8 △	0.43	3.5×10^{-4}	1.3×10^{-4}	5.8	
9 ▲	"	8.0×10^{-5}	9.0×10^{-5}	25.5	0.20

†v = cm/sec; D = cm^2/sec;
R = (dS/dc+θ); t = hours;
θ = cm^3/cm^3

Fig. 5. As in Figure 4, only for the sandy Besor soil.

When evaluating the results in study case a, it should be noted that values denoted to v due to variations in θ were subject to the assumption that a steady state, unit water-head gradient existed in the soil profile at each θ. Under such conditions, $v \approx K_h(\theta)/\theta$, and K_h can be estimated for the given θ from Figure 1. Since v thus estimated is very arbitrary, its effect on C_K distribution should be considered on its own merit, not necessarily in conjunction with variations in θ.

In the Bet Dagan soil, which represents a matrix of high K-retention and relatively slow v ($< 2.5 \cdot 10^{-5}$ cm/sec), the maximal K penetration into the soil (d, cm) can be estimated by $d=(2 \cdot D \cdot t)^{1/2}$. A straight line connecting the points $C/C_{in} = 1$ and $x=d$ gives a reasonable estimate of the C_K/C_{in} distribution in the soil after time t.

In soils with a lower buffer capacity and faster v *(e.g* the Besor soil), the contribution of convection to K distribution is appreciably greater than the combined effect of thermal diffusion and mechanical dispersion.

Study case b: K depletion by a planar sink.

The boundary condition at the absorbing plane is:

$$[D \cdot (\delta C_K/\delta x)+ v \cdot C_K]_{x=0}=\alpha \cdot C_K]_{x=0} \qquad (13)$$

The boundary condition at $x \rightarrow \infty$ and the initial condition are the same as in (11) and (9), respectively. The solution of (6) subject to (9), (11) and (12) was given by *Nye [1966]:*

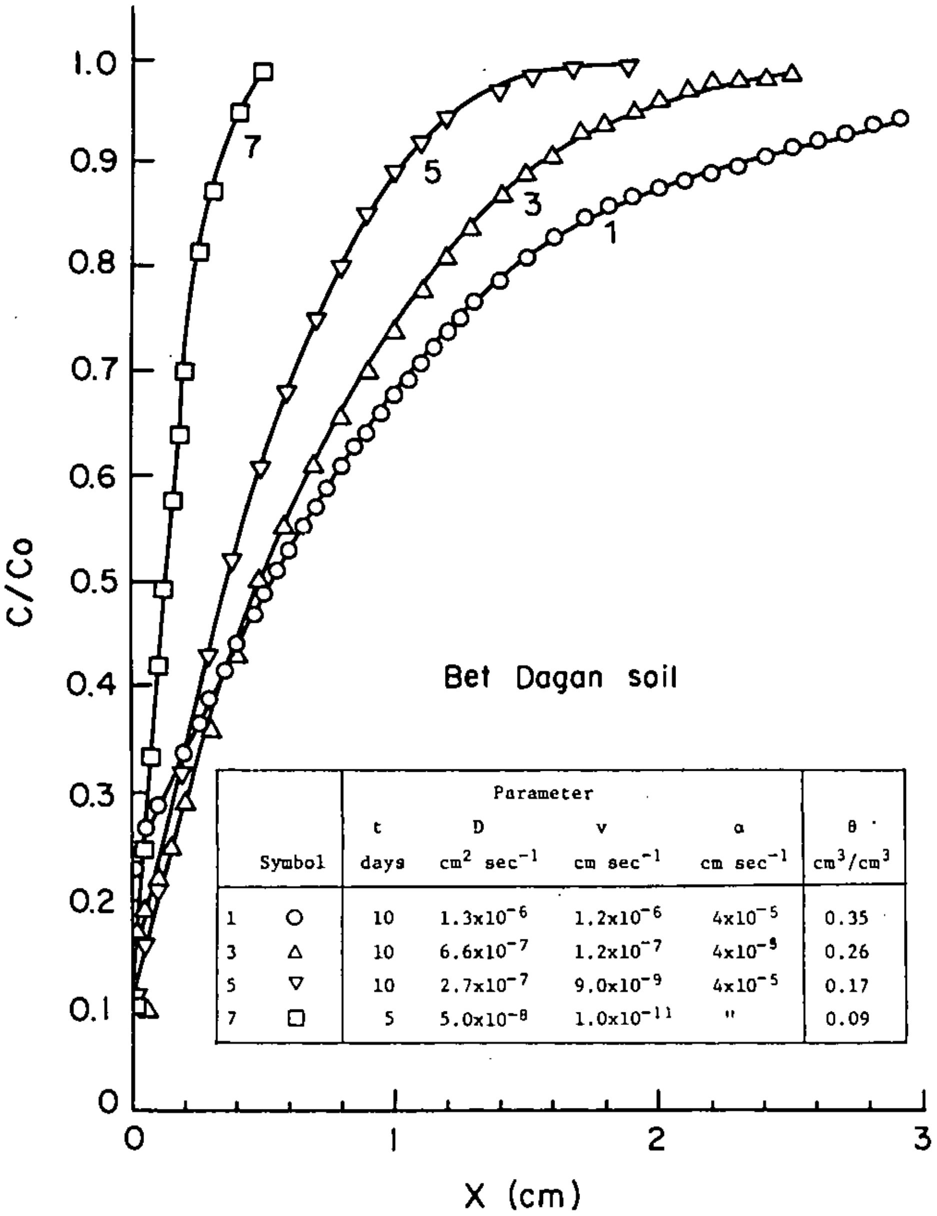
$$C_K/C_{Co} = 1\text{-}0.5 \cdot \{\mathrm{erfc}[\,(x+v \cdot t/R)/2 \cdot (D \cdot t)^{1/2}]+ [(\alpha\text{-}v/\alpha] \cdot$$

$$\exp(\text{-}v \cdot x/R \cdot D) \cdot \mathrm{erfc}[\,(x\text{-}v \cdot t/R)/2 \cdot (D \cdot t)^{1/2}]\}$$

$$+0.5 \cdot \{[(2 \cdot \alpha\text{-}v)/\alpha] \cdot \exp[(\alpha\text{-}v) \cdot (x+\alpha \cdot t/R)/(R \cdot D)] \cdot$$

$$\mathrm{erfc}[(x+(2 \cdot \alpha\text{-}v) \cdot t/R)/(2 \cdot (D \cdot t)^{1/2})]\} \qquad (14)$$

Water uptake is assumed to create a steady water flow (v, cm/sec) towards the sink. The flux of K uptake depends on C_K at the plane surface and on α (cm/sec). The value used for α was adopted from *Drew et al. [1969].* The K-depletion lines for the Bet Dagan clay soil are presented in Figure 6. At field capacity, v was given a value of 1.2×10^{-6} cm/sec, which is well accepted for water movement towards roots *(Olsen and Kemper [1968]).* D was denoted a value of 1.3×10^{-6} cm^2/sec. The difference between the current D and that of Figure 4 stems from the smaller D_{hd} in this case, due to the reduced v. Curve 1 represents K distribution at field capacity. At 75% field capacity, both D and v declined (inset Figure 6), and the result (line 3) is a steeper curve, a 15-20% smaller uptake with time, and 25% decrease in C_K at the sink surface relative to line 1. The reduced K-depletion as soil drying continues is shown for $\theta = 50\%$ and 25% of the water content at field capacity (lines 5 and 7, respectively). A similar trend with varying θ was obtained in the sandy Besor soil (data not presented).



		Parameter				
	Symbol	t days	D $cm^2\ sec^{-1}$	v $cm\ sec^{-1}$	α $cm\ sec^{-1}$	θ cm^3/cm^3
1	○	10	1.3×10^{-6}	1.2×10^{-6}	4×10^{-5}	0.35
3	△	10	6.6×10^{-7}	1.2×10^{-7}	4×10^{-5}	0.26
5	▽	10	2.7×10^{-7}	9.0×10^{-9}	4×10^{-5}	0.17
7	□	5	5.0×10^{-8}	1.0×10^{-11}	"	0.09

Fig. 6. Reduced K concentration in the soil solution (C_K/C_o, C_o being the initial concentration) as a function of distance from a planar sink. Parameters and times used for the presented lines are given in the inset Table. Calculation according to eq (13). Bet Dagan clay soil.

4.2 Effect of irrigation regime on K application to field crops.

Irrigation rate and frequency determine root growth and distribution in the soil *(Bar-Yosef et al [1980]; Bar-Yosef and Sagiv [1985])*. Under sufficient water supply, but high irrigation frequency (1 to 3 irrigations/day), the soil-root volume of tomato plants growing in the Besor soil was found to be approximately 1080 m^3/ha (or about 40 L/plant) *(Bar-Yosef and Sagiv [1985])*. At the time of peak K consumption rate, the crop used 0.33 mg K $[\text{kg soil}]^{-1}h^{-1}$. The potential rate of K transition from exchange sites in the soil to the soil solution was estimated in a batch experiment to be about 0.8 mg K $[\text{kg soil}]^{-1}h^{-1}$ *(Bar-Yosef and Sagiv [1985])*. Since under field conditions the K solubilization rate is expected to be appreciably slower than under batch conditions, the rate of K replenishment in the soil-solution may limit K uptake rate by plants even if exchangeable K in the soil is sufficiently large. To avoid such a possibility, K must be added via the water at critical growth stages. This is unlikely to be required at a larger soil-root volume per plant.

Bar-Yosef and Sagiv [1985] showed that a bi-daily trickle-irrigated sweet corn crop grown in a loess soils needs a C_K of about 0.08 mM at the root surface during the main growth season in order to sustain the required rate of K uptake by the plants. Consider an irrigation solution with K concentration of 1.5 mM, which is often used under field conditions. The data in Figure 4, line 2 (Bet Dagan soil), indicate that if applied on top of the soil, a C_K of 0.08 mM, or more will be obtained in the upper 7 cm soil layer after 20 days of continuous fertigation. Since $v = 2.5 \times 10^{-5}$ cm/sec, the accumulated water rate is 43 cm water, which is about the annual irrigation rate of sweetcorn in Israel. It is envisioned, therefor, that in Bet Dagan soil the control of C_K below 10-15 cm by means of K fertigation is practically impossible. In the sandy Besor soil, under conditions of high soil moisture (Figure 5, line 1), $C_K = 0.08$ mM or greater is obtainable after 1.2 hours at a depth of 20 cm. In this soil, care must be taken to avoid K leaching below root depth.

4.3 Monitoring soil-water and K concentration in the soil solution.

Soil water is being monitored under field conditions in order to ensure optimal water supply to plant roots. Tensiometers (if monitoring soil-water matric potential) or neutron probe access tubes (if monitoring volumetric soil-water content) are inserted into the soil within the expected soil root volume. Irrigation follows a pre-scheduled program intented to replenish water uptake by plants as predicted from environmental conditions, or to maintain a predetermined soil-water matric potential at a given point in the soil. Tensiometer or neutron probe readings are compared with values desired in the soil. If measured and pre-defined values deviate by more than a permitted range, irrigation rate, scheduling or both are modified, until the required level in the soil-root volume is maintained. Under trickle irrigation, the recommended soil-water matric potential should be between -8 and -15 and between -10 and -30 centibar in sandy and clay soils, respectively. Such ranges involve variations in θ (estimated from the soil-water retention curve, *e.g.* Figure 2) that were shown above substantially to affect K transport in soils.

The ionic composition of soil solutions is monitored to avoid extreme fluctuations in nutrient concentrations that may limit their uptake by plants. Soil sampling and saturated-paste extract analysis has the disadvantage of disrupting the real solution-to-soil ratio prevailing in the field, and the labor involved in sampling the soil and extracting it. Vacuum cups inserted in the soil allow collection of *in situ* soil solution, which is ready for chemical analysis. The convenient operation and low price of the vacuum cup system made it very popular with farmers. The most commonly used vacuum cup, which is constructed of porous ceramics *(Rhoades and Oster [1986])*, was used in the present study (Figure 3). The composition of the collected solution depends on the specific ion retention characteristics of the ceramic material and the soil volume around the suction cup from which the soil solution is being depleted. This depends on the suction applied and on the hydraulic conductivity of the soil.

Meiri et al [1985] compared C_K results obtained in vacuum cups and in saturated paste extracts. The results, obtained in the Besor soil in field plots which received 3 levels of K via the water, are summarised in Figure 7. Data points obtained at a given sampling date are corrolated better than the points of all the 4 sampling dates pooled together ($Y = 0.493\,X + 0.118$, $R = 0.70$). The slope of the linear correlation is not surprising, since the soil-water content in the field was approximately 50% of the water content of the soil at saturation. The low correlation coefficient reflects a large sampling variability, which is due mainly to temporal effects. The results do not indicate any consistent problem in determining C_K by means of a ceramic vacuum cup and definitely encourage further research to establish this fact with other, different soils.

Potassium concentration in the soil solution in the field experiment described in Table 2 was determined by means of ceramic vacuum cups. The soil-water matric potential during the growing season in the reported treatments is presented in Figure 8. To obtain an average potential of -25 centibars in the upper 40-cm soil layer (treatment 4), fluctuations between -9 and -40 cbar cannot be avoided. The extreme values characterise the soil a few hours after irrigation stopped, and just before irrigation started, respectively. The time interval between irrigations was 4-5 days. In terms of θ, the observed fluctuations correspond to variations between 0.20 and 0.06 cm^3/cm^3. In treatment 5, irrigation was applied daily in order to maintain a nearly constant water head in the 0-40-cm soil layer (between -6 and -10 cbars). The accumulated irrigation required to obtain this low tension was 468 mm, as compared with 300 mm applied in treatment 4.

The results of the vacuum cup-C_K as a function of time are described in Figure 9 and 10. In treatment 5 (-8 cbar) C_K in the 20-cm-deep cup increased almost linearly with time from 0.6 to 10 mM K. In the 40-cm-deep cup, only a slight increase in C_K (1.5 to 2.3 mM) was observed with time. The $NaHCO_3$-extractable K in the soil (Q_K) increased in the 0-10-cm soil layer until Feb 8, but subsequently declined. This is contrary to the vacuum cup-C_K values which continued to increase. Q_K in the 30-40-cm soil layer also decreased beyond Feb 8, but its absolute value was five fold smaller than in the 0-10-cm soil layer. A decline in K extractability by $NaHCO_3$ in various soils after a contact time of 50 to 100 days in the soil was reported by *Bar-Yosef and Akiri [1978]*. We deduce therefore that the cup-C_K results are correct.

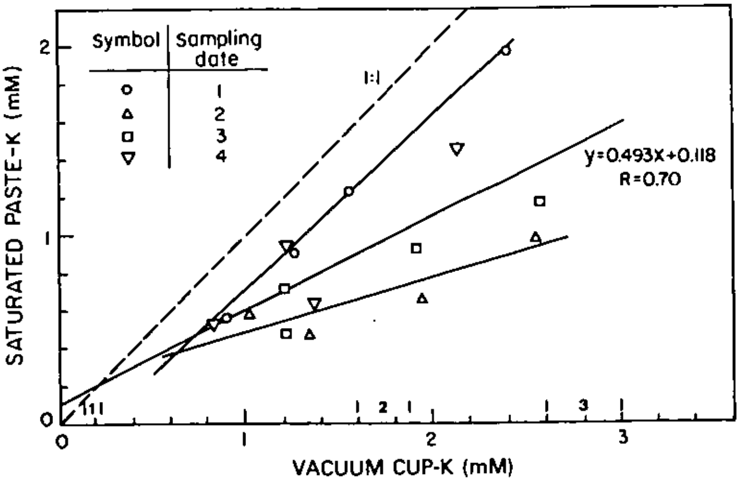


Fig. 7. Saturated paste-K *vs* vacuum cup—k (0-40 cm soil layer) in a field experiment in the sandy Besor soil. Soils were sampled 4 times at intervals of 1 month. The numbers and bars on the abscissa give the range of K concentration in the irrigation water in the 3 studied treatments.

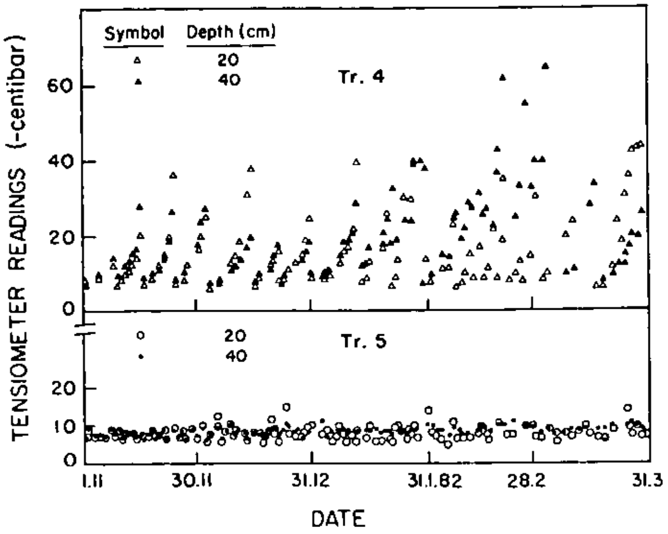


Fig. 8. Tensiometer readings during the growing season of glasshouse tomato plants (Besor soil). Treatments are described in Table 2.

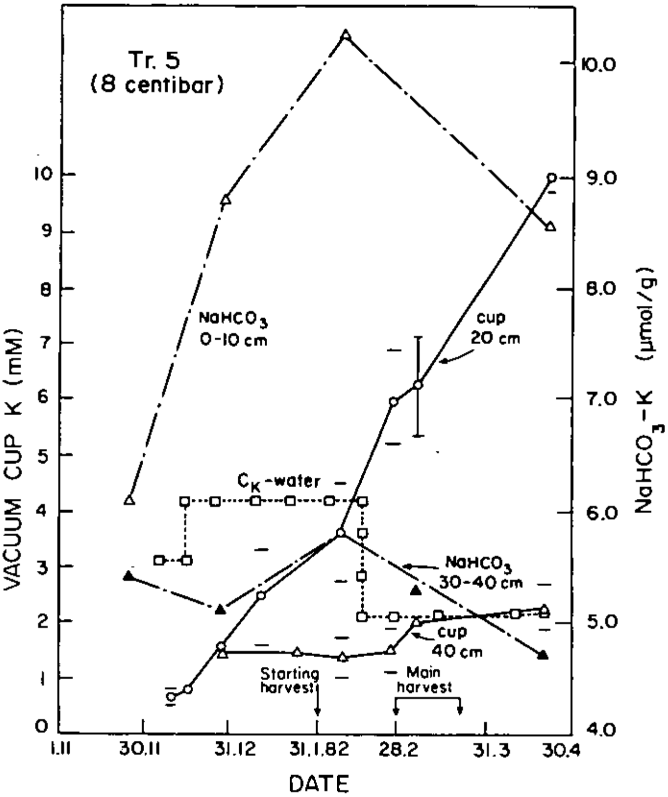


Fig. 9. Potassium concentration in the soil solution (mM) obtained by a vacuum cup, and NaHCO$_3$-extractable K in the soil (μmol/g) as a function of time during the growing season of glasshouse tomatoes. Besor sandy soil. Data given for two soil layers. Also presented is the K-concentration in the water during the growing season. Treatment 5.

Similar behaviour was observed in treatment 4 (Figure 10) but there the absolute C_K and Q_K values at 20 cm were lower than in treatment 5. The smaller concentration stemmed from the fact that total K applied in treatment 4 was 422 kg/ha, as compared with 693 kg/ha in treatment 5. In treatment 4, C_K at a depth of 40 cm exceeded, most of the time, C_K at 20 cm; in treatment 5 the opposite occurred. The difference could be explained if K uptake occurred mainly from the upper 20 cm soil layer. In this case, the smaller K quantity applied to treatment 4 could not provide the large increase in C_K observed in treatment 5.

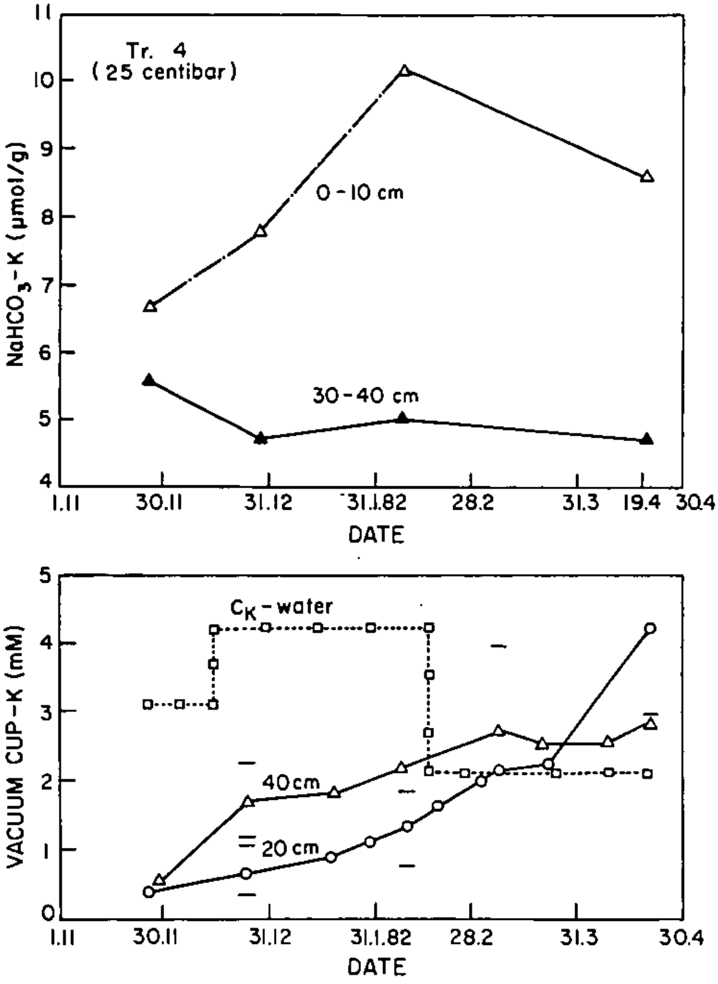


Fig. 10. As in Figure 9, only for treatment 4.

The concentration of K in the irrigation water is depicted in the same Figures. It was raised from 3.1 to 4.2 mM when K consumption rate by tomato plants reached its peak, and was reduced to 2.1 when the consumption rate was smaller, namely, towards the end of the fruit picking period. In treatment 5, C_K in the soil solution at a depth of 20 cm equaled C_K in the irrigation water 2 weeks after harvesting began, and surpassed it later on due to application rates that exceeded consumption by the plants. In treatment 4, C_K in the soil solution during the peak uptake period was appreciably below the input concentration. It equaled the inflowing K concentration only towards the end of the growing period.

The differences in soil-C_K between treatments 5 and 4 were reflected in %K in the plant dry matter, determined on Feb. 8: 4.1 and 3.3 in the canopy, and 5.7 and 4.5 in the fruits, respectively. The elevated %K did not result in higher fruit yield or improved fruit quality.

Monitoring C_K indicated that under limited water supply (treatment 4) K-uptake occurred mainly from the upper 20 cm soil layer. It also showed that K-fertilization beyond mid-March in treatment 5 could have been saved.

The slow increase in C_K with time at a depth of 40 cm in treatments 4 and 5 (Figures 9, 10) qualitatively agrees with the calculated results presented in Figure 5, if the inflowing solution volume is corrected for the uptake by plants. Constraints in estimating temporal water and K consumption by the tomato crop, and the fact that trickle irrigation rather than one dimensional water application was used, do not allow a quantitative comparison between the model computations and the field experiment results.

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Spatial Variability of Soil K-status

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Summary

This paper briefly reviews the short-, medium- and long-term elements of soil K-status. It then discusses the processes that contribute to the long-, medium- and short-range components of the spatial variability of soil K-status. In some cases temporal variability may equal or exceed spatial variability: this may confuse measurements of the latter.

It reviews published measurements of the variability of soil K-status. These demonstrate that the distribution of variability is usually not random. The non-random distribution of long-range variability in K status may be crudely described in term of soil classes or map units; these will still include the short- and medium-range components of the total variability, which may form a substantial part. Semi-variograms describe the spatial dependance of soil variability better, provided they cover all scales of variability. Even so, it may be useful to reduce the contribution of very short-range variability («noise») by bulking several soil samples from within an area round each sampling site.

It comments on methods for measuring spatial variability, emphasizing that measures of short- or medium-range variability must be distributed over the whole area of interest.

Potassium status

Several soil properties, operating in different time scales, control the potassium status of a soil.

Labile K.

The immediate availability of K to plant roots is determined by the *K-concentration* or the *K-activity* of the soil solution, according to whether it is the number of ions or their free energy that control the rate-determining stage of K-uptake. Both of these fluctuate with adventitious changes in the thickness of the diffuse double layers round exchange surfaces in the soil. Activity ratios (AR), such as

$$aK/\sqrt{a_{Ca}} \text{ or } aK/\sqrt{a_{Ca+Mg}},$$

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are more stable. *Activity ratios* measure the immediate availability of K relative to that of the dominant cation in the soil solution. They are related to the pool of labile, or «easily exchangeable»-K, by relations such as:

$$AR = a_K/\sqrt{a_{Ca+Mg}} = b' \cdot K_{eex}/(Ca+Mg)_{eex} \qquad (1a)$$

which reduces to:

$$AR = a_K/\sqrt{a_{Ca+Mg}} = b'' \cdot K_{eex} \qquad (1b)$$

when $K_{eex}/(Ca+Mg)_{eex}$ is relatively small. b" depends upon the charge density of the relevant exchange surfaces, on any non-ideal (specific) affinities of the exchange surfaces for K, Ca or Mg, and on their total charge. Figure 1 presents three examples of equation 1b *(Beckett [1964])*. The total quantity of immediately available K corresponds to ΔK, the fall in K_{eex} between the current AR of the soil (AR_o) and the «exhaustion» value (AR_e) below which K-uptake will cease. This quantity is the short-term component of the soil K-status.

At exhaustion $a_K/\sqrt{a_{Ca+Mg}} \approx .3 \times 10^{-4}$ in solution cultures, and about 5×10^{-4} in an «exhausted» soil, the result of the averaging of its more and less depleted volumes. The latter roughly corresponds to $K_{ex}/CEC \approx .7\%$. *(Beckett [1972])*.

Note that strong salt solutions, particularly M. ammonium acetate, tend to extract rather more K («exchangeable-K») than is immediately or easily exchangeable to the Ca or Mg ions in the normal soil solution.

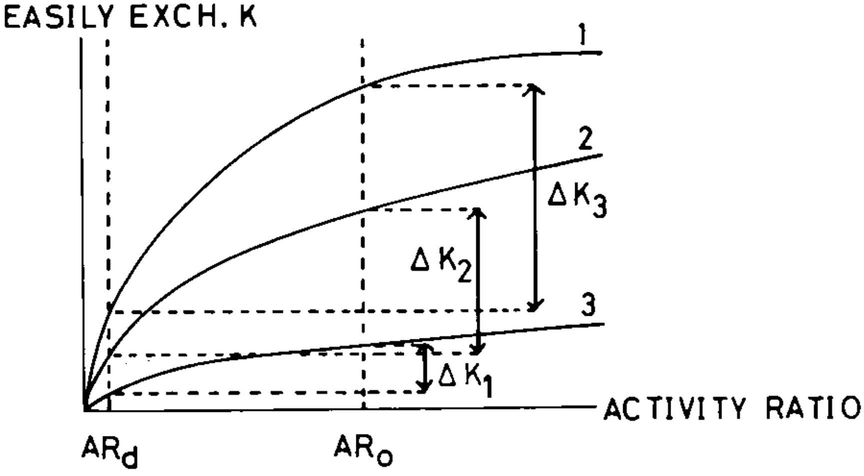

Fig. 1. Three Q/I relations (1-3) of the form of relation (1b): AR_o is the current activity ratio in the soil and AR_d is its exhaustion value, so ΔK_{1-3} are the quantities of K immediately available (labile K).

Non-labile K.

Once depleted, the pool of labile K may be replenished by the decay of plant residues. This is usually rapid: indeed, K may be leached out of mature or senescent tissues even before they fall as litter. In soils containing biotite, glauconite, and hydrous micas or illites *(Møberg & Nielsen [1983])*, the depleted K may be replenished by the release of *interlayer-K* on exchange with Ca, Mg, Na, (H_3O^+), etc. from the soil solution. This usually follows or leads to a loss of lattice charge *(Arnold [1960])* and so to the expansion of their crystals (10 → 12 → 14A, *e.g. Raman & Jackson, [1965]; Rausell-Colom et al. [1965]; Niederbudde & Fischer, [1980]; Møberg & Nielsen, [1983])*. A few non-micaceous materials release K at a useful rate on normal hydrolytic weathering, notably those in recent volcanic effluvia, but most non-micaceous minerals, and muscovite micas, release K very slowly and cannot be said to provide more than a very long-term reserve.

The release of «native» or *«core-interlayer» K* from unweathered crystals of biotite etc., progresses inwards from the edges (or lattice imperfections) of the crystals, so the expanded form of the crystals forms a concentric zone (Figure 2) *(Rausell-Colom et al. [1965])* which increases the extent and possibly the CEC of the exchange surfaces *(Beckett & Nafady [1967a,b]; Møberg & Nielsen [1983])*. The difference between the activities of K, and the replacing cations, within and without the crystal *(Mortland [1958, 1961])*, provides the driving force for release, and for each crystal there is a critical K-concentration or activity ratio in the surrounding solution above which release cannot take place. The rate of release, however, is limited by the rate at which replacing cations can diffuse into the crystal *(Rausell-Colom [1965])*, which appears to be greatest where the lattice charge is lowest. The *K-releasing capacity* of a soil thus depends on its clay content, on the constitution (particularly the lattice charge) of its clay fraction, and on the extent to which the soil solution is depleted of K by plant uptake, or by reagents such as sodium tetraphenyl boron.

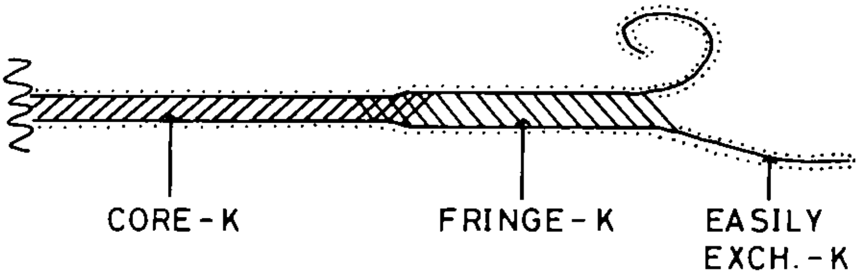

Fig. 2. Diagrammatic section of two layers of a weathering illite crystal.

On the other hand, if the K-concentration of the soil solution is raised substantially above its critical value for release, the corresponding increase in the proportions of exchangeable K cations in the expanded peripheral zones of the clay crystals may collapse them (14 → 12 → 10A). It is unlikely that the arrangement of the «fixed» K cations, with the Ca and Mg and water molecules entrapped with them *(Beckett & Nafady [1967a])*, will be well-ordered, so it is commonly observed that «fixed» K is more readily released than «native» K. More significantly, it would seem that repeated depletion and replenishment of soil K may lead to a substantial peripheral zone of *«fringe-interlayer-K»* whose extent and rate of K-release reflect the balance of gains and losses of K over a long while. Indeed, many workers have shown that not only is the K-releasing capacity of illite soils increased by a long history of K-fertilization, and thus depends on the magnitude of the pool of *fringe-K* (Figure 2), or vice versa *(Beckett & Nafady [1969]; Beckett & Clement [1973])*, but their CEC or the extent of their exchange surfaces may have been decreased by repeated K-fixation, or *vice versa.* These are the medium to long-term components of soil K status.

Under sustained K-depletion (Figure 3) such soils first release their exchangeable-K, then a further and finite quantity of K at a lower but still significant rate (presumably fringe-K) *(Reitemeier et al. [1947]; Barrow [1966]; Beckett & Nafady [1967a]; Waddy & Vimpany [1970]).* After this, further K release is at a much slower but more or less constant rate, presumably from core-K or from an intermediate zone between the fringe and core zones.

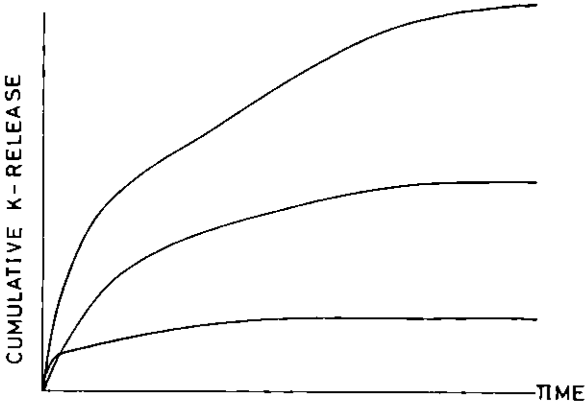

Fig. 3. Cumulative K-release with time from three soils, to illustrate the three stages.

In a rested soil, not recently depleted nor replenished with K, K_{ex}/CEC is roughly proportional to the release rate of fringe K *(Smith & Matthews [1957]; Arnold [1960]):* in an exhausted soil the constant, depleted value of K_{ex}/CEC appears to depend on the release rate of K from the core or intermediate zones *(Tabatabai & Hanway [1969]).* The *total-K* % of the clay fraction of an illitic soil may provide a measure of its K-release capacity, but less so or not at all for vermiculite, smectite or kaolinite clays.

Various attempts have been made to measure these pools of interlayer-K, or their rates of release. For example, *Haylock (1956)* and *Netson (1956, 1968)* exhausted soil or clay samples with successive aliquots of boiling *M* HNO_3. After 5-6 extractions the rate of release became more or less constant (K_c) and was assumed to measure the potential release of core-K: the extra K-release during the first 3-4 extractions («step K») comprised exchangeable- and fringe-K and measured the medium-term K reserve. The latter corresponded fairly closely to the resin-K extracted over 20 hours by a cation exchange resin at 80 °C *(Waddy & Vimpany [1970]).*

In addition the many empirical extractant solutions, such as citric acid, lactic/lactate, acetic acid, ammonium nitrate, sodium bicarbonate, etc., attempt to provide rough estimates of the combined short- and medium-term K reserves of a soil.

Components of variability in soil K status

The *total K* of sites in a soil-less landscape is determined by the composition of their rocks *(e.g.* igneous rocks contain about 2%, shales 2%, sandstones 1%, limestones 0.3%, *(Bowen [1966]).* The total K of young soils reflects their parent rocks also. In these early stages of soil development K-release depends as much on which minerals are present as on their total K; it also depends on the prevailing soil temperature, the intensity of biological activity, and on the soil being moist. As the soils develop and deepen, the total K in their upper horizons falls off; the least resistant, high-release minerals weathering more rapidly. In releasing K their mica and illite fractions lose charge and expand, which increases their CEC. Seasonal changes in topsoil K *(e.g. Childs & Jencks [1967]; Briggs, 1974; Martel & Zizka [1978]; Weaver& Forcella [1979]; Mollitor et al. [1980]; Gibson [1986])* build up fringe K within the weathered edges of illitic crystals. Their organic matter content increases, too. Thus, throughout the early and middle stages of soil development (which comprise most of the soils of Europe) the short-and medium-term K-reserves of a soil tend to increase as its long-term reserves decrease, both in proportion to the geomorphic age of the site and/or the degree of pedological development in the profile. Soil K-status in different landscapes on the same parent rock should reflect their relative ages or relief; in landscapes of the same age soil K-status should reflect the proportions of weatherable minerals in their parents rocks.

So in all but the oldest landscapes the patterns of parent rocks provide the main component of the long-range spatial variability of soil K-status. Long-range gradients in climatic factors that affect soil development may create long-range trends in K-status. Thus a sequence of soil profiles, on comparable sites and on comparable Drift parent materials, along an 813 km transect from Illinois to Nebraska (over which rainfall falls from 99 to 69 cm) showed a steady increase in the total K content of the < 0.001 mm clay fraction of the B horizon, and a decrease in the depth to the horizon of maximum clay content *(Wells & Riecken [1937]).*

Within one landscape on one parent rock, the older soils will tend to occur on the flatter sites, and vice versa. So, ideally, the K-status of different sites in a landscape should reflect their gradient or their relative physiographic age *(Campbell [1973]).* Similarly, the K-status of different parts of multicyclic landscapes should reflect the relative durations of the different cycles *(Campbell [1975])*. To some extent potassium may become concentrated in the lower parts of the landscape that receive local drainage. However, temporary excesses of labile K tend to be retained in the fringe-zones of illitic clays, so it is unlikely that K will be as concentrated in this way as, for example, Ca or Fe. Local geomorphic contrasts such as these contribute to the medium-range variability of soil K-status. Recurrent local alternations of natural erosion and stability as in the landscape examined by *Webster and Butler [1976]*, or the operation of short-range geomorphic processes such as sheet-wash, wind erosion, or solifluction, may impose relatively short-range variability too.

Super-imposition of secondary or transported soil parent materials may impose further trends in K-status, or juxtapose materials of different origin or different degrees of weathering. Thus, the very fine sand fraction of a thin loess cover in S.W. Saskatchewan decreases and the silt fractions increase with distance from its source, while the proportion of mica in the very fine sand and coarse silt increases with distance, but decreases in the fine silt fraction. The «total» K and presumably K-status, follows the trend in the mica *(Souster et al. [1977])*. Similarly the thickness of a loess deposit from the Wabash river decreases with distance while the quartz/feldspar ratio of the medium silt fraction rises *(Caldwell & White [1956])*. Some processes, such as water transport, may accelerate weathering to produce deposits of reduced K-status: others, such as glacial or frost action, or wind blasting, may expose fresh facets of weathering minerals. So transported parent materials may superimpose short-to long-range patterns of variation in K-status.

Drees & Wilding (1973) found that the variability of total K (within the fine silt or coarse silt fractions) in corresponding horizons of profiles within 4 m^2, varies with parent material, in the order loess < till < glacial outwash: *Mollitor et al. (1980)* found that the K-variability within small areas of flood plain forest was greater on channel or accretion deposits than on overbank flood deposits: *Courtin et al. (1983)* found that variability in available K increased in the order alluvial < moraine < glaciofluvial deposits.

Many of the patterns derived from the distribution of parent rocks, or the transport of their weathering products, become muted in old landscapes, which are usually dominated by profiles of deep weathering and by concave-upwards wash slopes (pediplains). In extreme cases the soil reserves of weatherable minerals, and of 2:1 clays, may be almost exhausted, and with them the long- and medium-term K-reserves of the soil. If so, the soil K-status may come to depend wholly on the short-term reserves of the standing vegetation and the soil organic matter. Indeed, this may also be the case even in young soils forming on quartzitic or weakly arkosic sandstones, which may give rise to highly developed soils even in young landscapes.

Horizonation within soil profiles usually increases with age and we may expect to find higher proportions of expanded clays, and lower proportions of easily weatherable minerals in the topsoil than the subsoil. Since the topsoil is also the zone of greatest annual fluctuations in K-status, there will probably be more fringe-K in the topsoil than in the subsoil, and proportionately less core-K until, in really old soils, the whole K-reserve lies in the organic components of the litter and topsoil.

The prolonged weathering and mass-wasting necessary to produce old landscapes commonly results in isostatic uplift. The resulting changes in regional base levels lead to successive cycles of rejuvenation by dissection, which in their turn lead to successive cycles of soil development, and impose strong, long- to medium-range, patterns of K-status (and other soil properties) in the soils of old and stable continents.

Superimposed on the patterns of K-status that derive from patterns of parent rock and patterns of landscape development, and from the geomorphologic processes that have formed the landscape, there will be patterns imposed by contrasts in natural vegetation, according to whether the main species are monocotyledons or dicotyledons (this contrast is particularly important for K), are annual or perennial, have long or short growing seasons, or have shallow or deep root systems, etc. In some cases, near ecological tension zones, vegetation contrasts may lead to different paths of soil development *(e.g.* to podzols or brown earths in Western Europe, or to Black or Grey Wooded soils in Alberta); in other cases contrasts in natural vegetation introduce differences in degree. Within one vegetation type the cycles of tree fall and recolonisation in natural woodland, or of fires in grassland, introduce local patterns of shorter range. Similarly, different crops (tree or herb, with high or low K requirements, with high or low recycling of K in residues, with deep or shallow roots, receiving high or low K-fertilisation), or different crop rotations, or, indeed, adjacent farmers practising more or less intensive management in the same environment, will affect the rates of K-release. They will particularly affect the magnitude and the critical activity ratio of the fringe-zone. All these contrasts introduce medium-or short-range variability.

Within the elements of the patterns of K-status due to different types of natural vegetation, or different crops, there will be finer contrasts, attributable to tree throw and decaying timber, animal burrows, the concentration of canopy drip and litter round trees (with bark concentrated near the trunk, and leaves further away) *(e.g. Zinke [1962]; Grieve [1977]),* or to row crops, ridge and furrow, drainage or deep ploughing, accelerated sheet-wash or splash erosion, etc. Some soil processes, such as solonisation, may also introduce short-range patterns of K-status. The spotty distribution of dung or urine patches *(e.g. During & Mountier [1967a,b]),* and the tendency of some varieties of sheep to congregate and to leave concentrations of faeces will also have a marked effect on the variability of K-status *(e.g. Hilder & Mottershead [1963]).* These contrasts are unlikely to be the result of stock ingesting soil with their feed. Though sheep faeces may contain up to 30-60% soil under some circumstances *(Headley & Drew [1970]),* their feed usually contains more K than the soil, so the ingested soil does not increase their excretion of K.

Over even shorter ranges, soil cracks or worm burrows may create K-contrasts, and at finer scales contrasts between the interior and the faces of blocky and granular peds, and concentration gradients towards feeding roots, create yet finer patterns in K status, and so on down to the smallest imaginable fractals.

Statistical distribution of parameters of K-status.

Some of the inequalities discussed above are random in their origin, and the histograms of their effects may show a normal distribution. Others show stepwise variation, and discontinuous histograms, of which the peaks will gradually merge as the soil and landscape become older. Also some irregularities create their own restoring processes *(e.g.* by diffusion, or by the mixing of soils by fauna, possibly concentrated in the high spots) proportional to Log (activity) or Log (K_{ex}/CEC) in the first case, and possibly to K_{ex} in the second, which may skew the histograms. Some processes tend to produce high spots *(e.g.* urine or ash patches) and others low spots *(e.g.* erosion of superficial organic matter), while some restoring processes operate more actively on the lower limb of the normal histogram *(e.g.* K-release) and some on the high spots *(e.g.* K-fixation), but not necessarily at the same rate. All possible kinds of distribution have been reported, and workers have used every possible kind of transformation to normalise the histograms of their measures of K-status. Thus *Adams & Wilde (1976)* found that total K had a normal distribution, but not K_{ex}: *Bie & Beckett (1973)* log-transformed K_{ex} available P, Na_{ex}, Mg_{ex} but arc-sin-transformed $CaCO_3$ % and Clay %; *Uehara et al. [1985]* had to log-transform Ca_{ex} and Mg_{ex}, but K_{ex} had a normal distribution: *Webster and Butler (1976)* log-transformed available P, but square-root-transformed available K, etc. There is no general rule of thumb. Some of the data presented below had been transformed by their authors and some not.

Measured variability

A earlier review *(Beckett & Webster [1971])* presented data from 27 studies on the spatial variability of available K, which may be summarised in Table 1.

Table 1. Spatial variability of the Coefficients of Variation (%) of point values for available K or exchangeable K (medians in brackets)

	Within-field		Between	Areas larger
1 m²	0.1 ha	field	fields*	than one field
11-40 (30)	11-112 (35)	21-142 (70)	 (40)	35-125

* variability between one sample per field, each bulked from several point-samples.

Tables 2 and 3 present further measurements of variability in K-status for agricultural and forest lands respectively. Table 13 in the appendix briefly reports the source of each data set. As far as possible they are presented in the order of the size of the areas they represent. There are difficulties in reducing such a range of material to standard format, and it is not always totally clear whether a particular value related to variability *within* a given area, or between several such areas, nor whether single soil samples were analysed separately or were bulked before analysis. However, the variability of these variabilities is at least as large as the possible effects of these uncertainties. «Site-bulked» means that several samples were collected within one or a few square metres round each sample site and bulked before analysis, to damp down the contributions of very short-range «noise».

Table 2. Coefficients of Variation for agricultural lands

Ref.	Area-within (ha)	Bulking	Depth	Coefficients of Variation (%) K_{ex} or K_{av}	K_c	Total K
1a	.003		0-20	26-73		
2a	.004		Specific			2-3
c	.11		horizons	9		
3a	.01		Topsoil	8		
4a	.01		Ap	8		
			Bnt	9		
			C	10		
5	.01		0-15 cm	12		
6a	.02	Site-bulked	Bnt	19		
7	.1		Topsoil	53, 13, 60	10, 5, 7	
3b	.1		Topsoil	10		
c	1		Topsoil	12		
8	1	Site-bulked	Topsoil	30		
4b	Fields		Ap	28		
9			B2t	27		
			C	26		
9	Fields		Topsoil	26-64		
10a	Fields		0-15	19-33		
b	Fields		0-15	15-33		
			15-30	19-34		
			30-61	19-27		
3d	10		Topsoil	19		
11	A few ha		Topsoil	> 35		
12	10		0-30	23		
			30-60	45		
			60-90	70		
13	40-60	Site-bulked	0-30	12-15		
14	150		Lower A			10-20
			mid-profile			7-11
			C			7-15
6b	Region	Site-bulked	Ap	52		
			B2t	31		
			Csk	34		
15a	Admin.Dist		0-15	59		
b	Admin.Dist		0-15	21		
16	100,000		0-15	70		
			15-45	100		

Table 3. Coefficients of Variation for forest lands

Ref.	Area-within (ha)	Bulking	Depth (cm)	Coefficients of Variation (%)		
				Solution K	K_{ex} or K_{av}	Total K
16	.00		Forest floor			30
17a	.01	Site-bulked	F & H		11-30	
			0-20 (min. soil)		20-41	
b	.01	Site-bulked	F & H		21	
			0-20 (min. soil)	19		
18	.03	Site-bulked	LF		25	
			H		35	
19	.04		5		181	
			50		39	
20	.02-.09	Bulked round each tree	0-8		22	
			8-15		22	
			B		21	
21	.08		A2		41	
			B		41	
22	.09		L		14	
			F		36	
			H		54	
23	.1		Base of Ah		31-45	
17b	.25	Site-bulked	F & H		21	
			0-20 (min. soil)		22	
c	.5		F & H		25	
			0-20 (min. soil)	23		
d	1		F & H		32	
			0-20 (min. soil)		23	
24a	.8-3.3	Site-bulked	0-30 (min. soil)		43 Low fertility	
					55 High fertility	
b	Region	Plot-bulked	0-30 (min. soil)		14 Low fertility	
					35 High fertility	

It would appear that forest sites, and particularly the forest floor, show more short-range variability than most agricultural sites. Many workers have reported that the variability of soil properties, particularly of the nutrient elements, is increased by tillage, fertilization or grazing. *Hemingway [1955]* reports that the within-field CV for available K is raised from about 30% to about 70% by cultivation, grazing, etc. As would be expected, the total variabilities within large areas are much the same. The labile pool (K_{ex} or K_{av}) is more variable than non-exchangeable or total K *(cf.* Table 5).

Childs & Jencks [1963] found greater seasonal changes in available K in the topsoil than the subsoil: *Martel & Zizka [1978]* found K_{ex} changes more with the seasons in a sandy than in a clay soil: *Mountier & During [1967]* found that spatial changes in topsoil K in a grazed paddock were four and a half times greater than temporal changes: *Frankland et al. [1963]* found the mineral horizons of a woodland soil to show greater spatial variability and smaller temporal variability than the litter layer; *Mollitor et al. [1980]* found that topsoil K shows greater spatial variability than at 50 cm.

Variability within soil classes or mapping units

Soil Classes are defined, or mapped, in order to help their user to specify the local distribution of soil variability. The within-class or within-unit variability of each soil property measures the precision with which the classification or the map can predict that property – the higher the variability the lower the precision.

Beckett & Webster [1971] summarized data from 27 studies on the variability of available K within soil classes or map units (Table 4). It should be noted that most of the data sets covered only small parts of the total extent of each class or map unit.

Table 4. Coefficients of Variation (%) of available or exchangeable K within the topsoils of Soil Classes

Within Series	
Randomly chosen profiles	30, 55
«Typical» profiles	5, 54
Between fields	21, 34, 51
Within Families	
Between fields (or equivalent)	75, 83

They reported that available K, Mg, Ca and P were the most variable of the soil properties commonly measured.

It would be expected that labile-K would be more affected by management or short-range disturbance than interlayer-K or K-release-capacity, and *Lee et al. [1975]* did find that K_{ex} within areas of 0.1 ha was more variable than K_c: on the other hand *Piper and de Vries [1960]* found that prolonged management had changed K_c more than K_{ex} (by cold *M* HNO_3). Table 5 presents a more detailed comparison

Table 5. Coefficients of Variation (%) of various components of soil K-status

	Within soil types		Between soil types	
	(a)	(b)	(a)	(b)
Water-soluble K	72	—	13	—
Exchangeable K	39	52	94	206
Available K (acid Na-acetate)	51	34	105	140
HNO_3-soluble K	35	—	64	—
K-uptake by exhaustive cropping				
(i) Neubauer test	—	35	—	172
(ii) Glasshouse trial	—	36	—	285

(a) *Bishop, Maclean et al. [1954]* – 9 fields on each of 10 soil types.
(b) *Maclean et al. [1957]* – 6 fields on each of 5 soil types.

Subsequently *Adams & Wilde [1976]* examined the whole extent of the Westmere silt loam as mapped in New Zealand at 1:31 680. Their measures related to the whole map unit, and therefore did not reject the 20% of «impurities» (wrong soil class) present. On this basis they found (Table 6):

Table 6. Coefficients of Variation (%) within Westmere silt loam map unit

Depth (cm)	K_{ex}	Total K
0-10	66	10
10-20	80	11
20-30	106	12
30-40	117	13
40-60	117	13
70-90	181	15

They also plotted the K profiles (K-value against depth) for exchangeable K and total K at the 32 sites and measured how many of them lay within the envelopes defined by ± 10%, ± 25%, ± 50% of the mean profiles for exchangeable and total K respectively (Table 7):

Table 7. Variability of K-profiles within Westmere silt loam map unit

	± 10%	± 25%	± 50%
K_{ex}	0	0	9
K total	17	31	32
(compare Mg_{ex}	1	15	27
Ca_{ex}	0	12	30
Ca total	9	26	31)

Tables 6 and 7 both illustrate the high variability of labile K.

Later *Gibson et al [1983]* re-measured the variability of areas within the same map unit, and specifically S_1^2 the variance between profile means, and S_2^2 the variance between different depths within a profile, and found what is presented in Table 8:

Table 8. Components of the short range variability of Westmere silt loam map unit

	0.1 ha		10 ha		Whole map unit	
	K_{ex}	K_{tot}	K_{ex}	K_{tot}	K_{ex}	K_{tot}
S_1	0.6	0.06	0.8	0.1	0.7	0.1
S_2	0.3	0.07	0.5	0.1	0.4	0.05

They were forced to conclude that the 10 ha area had included a rather discrepant part which may have weighed rather more heavily within the10 ha sample area than it might have within the mapping unit as a whole.

Cipra et al. [1972], on the other hand, measured the local variability of the K-status of the Richfield silt loam map unit within seven widely separate fields, one in each of seven counties in S.W. Kansas. They found (Table 9):

Table 9. % of total variation in different subdivisions of Richfield silt loam

	Ap	B2t	C
Between fields within 7 counties	34	59	80
Between 25 m^2 plots within fields	48	25	12
Within 25 m^2 plots	15	12	7

Clearly much of the topsoil variability is of short-range, whereas most of the subsoil variability is of long range.

Ike & Clutter [1968] examined 123 sample plots of 800 m^2 in the Blue Ridge mountains (U.S.A.) and found that their Coefficients of Variation were:

	A2	B
Between all plots	49%	50%
Between plots within series	41%	41%

In this case the soil classification has described only 10% or so of the total between-plot variability. The within-plot variance varied between 1/4-3/4 of the total between-plot variance.

For an area on the Tablelands of New South Wales, *Webster and Butler [1976]* compared the efficacy of three soil classifications, and a 1:25 000 soil map, at predicting levels of available potassium (square-root-transformed) and found that they accounted for only 19, 3, 9 and 12% of the total K variability. Similarly *Bie and Beckett [1973]* compared the efficacy of separate soil surveys in S.W. Cyprus by four air photo interpreters; they also measured how much of the total variability of exchangeable K (log-transformed) their soil classifications and maps had accounted for (Table 10).

Table 10. % of variance of available K described by soil classes and map units

	Interpreters			
	A	B	C	D
No. of soil classes	8	25	18	10
% of variance described by each soil classification	3	3	5	12
No. of map units	8	25	9	10
% of variance described by each soil map legend	11	26	9	30

Yost & Fox [1981] examined the results of a hierarchical subdivision of the soils of the Andept suborder in Hawaii, and found:

	Great groups	Subgroups	Families	Series
% of total availability of exchangeable K accounted for:	78	4	7	10

Tidball [1976] performed a similar exercise on the soils of Missouri, and expressed each component of variance as its percentage of the total variance of total K:

Within 0.09 ha sites	5%
Sites within series	13%
Series within subgroups	50%
Subgroups within suborders	0%
Suborders within Missouri	31%

Some of these examples confirm how much of the total variability of K-status is of short- or medium-range, and therefore not described by a soil classification or soil map.

Part of the variability may be the result of long cultivation which superimposes new patterns on the patterns originally imposed by geology and pedogenesis. Thus in the Oxford area, *Ogunkunle [1979]* estimated exchangeable K and Mg, and available P, in six topsoil samples (each bulked from six sub-samples from within 1 m^2) from each of an average of five fields (each chosen to contain only one soil series) within each of 13 farms. He found (Table 11):

Table 11. Coefficients of Variation of topsoil properties

	Mg_{ex}	K_{ex}	Av.P
Between different series within one farm	248	152	34.8
Between different farms within one series	35.2	125	230
Between fields within one series within one farm	—	32.3	—
Residual – between sites within one field	28	31.2	51.2

There is a clear gradation between topsoil-Mg which, until recently, farmers have not attempted to change, and soil-P which they have been modifying from the Neolithic period. Potassium lies in the middle: in this range of clay, limestone and sand soils inter-farm differences due to varying levels of fertilizer and bought-in fodder nearly match the effects of different series.

Spatial dependance of the variability of soil K-status

The simplest predictor of the value of the K-status within an area is the mean value for the area. This assumes that its variability is randomly distributed, which is uncommon. Soil classes are defined and mapped in order to describe some of the non-random components of soil variability, mainly those of longer range. It is assumed that class or map-unit means provide better local predictors than the mean for the whole area. The preceding section shows that this is not always the case, particularly if there remain significantly non-random variations within the map unit, as in the Westmere map unit *(cf. Gibson et al. [1983])*.

However these are crude ways of describing soil variability, since Figure 4 (after *Beckett and Webster [1971])* and Tables 2 and 3 above, clearly show that though the scale of variability tends to increase with the size of the area sampled, often a substantial fraction of it is of very short range.

A semi-variogram plots the average of the variance between the values of a soil property at two points at a specified distance apart, for a number of such spacings (lag distance): it describes spatial variability more sensitively. It is related to the correlogram which plots the correlation between the two sets of values against the distance between them, and to the corresponding graph of the variance within sample plots against the areas of the plots (Figure 4).

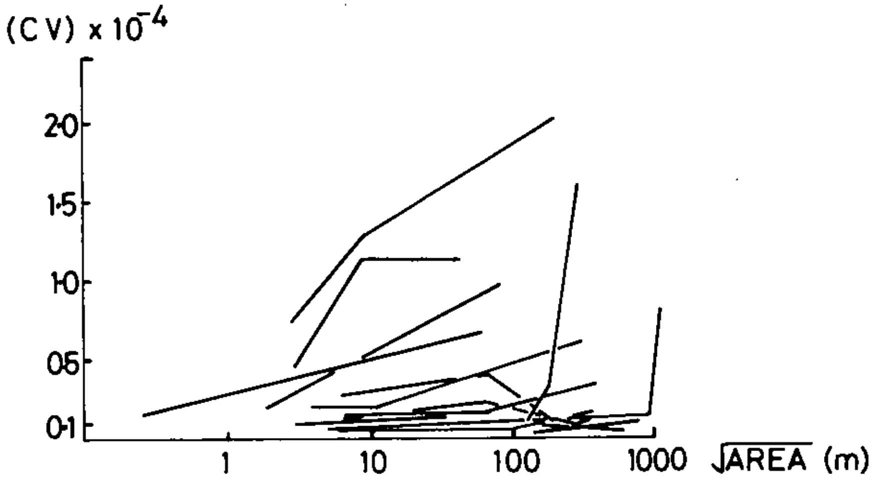

Fig. 4. Variance of available K within areas of varied size – each line represents one set of data – plotted against $\sqrt{\text{area}}$: replotted from *Beckett & Webster [1971]*.

Each of the components of variability discussed above (pp 6-11) may be described by a simple semi-variogram (Figure 5 [a]). The *sill* height represents its full effect: the *range* is the distance beyond which its contribution to soil variability does not increase further-every pair of sites includes the full effect: a *nugget variance* appears when there is substantial short range variability within the minimum lag distance. This is not necessarily described by extrapolating the semi-variogram to zero. Figure 5(b) illustrates separate semi-variograms for three components of variability of different range and magnitude – these two aspects are not necessarily correlated. When added they produce the less simple semi-variogram (1 + 2 + 3) that would be measured in the field. As drawn, its points of inflexion reveal the ranges of components 2 and 3. Strictly perhaps, the semi-variogram should be presented as in Figure 5(c) without surmises about its form below the shortest lag distance. In principle X might be reduced by taking N samples in an area of L^2 round each sampling site, and bulking them for a single analysis. This would reduce the within-site variance by a factor of 1/N *if* the the values of the property to be measured were normally distributed within each sample, and would raise the lag axis by X (1 – 1/N), or proportionately less if the area sampled were less than L^2.

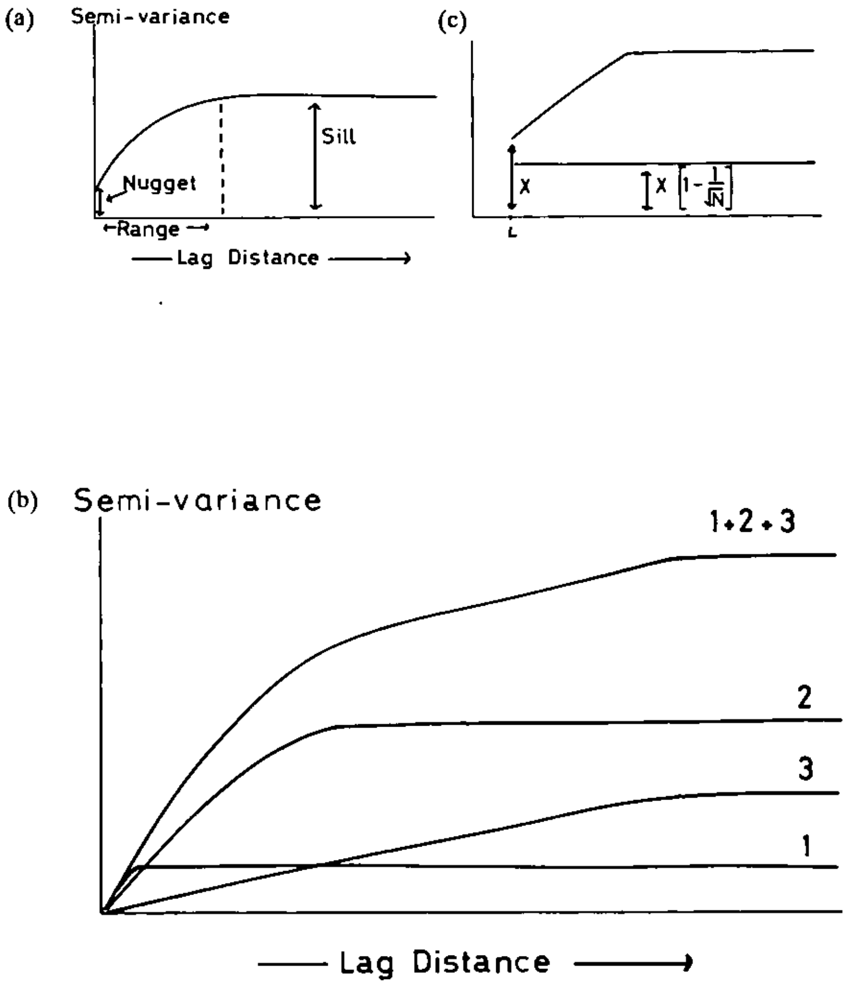

Fig. 5. (a) Idealised semi-variogram.

(b) Idealised semi-variogram (1 + 2 + 3) for a landscape in which there are three components of variability, of short-(1), medium(2) and long-range(3).

(c) Idealised semi-variogram with a substantial nugget-variance (X). If each sample had been bulked from N soil samples from within an area L^2, then this would have had the effect of reducing the nugget-variance to X/N, or raising the distance axis by X (1-1/N).

Table 12. Spatial dependence in the variability of K-status.

Ref.	Depth (cm)	Minimum Lag	Nugget variance (as % of sill variance)	Range	K-property
3	0-10	> 15 m	21%	100-200 m but semi-variogram still rising to another sill at > 500 m	K_{ex}
12	0-30	30 m	50%	Semi-variance increasing linearly with lag distance up to > 180 m	K_{ex}
	30-60		30%		
	60-90		32%		
25	0-15	1-2 km	7%	10 and 32 km	K_{ex}
	30-45		21%	14 km	
26	0-15	2 km	No spatial dependence, nugget = sill variance: any spatial dependence must be of range 2 km		Total K
27a	Topsoil	80 km	No spatial dependence		Available K
b		1.6 km	No spatial dependence		
c		90 m	Semi-variogram rising from 90-1000 m		
d		90 m	No spatial dependence for lag distances of 100-900 m		
e		45 m	Semi-variogram rises from 100-150 m		

Table 12 presents examples of spatial dependance in K-status, in the order of their minimum lag distance. The first (*ref.* 3 in Table 13) relates to a complex, multicyclic landscape and shows that 21% of the total variability occurs within distances of 5 m or less: the principal medium-range component of variance has a range of 100-200 m, but there appear to be others with ranges of more than 500 m, the limit of the semi-variogram. In the second case (*ref.* 12) the short-range (< 30 m) nugget variance of exchangeable K is highest in the topsoil: the semi-variance at every depth is still rising at 180 m. In the Hawaiian example (*ref.* 25) there appear to be two principal components of variability in topsoil K with ranges at 10 and 32 km, and one for subsoil K with a range of 14 km. Other properties also showed ranges of 10-15 km. The example from China (*ref.* 26) shows no component of variability in total topsoil K that had a range > 2 km: this does not preclude significant spatial variabilities with smaller ranges. The last example *(ref.* 27) includes several fragmentary semi-variograms from transects of 180 m to 1450 km in Central Australia, with minimum lag distances of 45 m to 80 km. As can be seen there is no spatial structure in the variability of available K for ranges greater than 80 km along a N-S traverse on the Stuart Highway, nor for ranges greater than 1.6 km across a pediment plain. There were marked structures with ranges from ½ km to more than 1 km across the pattern of a dissected laterite peneplain, and with ranges of 100 m or so across gilgai, but no structure with ranges of more than 90 m across an area of patterned vegetation with a recurrent frequency of the order of 100 m.

These examples emphasize the importance of sampling for both short-and long-range variability. The question of bulking samples to damp down short-range variability should be seriously considered in any project where short-range variability is of limited interest because management practices will bury it in a mean value.

Measurement of soil variability

Corresponding to the above there are three levels of approach:

(i) An overall mean and variance for the whole area of interest, based upon uniformly distributed (systematic or stratified random) sample sites.

(ii) Stratification of variability by means of mapped soil classes (simple map units), or by iso-lines of the values of K-properties. These are likely to be more useful for describing variability in the non-labile than in the labile forms of K. Stratification into fine divisions is likely to produce map units for which the $\sqrt{\text{area}}$ is comparable to the range of the corresponding semi-variogram (iii) which will be more useful. A less fine stratification might provide a useful basis for within-stratum semi-variograms, and obviate the need to measure long-range components of variability.

(iii) Semi-variograms of K-properties, for the whole area, or within broad strata (ii) defined on soil, geology or other environmental factors.

For all three of these it may be useful and reduce sampling effort if the basic measurement is based upon a bulked sample, fully representing a specified area round each sample site. To sample even 30m^2 round each site (a circle of 3 m radius) would filter out much short range noise, and there are not many kinds of land management that take account of variations within such small areas.

If the short- and medium-range variability in a large area can only be measured in sample areas, then the sample areas must be fairly distributed over the whole area – one set of nested plots is rarely adequate. In the case of a semi-variogram, a regular grid of sites at a spacing of say ⅙ of the mean width of the area or stratum to be sampled, provides a range of long distances up to half the width (which should be the limit). Satellite sites in random orientations to half of these, at set distances down to the minimum lag distances required, should provide a sufficient range of shorter spacings.

APPENDIX

Table 13 Sources of data for Tables 2, 3 and 12.

1.	UK, Dune grassland: available K by «resin-bag» procedure.	*Gibson [1986]*
2.	USA, Ohio: Farmland a) total K in silt fractions of corresponding horizons in six profiles round one pit.	*Drees & Wilding [1973]*
	b)	*Wilding & Drees [1978]*
3.	Australia, NSW: 400 ha. pasture on Tablelands: 111 sites on 180 m. grid with added «twin» sites at spacings of 5,18 & 56 m: semi-variogram for lag distances 5-500 m. Values square-root transformed.	*Webster & Butler [1976]*
4.	USA, Kansas: fields unutilised and unirrigated	*Cipra et al. [1972]*
5.	Canada, Alberta: rotation crops.	*Briggs [1974]*
6.	W. Canada: solonetzic soils.	*Carter & Pearson [1985]*
7.	New Zealand: one field on each of three soil types; pasture.	*Lee et al. [1975]*
8.	Canada, Quebec: rotation crops.	*Martel & Zizka [1978]*
9.	Finland	*Jokinen et al. [1983]*
10.	Canada, Alberta: 3 widely separated fields under rotation cropping.	*Cameron et al. [1971]*
11.	USA, Ohio.	*Wilding & Drees [1978, 1983]*
12.	W. Germany: $CaCl_2$ – extractable K on 30 × 30 m grid, with lag-distances 30-180 m.	*Dahiya et al. [1985]*
13.	N.W. USA; central-pivot irrigation area.	*Dow et al. [1980]*
14.	UK, Oxon: selected areas of clay soils.	*Bascomb & Jarvis [1976]*
15.	India, Tamil Nadu a) Alluvial landscape b) Lateritic landscape	*Mosi et al. [1975]*
16.	N.W. USA; Douglas fir forest.	*Grier & McColl [1971]*
17.	UK, Scotland: Sitka spruce forest a) was measured over a wider range of forest than b)	*Blyth & McLeod [1978]*
18.	W. Canada: three forest types.	*Quesnel & Lavkulich [1980]*
19.	N E USA: floodplain forest.	*Mollitor et al. [1980]*
20.	S E USA: 9 year Loblolly pine plantation on former cotton fields.	*Metz et al. [1966]*
21.	S E USA: Blue ridge forest.	*Ike & Clutter [1968]*
22.	S E USA: Red pine plantation.	*Hort et al. [1969]*
23.	UK: Mixed oak woodland, values show that spatial variation changes with season.	*Grieve et al. [1984]*
24.	W Canada. Douglas fir: Low (L) and High (H) fertility plots: «plot-bulked» means that all the samples within plots of .5-3.3 ha were bulked before analysis.	*Courtin et al. [1983]*
25.	Hawaii, 80 sites at 1-2 km intervals, along transects more or less perpendicular to the coast, samples bulked over .3ha, values log-transformed.	*Yost et al. [1982]*

26. China, Zhangwu county: 102 profiles in 3635 km^2; semi-variogram calculated for lag distances 2-50 km. *Xu & Webster [1984]*
27. Central Australia, natural vegetation, all samples bulked within 25 m^2 areas round each site.
    a) Along 1450 km of the Stuart Highway, sampled at 80 km intervals.
    b) Along 58 km across pediments of Hammersley range, sampled at 1.6 km intervals.
    c) 900 m transects perpendicular to drainage in a strongly dissected landscape, sampled at 90 m intervals.
    d) 550 m across striped vegetation pattern, sampled at 90 intervals.
    e) 180 m across gilgai area, sampled at 45 m intervals *Beckett & Bie [1976]*

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Interpretation of Long-Term Experiments with K Manuring

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Summary

Results from 3 long-term (30 year) experiments are presented and discussed leading to the following conclusions:

1. Conventional soil analysis of surface soil (CAL, $BaCl_2$, H_2O, EUF) does not fully reflect the effect of long term differential K fertilizer treatment. Taking into account texture, K fixation and supply of K from subsoil brings about improvement. Correction of CAL K for % K of the sum of basic cations improves interpretation.
2. So far as dressings for individual crops are concerned, conventional methods are helpful but not predicting requirements for ameliorative dressings.
3. Limitations of conventional determinations on topsoil are made clear by the fact that on nil K plots, change in CAL K accounts for only 0.1-3% of crop uptake and on high K (300 kg/ha/yr) plots for only 2-12% of the excess of K application over removal. Obviously non-exchangeable and subsoil K is important.
4. Needs in terms of both K dressing and soil K content contrast as between rootcrops and cereals. Economically optimum results with cereals are obtained at CAL K values from 6-12 mg K_2O/100 g soil and K fertilizer rates from 0-110 kg/ha K_2O. For rootcrops the relevant values are 6-19 mg/100 g and 160-290 kg/ha/yr K_2O. Sugar content of beet and dough elasticity of wheat are positively correlated with soil-K content. Starch content of potatoes is slightly decreased by K supply, but this is compensated by higher tuber-yield.
5. Economically optimum K dressings increase crops up to 60% (cereals) and 90% (roots) of the maximum yield responses by K. They produce net yield increases (fertilizer cost already deducted) of 5.5 t beets, 2.4 t potatoes and 0.1 t cereals/ha/yr.

1. Introduction

The general improvement in soil fertility of our agricultural land – especially arable land – means that today it is very difficult to find sites for experiments to confirm the correctness of K fertilizer recommendations and to establish norms for soil K content, ranging from deficiency to excess of K supply. This is because crops obtain

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their K needs increasingly from reserve sources, either natural or resulting from residues accumulated from previous fertilizer treatment and only partially utilise freshly applied K. K uptake is confined to the soil within a short distance from the root surface to which non-exchangeable K makes a significant contribution *(Claassen and Jungk [1982])* and this principal fact reduces utilization of fertilizer K in the bulk soil in the season following applications. From this it follows that generally, and especially on high K soils, full economic evaluation and differentiation between past and present K-fertilizer application is not possible. Unutilised residues which compensate for removal from soil sources or increase soil reserves would not be taken into account.

These difficulties can be overcome only in long-term experiments preferably on soils which have previously received little fertilizer. This allows the taking into account of the value of fertilizer residues accumulated in the soil and their proper evaluation. Long-term experiments have a subsidiary advantage in that they take into account seasonal variations in yields.

This paper discusses results from long duration (30 years) trials of K manuring as they indicate how soil K status of different soils is affected by level of fertilization, how crop yield and quality are affected by this and how the results can be used to indicate the K fertilizer amounts and soil K levels which are needed for optimum crop production. Finally it mentions results from survey experiments designed to improve the interpretation of soil analysis.

2. Materials and methods

The experiments are sited in three contrasting areas of Lower Austria and were laid down by *Reichard* in 1956. Data relating to the experimental sites are given in Table 1.

The sites contrast not only as regards altitude and rainfall but also as regards soil type, parent material and texture. The Rottenhaus soil is especially compact and heavy (silt + clay 97%). These contrasts results – as well be shown – in great differences in response to K fertilizations.

Rates of potash applied at Fuchsenbigl and Rottenhaus were 0, 150 and 300 kg/ha/yr K_2O and at Zwettl 0, 50, 100, 150 on account of the high K content of parent material at the latter site. NP dressings were adequate, especially the rate of nitrogen was adjusted to crop and yield potential every year. Only data from the 2nd and 3rd ten year cycles are discussed because there were changes in fertilizer treatment in the early years and in 1965/66 the DL method of extraction was replaced by CAL *(Schüller [1969])* so that soil analysis data since then are not comparable with the early years. By taking the shorter period the evaluation is based on varieties with similar yield potential.

The other series of experiments, mentioned briefly in section 3.6, covered a wide range of sites varying in K status (8-52 mg K_2O/100 g) and soil criteria (type, texture, organic matter content etc.) in Lower Austria and the northern Burgenland. Rates of potash applied were per annum: 0, 75, 150, 300 kg/ha K_2O and the aim was to calibrate soil-examination methodology *(Köchl [1979])*. 6 years' results are taken into consideration.

The methods compared in long duration trials and discussed in this paper were as follows:

CAL	Ca-acetate (0.05 m) Ca-lactate (0.05 m) method of *Schüller [1969]*
EUF	Electro-ultrafiltration of *Németh [1979]*
$BaCl_2$	$BaCl_2$ (0.2 m) – triethanolamine solution of Mehlich pH 7.5, 1:20, 1h
H_2O	Extraction with water; 1:20, 1h
K (fix)	K fixation. KCl (120 mg/100 g soil) addition and exchange with 1 N NH_4Ac; 2 × 1 h. Parallel determination of CAL K.

Table 1. Characteristics of experimental sites

Site	Fuchsenbigl	Rottenhaus	Zwettl
m.a.s.l.	150	290	550
Annual rainfall mm	541	836	740
Mean annual temperature (deg C)	9.1	8.5	6.8
Parent material	Loess	Silt	Silicate
Soil type	Chernozem	Brown earth	Brown earth
Texture	Sandy loam	Silty loam	Sandy loam
pH $CaCl_2$	7.5	6.5	6.0
$CaCO_3$ %	15	0	0
Organic matter %	2.1	2.9	1.9
CEC me/100 g	25.4	28.0	11.6
Sand/silt/clay (%)	40/42/18	3/67/30	48/36/16

3. Results and discussion

3.1 K content of long-term plots as related to K fertilizer rate and duration

The value of soil analysis for advisory purposes depends upon how well it reflects nutrient content of the soil and previous fertilizer treatment. Hence long term experiments in which the history is accurately recorded are of particular value in assessing the value of different methods. This is especially true for the CAL extracted K since this was investigated regularly over the full experimentation period.

All methods show differences in K supplying power between the experimental sites. This holds to some extent for the control (K_0) plots as would be expected but also for the K content under fertilizer treatments. Differences in K removal due to different crop successions do not explain these differences. Rottenhaus is distinguished from the other sites by its low K status as indicated by CAL or water extracts (5.2 and 1.33 mg/100 g respectively). At Rottenhaus the effect of K fertilizer on easily soluble soil K is slight. Without knowledge of the fertilizer history, the value of 6 mg/100 g for the 300 kg/ha treatment would be taken to indicate K deficiency. At Fuchsenbigl and Zettl, applying 150 kg/ha K_2O increased the CAL or EUF values by ten times as much as at Rottenhaus. This is correlated with the noticeably higher rate of K fixation at this site but this does not – as a long-term experiment using very high K rates (up to 900 kg/ha) has shown – indicate a need for extremely high K dressings. Corresponding with the low K (CAL) values a high fertilizer efficiency at Rottenhaus was found (Figure 2); however, the fertilizer

Table 2. K_2O content of soils by different methods (mg K_2O/100 g soil)

Site	kg/ha/yr K_2O				
	0	50	100	150	300
CAL, Ø 1966-1983					
Fuchsenbigl	7.8			11.7	19.4
Rottenhaus	5.2			5.7	6.6
Zwettl	10.3	12.0	14.2	18.4	
$BaCl_2$, Ø 1980-1982					
Fuchsenbigl	9.1			14.3	23.1
Rottenhaus	8.9			9.7	11.7
Zwettl	12.3	13.2	15.6	18.3	
H_2O, Ø 1979-1981					
Fuchsenbigl	2.50			4.79	9.87
Rottenhaus	1.33			1.65	1.87
Zwettl	2.98	3.30	3.54	4.47	
EUF I (30', 20 degrees, 200 V), Ø 1978-1980					
Fuchsenbigl	5.65			9.78	16.42
Rottenhaus	5.25			5.74	6.78
Zwettl	7.67	8.89	11.52	12.58	
EUF II (5', 80 degrees, 400 V), Ø 1978-1980					
Fuchsenbigl	3.82			5.94	8.59
Rottenhaus	2.69			2.84	3.65
Zwettl	3.21	3.62	4.55	4.78	
K fixation, Ø 1982-1983					
Fuchsenbigl	20.3			14.8	12.7
Rottenhaus	88.2			74.7	70.8
Zwettl	17.7	14.1	13.9	12.2	
CAL, Ø 1978-1980					
Fuchsenbigl	8.20			12.74	22.44
Rottenhaus	5.77			6.97	8.57
Zwettl	10.7	10.5	12.8	16.2	

requirements do not lie outside the normal range inspite of a remarkable K-fixation capacity. K supply from the subsoil has probably played a part in supplying the crops. Analysis of the 40-60 cm soil layer, well below plough depth, shows extremely slight differences between the sites (Table 3) so that K from this source can be said to be equally available to crops on all sites. After all, cereals can obtain up to 50% of their K needs from this source ***(Grimme et al [1981]; Kuhlmann [1983])***.

As Table 4 shows there is good general agreement between the different methods of analysis used on the surface soil. Apparent discrepancies between CAL, H_2O and EUF II disappear when they are compared on the same year basis. The negative correlation between extractable and fixed K is in the line with expectations and indicates that a knowledge of K fixation capacity – especially when there is a lack of information on particle size distribution – would assist in interpretation of results. The results for Rottenhaus (6 mg CAL-K, 80 mg K fixation) would indicate requirement for above-average K dressings but no need for supplementary ameliorative applications.

Figure 1 shows soil K content plotted against time and indicates that soil K has varied with crop succession; it declines following root crops and legumes. This indicates that soil analysis reflects K addition and removal accurately. The traces at the different levels of K application are substantially parallel. All this demonstrates that – careful soil sampling provided – soil testing in regular intervals gives quite a reliable information about changes in K availability. Field records and extension services, therefore, call for regular soil testing.

Table 3. CAL K values for 20-40 cm depth (mg K_2O/100 g soil)

Site	annual K_2O rates in kg/ha 0	50	100	150	300
Fuchsenbigl	4.3			4.4	6.4
Rottenhaus	5.5			5.4	6.2
Zwettl	6.1	6.0	7.1	7.9	

Table 4. Correlation between different methods of soil analysis

Method and years taken into account	CAL 78-80	$BaCl_2$ 80-82	H_2O 79-81	EUF I 78-80	EUF II 78-80	K-FIX 82-83
CAL 66-83	0.95	0.95	0.84	0.96	0.78	– 0.77
CAL 78-80		0.99	0.96	0.98	0.92	– 0.67
$BaCl_2$ 80-82			0.92	0.99	0.88	– 0.61
H_2O 79-81				0.92	0.97	– 0.60
EUF I 78-80					0.88	– 0.65
EUF II 78-80						– 0.55

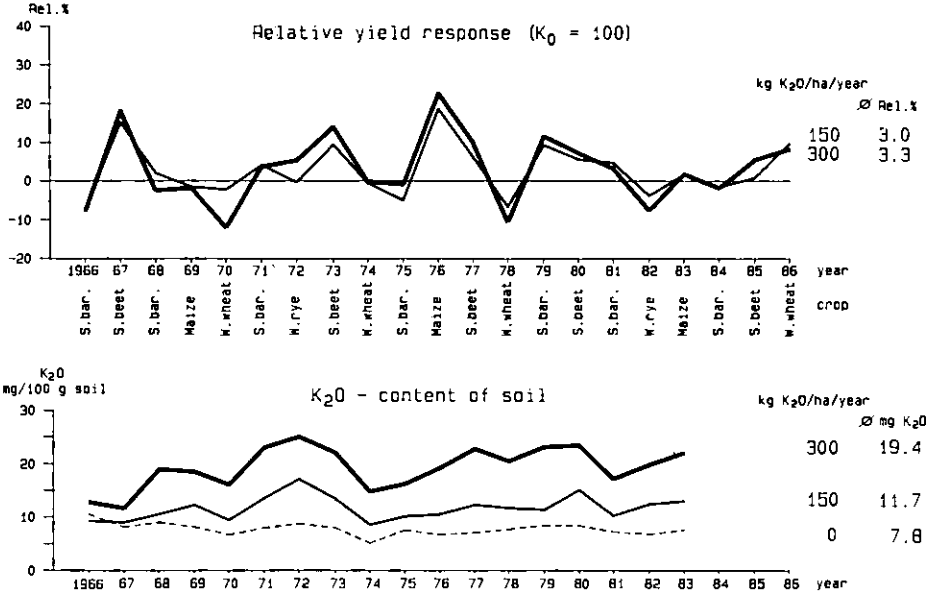

Fig. 1. The effects of K fertilizer on yield and K_2O (CAL) content of soil. Years 11-30 of long-term experiment at Fuchsenbigl.

3.2 Effects and profitability of K application

The effects of fertilizer treatment on yield show variation between years and between crops. From Figure 1 it was apparent that at Fuchsenbigl beet is the most responsive crop followed by grain maize and spring barley; winter sown crops show negligible or even negative response. On the average over the whole period, in Fuchsenbigl yield of rootcrops is increased by 12%; cereal yield is not increased. The same applies at Zettl but, at Rottenhaus, both roots and cereals respond (+ 18% and + 11% respectively). On this heavy soil with much clay and silt, silage maize responds to K fertilizer by up to 60%.

The contrast between crops and sites in their reaction to K fertilizer is clear from Figure 2. Positive responses are shown as curves (IY) derived from the Mitscherlich equation ($y = A(1-10^{-c(x+b)})$ with iterative computation using varying values for c until the curve passes through the experimental points. Negative responses are shown by the lines (DY) jointing the recorded yields. Cost/price ratios and cash returns are also plotted and the economic optima indicated by broken vertical lines. The cost/price ratios (sugar beet roots 7 kg, cereals 1.6 kg and potatoes 5.75 kg per kg K_2O) are used to adjust the diagrams (lines FC parallel) in order that visual comparison is facilitated. Except for potatoes at Zettl cost price ratios are based on the price of chloride-based K fertilizers. The steeper FC line for Zwettl results from

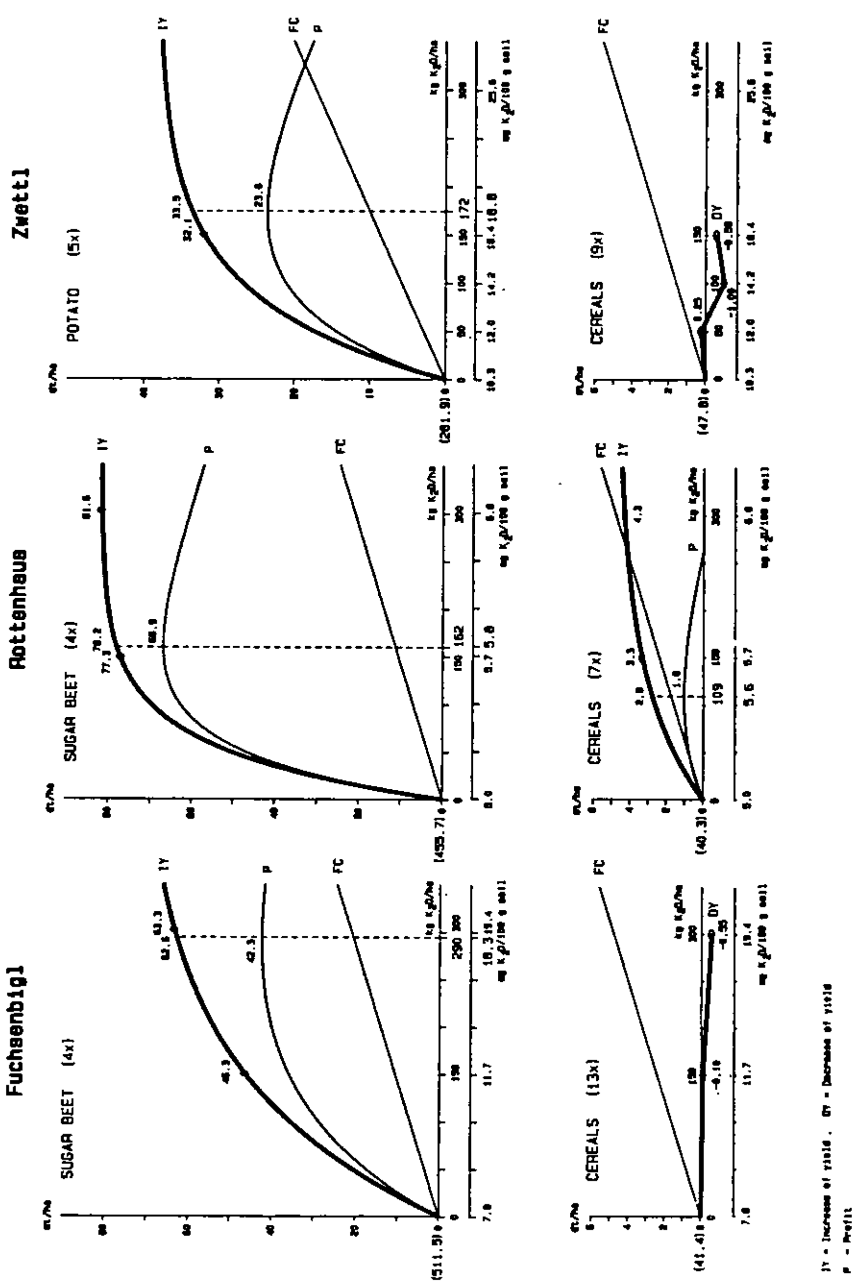

Fig. 2. Profitability of K dressings and derivation of optimum soil K supply for sugar beet, potatoes and cereals based on 42 annual results from long-term experiments at Fuchsenbigl, Rottenhaus and Zwettl.

the substitution for chloride by the more expensive sulphate of potash or sulphate-of-potash-magnesia.

Both curves for gross return (IY) and net return (P) show that the return from K fertilizer is much higher for root crops than for cereals (nil or negative except at Rottenhaus).

Maximum and economically optimum yield responses and K rates corresponding with the latter are listed in Table 5. For beet the economically optimum increases are 6.26 and 7.82 t/ha roots and for potatoes 3.35 t/ha tubers; these are from 4-14 % below maximum responses. Cereals responded only at Rottenhaus with economically optimum response of 0.28 t/ha (max. response 0.48). After deduction of cost of fertilizer, the profit remaining amounts to 4.2 or 6.7 t/ha beet, 2.4 t/ha potatoes and 0.10 t/ha grain (Rottenhaus) per ha per annum. K fertilizer is at least ten times more profitable on beet than on cereals.

Table 5. Economic results of K manuring (42 annual yields on long-term experiments)

Crop	Site	Yield increase (dt/ha) maximum	optimum	Optimum rate kg/ha K_2O	Cost of fert. dt/ha/crop	Margin dt/ha/crop
Sugar beet	Fuchsenb.	73.1	62.6	290	20.3	42.3
Sugar beet	Rottenh.	81.8	78.2	162	11.3	66.9
Potatoes	Zwettl	38.3	33.5	172	9.9	23.6
Cereals	Fuchsenb.	–	–	–	–	–
Cereals	Rottenh.	4.8	2.8	109	1.8	1.0
Cereals	Zwettl	–	–	–	–	–

3.3 Optimum soil K levels

The soil K(CAL) values and optimum K dressings for attainment of optimal yield are shown in Figure 2 at the base of the vertical line and are supplemented with results of the other soil testing methods in Table 6. Rootcrops, according to site, require 160-290 kg/ha K_2O and cereals 0-110 for highest economic return. These rates lead to the optimum only if K residues in the soil are taken into account. As the data show, rootcrops at Fuchsenbigl and Zwettl must have access to 18-19 mg K_2O/100 g soil (in addition to the indicated fertilizer rates) if optimum yields are to be obtained. On the other hand, 8-10 mg suffices for cereals. Spring cereals, whose K requirement is generally higher (Figure 3), require at Zwettl 12 mg plus 30 kg/ha K_2O fertilizer, at Rottenhaus 6 mg/100 g suffices together with the optimal fertilizer rate given in Table 6 for both crop groups besides of the optimal dressings.

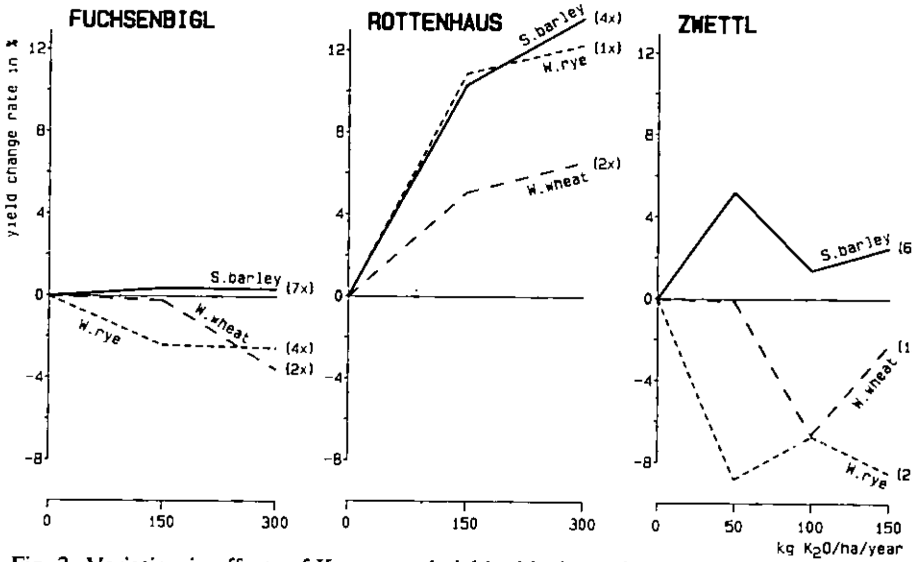

Fig. 3. Variation in effects of K on cereal yield with site and crop.

Table 6. K_2O rates and optimum soil K values for economically optimum production

Crop	Site	Opt. K_2O kg/ha	Opt. soil K (mg/100 g K_2O) CAL	EUF I	EUF II	EUFI+II	H_2O	$BaCl_2$
Sugar beet	Fuchsenb.	290	18	16	8	24	9	23
Sugar beet	Rottenh.	162	6	6	3	9	2	10
Potatoes	Zwettl	172	19	14	5	19	5	23
Cereals	Fuchsenb.	0	8	6	4	10	3	8
Cereals	Rottenh.	109	6	6	3	9	2	10
Cereals	Zwettl	0	10	8	3	11	3	17

3.4 Optimum K supply and crop quality

Long term experiments offer a good basis for assessment of effects of fertilizers on quality. Table 7 shows that K fertilizer increases sugar yield more than it increases root yield. Improvement in sugar formation is always accompanied by increase in K and Na uptake to the detriment of extractability. Even so, the refined sugar yield is still increased slightly more than root yield (+ 15% against + 14%).

On the other hand, in potatoes, starch content slightly decreased with K supply (Table 8). While starch yield increases up to 150 kg/ha K_2O, the slight increase for the last increment of potash indicates that it is safer to underestimate than to overestimate the economically optimum K rate.

So far as concerns winter wheat at Fuchsenbigl, 8 mg soil K is enough for optimum yield. If quality wheat is grown, dough elasticity increases significantly if N dressings above 100 kg/ha are accompanied by potash. 75 kg/ha K_2O is the appropriate rate.

Table 7. Effect of long-term K manuring on root and sugar yield (7 year summary). Fuchsenbigl and Rottenhaus

	Yield					
K_2O	Roots		Sugar		Refined sugar	
kg/ha	dt/ha	Rel.%	dt/ha	Rel.%	dt/ha	Rel.%
0	485	100	88.4	100	80.3	100
150	544	112	101.1	114	91.0	113
300	551	114	104.0	118	92.7	115

Table 8. Effect of long-term K dressings on yield and quality of potatoes (4 year summary). Zwettl

kg/ha	Tuber yield		Starch content (%)		Starch yield	
K_2O	dt/ha	Rel. %	%	Rel. %	dt/ha	Rel. %
0	298.4	100	16.18	100	48.2	100
50	310.0	104	16.13	99.7	49.8	103
100	326.3	109	15.94	98.5	51.7	107
150	330.9	111	15.91	98.3	52.4	109

3.5 Change in K content of topsoil in relation to K balance

Changes in CAL K contents of topsoil are listed in Table 9 together with K applications and removals in crops. K_2O removals from the nil K plots at Fuchsenbigl (CAL K 8 mg K_2O) and Rottenhaus (CAL K 5 mg) were respectively 127 and 136 kg/ha/yr K_2O. Of these amounts 97% originated from non-exchangeable sources or from the subsoil at Fuchsenbigl and 99% at Rottenhaus. The equilibrium between CAL content and other K fractions on the control plots reflects the ability of the natural soil to supply K.

At the other extreme, 300 kg/ha/yr K_2O, most of the excess of K applied over uptake has gone into increasing the non-exchangeable and subsoil K. Only 12% of the K balance is accounted for in CAL K at Fuchsenbigl and only 2% at Rottenhaus.

Table 9. K balance at Fuchsenbigl for period 1966-81 (62.5% cereals, 25 % sugar beet and 12.5% grain maize) and Rottenhaus 1968-81 (47% cereals, 26% sugar beet, 7% field beans, 13% silage maize, 7% spring catch-crops) kg/ha/yr K_2O.

	Fuchsenbigl			Rottenhaus		
Fertilizer	0	150	300	0	150	300
Removal	127	148	168	136	162	172
Difference	− 127	+ 2	+ 132	− 136	− 12	+ 128
Change in CAL K 0-25 cm	− 3.8	+ 4.1	+ 15.4	− 0.1	+ 0.3	+ 2.3
From non (CAL) exch. K	123	2	–	136	12	–
Into non (CAL) or subsoil	–	–	117	–	–	126
% of balance accounted for as CAL K	3%	12%	0.1%			2%

3.6 Site distinguishing factors

As shown by a series of survey experiments (70 sites, 6 years), easily soluble soil K on its own is not an infallible guide, except in very few cases, for K fertilizer recommendations. The correlation between yield response to K fertilization and CAL ($pH \geq 6$) or DL ($pH < 6$) K content of topsoil amounts to as little as $r = 0.2$. H_2O or 1 M NH_4-Ac + 1 M HAc + 0.002 M DTPA are not better. But indications can be improved by including factors which influence K activity. From a large number of factors tested statistically, the following seem significant: % coarse material, sum of exchangeable basic cations, K in % of exchangeable bases, % clay, K fixation capacity and deep subsoil (50-75 cm) K. Naturally, the effect of K fertilizer is also dependent on subsoil (25-50 cm) K content but, because this is closely related to the values for topsoil K ($r = +0.82$) it is of little practical use compared with deep subsoil K.

K saturation is particularly useful and this should be included in all routine analysis also because it yields information on Ca, Mg and Na status of the soil. By taking into account K saturation together with deep subsoil K, the correlation is improved to $r = 0.43$ and, if soils with more than 20% clay are excluded, to 0.70. If additionally, fixation capacity and rainfall are taken into account we arrive at a value for r of 0.91.

4. Conclusion

The first conclusion to be drawn from the 3 long-term experiments is that soil analysis accurately reflects inter-treatment and inter-crop differences in reaction to K fertilizer on one site. However, the effects of differential K application over 3 decades has resulted in great differences between sites as regards change in easily soluble K content of topsoil which indicates that this criterion on its own is of limited use. Without knowledge of other soil factors there is no guidance as to what dressings may be needed to build up soil fertility or at best only with considerable reserve (*e.g.* restriction of additional dressings to the economic optimum). According to the results of the 3 long-term trials the EUF method gives no better guidance (high correlation between methods, no evident difference in EUF I – EUF II ratio between sites). Interpretation is improved by taking into account site properties and further soil data – texture, K in deep subsoil (below 40 cm) and K fixation. Such information is obtained relatively cheaply since the analyses do not or not frequently have to be repeated. The indication from the 70 survey experiments is that furthermore the proportion of K in exchangeable bases is useful.

If, for the sake of simplicity, soil investigation is limited to determination of K content of the topsoil, this is an adequate guide to fertilizer rates, provided no amounts above the optimal ones are applied and differences between crops are taken into account. Within the range of soil K indicated for cereals (6-12 mg/100 g K_2O) optimum K dressings range from 0-110 kg/ha K_2O (higher values and rates for spring barley, lower for winter-sown crops). Quality wheats should receive 75 kg/ha K_2O. Above 12 mg the results of the long-term experiments indicate that K dressings could be reduced. The survey experiments gave somewhat different indications: even within the range 15-28 mg/100 g CAL K_2O, 75 kg/ha K_2O gave economic returns from spring barley.

Economic evaluation of the results has shown that for rootcrops, 6-19 mg CAL K_2O/100 g and 162-290 kg/ha/yr should suffice. Somewhat lower dressings are suggested for potatoes because of the reduction in starch content, though if rates are cut too far, there is a danger of blue spot or after-cooking-blackening especially on high clay soils *(Marschner and Krauss [1980])*. The positive effects of K fertilizer on % sugar in beet and yield of refined sugar are to be noted. Dressings to sugar beet could be in the lower range if there were no irrigation in the dry area (Fuchsenbigl) *(Köchl [1985])*.

The marked difference in K requirement between rootcrops and cereals is confirmed by *Heimes [1971]*, and *Kuhlmann and Wehrmann [1984]* while *Mengel [1974]* citing results from *Harrach* and *Németh* gives requirements of sugar beet at 1.3 me K/l soil solution and 0.7 for winter wheat. *Bucher et al [1981]* place winter wheat in the same category as the above, less K responsive than spring barley or – as in a 26 year experiment *(Mraczek [1979])* – as unresponsive as winter rye.

These differences are not due only to the lesser K removal by cereals but to the more intensive rooting of monocotyledons *(Fink [1969])* which are able to extract large quantities of non-exchangeable K *Claasen and Jungk [1982]; Kuchenbuch and Jungk [1984]; Kuchenbuch and Claasen [1985])*. Utilisation of deep subsoil K is particularly important in dry regions. Transfer of K between exchangeable and non-exchangeable forms is responsible for the constant soil K values and for the substantially annual uptakes (127-136 kg/ha/yr K_2O) for the control plots.

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Assessment of Optimum Application Rates of Fertilizer K on the Basis of Response Curves

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Summary

K-response curves of 39 K-fertilizer trials with potato are described by a quadratic and a modified exponential equation. In all experiments the modified exponential equation was better when the residual sum of squares (RSS) was taken as a measure of the degree of fit. The economically optimum application rates of fertilizer K, which were calculated on the basis of the modified exponential equation, covered the entire range of fertilizer-K_2O levels tested, viz., 0-400 kg ha^{-1}. The confidence intervals ($p > 95\%$) for the optimum K-application rates were frequently very wide. In 18 trials the confidence interval covered the entire range of tested fertilizer levels. Although the calculations were done to demonstrate the method and not to make fertilizer recommendations, the implication is that care should be exercised in using optimum application rates of fertilizer K for making fertilizer recommendations.

1. Introduction

Fertilizer recommendations are usually based on results of field trials in which crop response to various rates of fertilizer application is determined. The response curve then provides the relationship between amount of fertilizer and crop yield for each trial. From this curve the economically optimum application rate of fertilizer, *i.e.* the minimum amount of fertilizer needed for maximum financial yield, can be derived. Then, fertilizer recommendations can be made by correlating the optimum application rates of fertilizer in the various trials with one or more field characteristics, for instance the amount of plant-available nutrient already present in the soil.

In the Netherlands numerous fertilizer trials have been conducted to establish the relationship between the amount of a plant-available nutrient in the soil and the optimum applicatin rate of fertilizer. Although it was seldom stated explicitly, interpretations of the experimental results were based on hand-drawn curves

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(Neeteson [1985], Neeteson & Smilde [1983], Prummel [1969], Prummel & Von Barnau Sijthoff [1984]. Van der Paauw [1956]) as were the recommendations *(Neeteson et al. [1984], Van der Paauw & Ris [1960])*.In drawing curves by hand the deviations of the points from the curve were minimized. A prerequisite was that the drawn curve should be in agreement with the generally accepted shape of response curves. This method of curve-fitting is rather subjective and time-consuming. Drawing curves by hand also makes it difficult to assess accurately the optimum application rate of fertilizer and to state its reliability.

Neeteson & Wadman [1987] re-evaluated results of 167 N-fertilizer trials with sugar beet and 99 with potato by determining response curves on the basis of mathematical functions. From the many types of response curves that can be used *(Wood [1980])* the quadratic and the modified exponential curve were chosen, the quadratic curve because it is widely used and the modified exponential curve because it was preferred to various other types of response curves in recent wheat research *(George [1983])*.

Neeteson & Wadman [1987] found that for both sugar beet and potato the modified exponential equation described response much better when the residual sum of squares (RSS) was taken as a measure of goodness of fit. In order to take account of the few occasions when the quadratic model was superior, it was suggested that both equations should be used for the data of each individual trial. The optimum fertilizer application rate and its confidence interval ($p > 95\%$) should then be calculated on the basis of the best-fitting equation. The confidence intervals for the optimum N-fertilizer application rate frequently were very wide. In 46% of the sugar beet trials and even in 60% of the potato trials the interval exceeded 300 kg N per ha *(Neeteson & Wadman [1987])*. The conclusion was that it is difficult to obtain reliable data on optimum N-fertilizer application rates. This conclusion agrees with results of *Sutherland et al. [1986]* and *Sylvester-Bradley et al. [1983]*. No data on the reliability of optimum K-fertilizer application rates could be found in the literature. This paper deals with results from 39 K-fertilizer trials with potato. For each trial the optimum K-fertilizer application rate and its confidence interval will be calculated on the basis of the best-fitting quadratic or modified exponential equation.

2. Materials and methods

2.1 Experimental design

In the period 1949-1958 39 field trials with potato (*Solanum tuberosum* L.) were conducted on sandy and sand/peat-mixed soils in the Northern part of the Netherlands (Table 1). With four exceptions the cultivar used was Voran. The trials consisted of five or six K-fertilizer application rates ranging from 0 to 300 or 400 kg K_2O per ha with from 2 to 6 replications. The fertilizer (potassium sulphate) was applied as a single dressing in early spring. Each experimental field was uniformly fertilized with N and P.

Table 1. Distribution of the trials over the years.

Year	Trial number
1949	1
1951	2
1954	3 - 5
1955	6 - 32
1956	33 - 38
1958	39

2.2 Determination of optimum application rate of fertilizer K

Response curves are described by both quadratic and exponential equations.

The quadratic response curve has the form

$$Y = b_o + b_1 K + b_2 K^2 \tag{1}$$

where

Y is yield in t ha^{-1}, K is applied fertilizer in kg K_2O per ha, and b_o, b_1 and b_2 are coefficients which are calculated by linear regression analysis.

The economically optimum application of fertilizer K, K_{op}, is calculated by

$$K_{op} = (P\text{-}b_1) / 2\ b_2 \tag{2}$$

where

P equals the ratio of the cost of 1 kg fertilizer K_2O to the price of 1 ton crop yield.

The modified exponential response curve has the form

$$Y = b_o + b_1 K + b_2 e^{aK} \tag{3}$$

where

Y, K, b_o, b_1 and b_2 are the same parameters as those in equation (1) and a is a constant which was set equal to one of nine predetermined values to avoid non-linear regression analysis. *(Neeteson & Wadman [1987]).*

For each value of a the response curve was calculated. The response curve which yielded the lowest residual sum of squares (RSS) was considered to be the curve of best fit. The exponential curve was termed «modified» because of the addition of a linear term (b, k) to allow for decreasing yields at fertilizer levels in excess of the level for maximum yield *(Wood [1980]).* From equation (3) it can be derived that the economically optimum application of fertilizer K, K_{op}, is

$$K_{op} = \ln\ [(P\text{-}b_1) / a\ b_2] / a \tag{4}$$

where

P represents the same as in equation (2).

Details about the response curves and the calculation of the confidence limits ($p > 95\%$) are given in another paper *(Neeteson & Wadman [1987])*.

3. Results

3.1 Optimum application rate of fertilizer K

In all trials the residual sum of squares (RSS) was lower when the modified exponential equation was used. Next, the optimum K-fertilizer application rate was calculated for each trial on the basis of the modified exponential equation. In doing so the monetary ratio of fertilizer cost to crop value, P in equation (4), was fixed at 0.006 (a monetary ratio of 0.006 means for instance that the cost of 1 kg fertilizer K_2O is DFL (Dutch guilders) 0.90 and the price of 1 tonne (industrial) tubers is DFL 150.00). These values are currently valid in the Netherlands **(PAGV [1986])**. Figure 1 shows the frequency distribution of the optima as determined with the modified exponential curve. The optima of 17 trials fell outside the range of tested levels of fertilizer K. These trials were omitted because the optima were derived after extrapolation, which may considerably decrease reliability. The remaining 22 trials showed optima which covered the entire range of fertilizer-K levels tested (Figure 1).

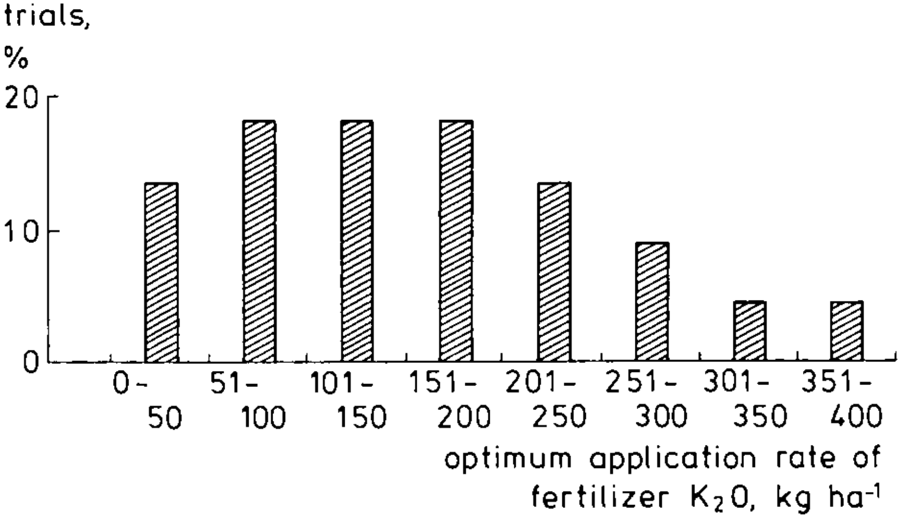

Fig. 1 Optimum application rate of fertilizer K for potato. Only those optima are shown which lay within the range of applied fertilizer K_2O: 0-400 kg ha^{-1}. Number of trials = 22.

3.2 Confidence interval for optimum application rate of fertilizer K

For each calculated optimum application rate of fertilizer K, including the optima which fell outside the range of tested fertilizer levels, the confidence interval ($p > 95\%$) was determined to distinguish between the degrees of reliability of the optima obtained. In Figure 2 only that part of the confidence intervals is indicated which lay within the range of applied fertilizer K, *viz.*, 0-400 kg K_2O per ha. For example, for trial 11, 264-400 kg K_2O per ha is indicated because the calculated confidence limits for the optimum application rate were 264 (lower limit) and 626 kg K_2O per ha (upper limit). Figure 2 shows that the confidence intervals of the optima were generally very wide. In 18 trials the confidence interval covered the whole range of tested fertilizer levels.

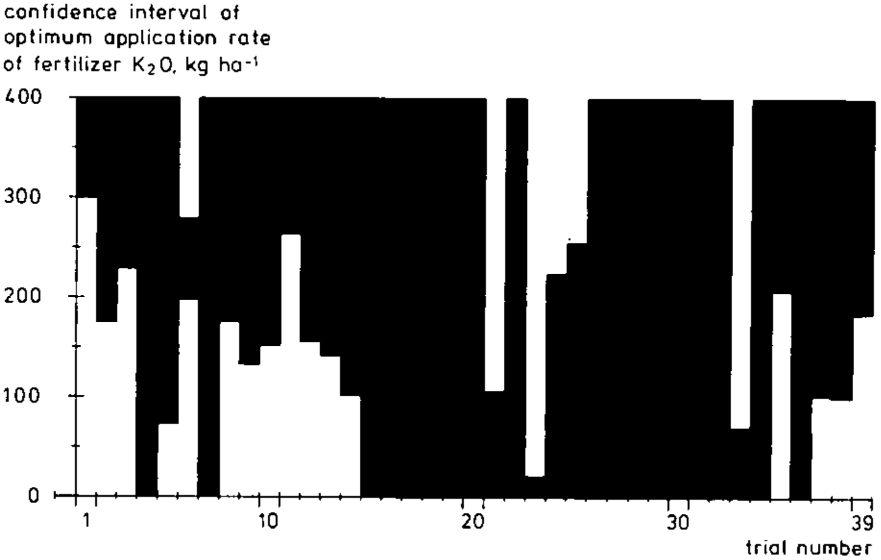

Fig. 2 Confidence interval (black bars) for the optimum application rate of fertilizer K for potato. See Table 1 for trial numbers. Only those parts of the confidence intervals are shown which lay within the range of applied fertilizer K_2O: 0-400 kg ha^{-1}. Number of trials = 39.

4. Discussion

4.1 Optimum application rate of fertilizer K

In agreement with previous work to describe N-response *(Neeteson & Wadman [1987])* it was found that the modified exponential equation described K-response better than the quadratic equation. To describe response of wheat to N-fertilizer, however, *Dilz et al. [1985]* found that the quadratic equation was superior to an exponential equation, but they used an exponential equation without including a linear term that would allow for decreasing yields at fertilizer levels in excess of the level for maximum yield.

In this paper the optimum application rate of fertilizer K was calculated on the basis of the modified exponential equation, because for all experimental data this equation described K-response better than the quadratic equation. The calculated optimum application rates of fertilizer K (Figure 1) could lead to the wrong conclusion concerning the amount of fertilizer K the potato crop generally requires, as the results of 17 trials were omitted because the optima fell outside the range of tested levels of fertilizer K. In seven of these trials the optimum was much higher than 400 kg K_2O per ha. In three of them, however, the optimum was likely to be less than zero, whereas in the remaining seven trials the optimum could not be calculated because the curves were concave. The large number of trials which yielded an optimum outside the range of tested levels of fertilizer K is probably due to the fact that the range of tested K-fertilizer levels was too narrow and/or that too few replications or fertilizer levels were included.

4.2 Confidence interval for optimum application rate of fertilizer K

The confidence interval for the calculated optimum application rate of fertilizer K was generally very wide (Figure 2). The magnitude of the confidence interval depends on the magnitude of the RSS and on the shape of the curve, *i.e.* on the significance of (P-b_1) and b_2 in equations (2) and (4). Confidence intervals for optimum fertilizer application rates are wide when the RSS is as is the case with heterogeneous fields. Confidence intervals are also wide when the curves are flat and do not decline significantly beyond their maximum, which often occurs with potassium sulphate response curves. The reliability of an optimum also depends on the place of the optimum within the range of fertilizer levels tested. When the optimum lies in the middle of the range, it is likely to be more reliable.

A point that deserves attention is the low yield level which was obtained in the K-fertilizer trials: on average maximum yield was about 35 t tubers per ha. This is probably due to a lower standard of crop protection and to the low productivity of the cultivars used: the trials were conducted in the late 1940s and in the 1950s.

Moreover, it is likely that too little fertilizer N was applied in the K-fertilizer trials: on average 128 kg N per ha. This is about half the amount which is currently applied. Perhaps too little fertilizer P was applied as well: on average 110 kg P_2O_5 per ha. The old data were used because results of recent trials on sandy soils with five or more application rates of potassium sulfate were not available.

It can be expected that response curves of recent K-fertilizer trials are less flat than those of old trials due to a higher standard of crop protection and to sufficient application of other nutrients. It is therefore quite possible that in recent trials the confidence intervals of the optimum application rates of fertilizer K are narrower than those shown here (Figure 2). However, we expect that they still are rather wide. In recent trials the reliability of optimum N-fertilizer application rates was poor *(Neeteson & Wadman [1987])*. There is no reason to expect that the reliability of optimum application rates of K fertilizer will be higher than that of N fertilizer.

Another point that deserves attention is that most trials were conducted in one year (1955; see Table 1), so that practical implications of the results presented cannot be derived.

The use of old data, which were obtained for the most part in one year, does not permit making fertilizer recommendations. However, in this paper it was intended only to show the method of calculation, which can be done with old data.

5. Conclusions

1. K-fertilizer response curves of potato can be described better by a modified exponential equation than by a quadratic equation.

2. The confidence interval for the optimum application rate of K-fertilizer for potato of individual one-year trials can be very wide. The implication is that care should be exercised in using optimum application rates of fertilizer K for making fertilizer recommendations.

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Coordinator's report on the 4th working session

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In spite of comprehensive and detailed scientific knowledge about the occurrence of potassium in soils and its availability (transport) to the root, the farmer and advisor are facing tremendous difficulties, when they have to synthesize the mosaic stones of knowledge into reliable K fertilizer recommendations accounting for both, the economical and ecological aspects. The dimensions of the complex relationships in soils and plants and of their interactions are nearly undefinable. Large- and small-scale pedogenesis, soil texture and soil structure, rainfall (irrigation) pattern, etc., all these are parameters contributing to nutrient availability in the soil and thus affecting fertilizer recommendation for cropping systems of different species and yield potentials.

It is therefore important to develop simple field methods which the advisor and farmer can use for improving fertilizer application and efficiency. In his review paper on the «Influence of soil structure on rooting, nutrient uptake and yield formation» *Harrach* has rigthly stressed the point that in modern agriculture with its high-yielding varieties and improved husbandry techniques priority in research must be given to soil structure and soil moisture availability rather than to further amendments of chemical soil analysis. Root elongation is inhibited by mechanical impedance, reduced gas exchange and decreasing soil moisture availability. Nevertheless, these three parameters can occur in such combinations as to allow a more or less good root elongation. Deep rooting is a prerequisite for high yields. Only this guarantees a satisfactory and uniform water supply of the crop during the growing season or, in other words, contributes to a sufficiently great available water capacity.

The determination of bulk density is a convenient indicator of soil structure. But it has its limitations in so far as it does not really reflect packing density and soil compaction which determine the mechanical impedance to root growth. Penetrometers must therefore be used in addition, although readings by penetrometers are also dependent on other soil factors, of which the soil water content seems to be the most important one. The simplest way of diagnosing the soil structure appears to be the use of a flat, square-ended spade to obtain undisturbed samples of the uppermost soil layer (spade diagnosis after *Görbing*).

It has always been the obligation of science to deduce the general principle from observed effects of single factors or their interactions. These endeavours can be achieved in two ways: by an empirical agronomic approach *(Köchl, Neeteson)* and/or by simulation models characterizing soil parameters which are important for root development and nutrient availability *(Beckett, Bar Yosef)*.

From a series of long-term experiments in Austria *Köchl*, for instance, concluded that lower levels of exchangeable K would have sufficed for optimum plant productivity in an alluvial soil than those required in a sandy soil, the reason being the higher K buffering capacity in soils with higher clay content. But in spite of the higher K reserves in clay soils, actual K availability may quickly become critical, so that both root crops and cereals responded to K fertilizer. On the other hand, sandy loams require higher levels of exchangeable K/100 g soil and this quantity must be supplemented by K fertilizer to root crops, but not to cereals, although for good baking quality of wheat K fertilizer was found to be beneficial.

There is no doubt that the definition of site-specific fertilizer recommendations require long-term experiments. *Sensu strictu*, however, such recommendations are only valid for the particular site where the long-term experiment had been conducted. This was demonstrated by *Neeteson et al.* who statistically evaluated about 40 annual K fertilizer trials with potato in the period 1949–58. In these trials the confidence intervals for the prediction of optimum K application rates were frequently very wide, ranging between 0–400 kg K_2O/ha. Apart from the fact that correlations between fertilizer rates and yield response must become less close when the yield plateau is reached, one of the most important reasons for poor K fertilizer/yield relationships seems to be the enormous large- and small-range spatial variability of soils and plant-available K *(Beckett)*. Even if the soils are grouped together according to families, groups and soil series, the coefficients of variation for exchangeable K can range between 30–200%. Such wide ranges cast some doubts on concepts attempting to improve K fertilizer efficiency by chemical analysis of extrapolations from «benchmark soils». As long as soil porosity and soil moisture regimes are not taken into account, reliability of K fertilizer recommendations will be inadequate. This was demonstrated by *Bar-Yosef* who simulated the transport of K in a clay and a sand in dependence on hydraulic conductivity as well as on quantity and duration of irrigation. Though not generally applicable, such simulation models based on monitoring nutrient concentrations in the soil solution will definitely lead to a better adjustment of nutrients in the irrigation water with the nutrient demand of the crop.

For productivity evaluation of a field the advisor has to start from two basic requirements. Firstly, he needs information from the farmer about yield potential, climatic conditions and soil tillage practices at the farm. Secondly, he needs a manual of field techniques for the evaluation of a soil profile with regard to texture, soil moisture regime, redox potential, pH, compaction, root penetration, etc. Such guidelines were given by *Lichtfuss and Grimme* who also recommended the use of geological, soil and climatic maps in order to improve the interpretation of soil test data. This approach should be followed more closely than it has been done up to now.

In conclusion, progress in the improvement of fertilization recommendations can be expected from more detailed investigations but also in particular from considering the soil as an integral part of a landscape.

Chairman of the Closing Session

Prof. Dr. *O. Steineck*, Director, Institute of Crop Husbandry and Plant Breeding, Agricultural University, Vienna/Austria; member of the Scientific Board of the International Potash Institute

Closing Session

Methodology of Potash Fertilizer Recommendations

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Summary

Fertilizer advice is only of use to the farmer when it gives results. Advice is based on experiments and only long-term work can give reliable information. Short-term investigation can give misleading results. Survey results should be checked by experiment.

Nutrient removals, soil K content and leaf analysis are all valuable. The use of net K removal (K in marketed produce) is less subject to error in establishing the K balance than gross K uptake. Especially when soil K content is high chemical soil analysis must be supported by analysis of other factors and modified in the light of site factors and crop characteristics. The latter are more important than the development of new extraction techniques.

Fertilizer advice aims to achieve maximum economic return which is obtained when marginal cost of K application and marginal yield increase are in balance. This involves consideration of the whole response curve and of the ratio between produce price and fertilizer cost. The return from K fertilizer is to be found not only in crop yield but also in the build-up of soil fertility.

Potash fertilizer can be applied: to meet the needs of individual crops or for the rotation as a whole. On high K soils it may be preferable to apply K only to the K demanding crops. For deep-rooted long-term crops it is advisable to use a heavy dressing before establishment.

Introduction

Like other fertilizers, potash usage must satisfy several requirements simultaneously. It should increase crop yield, improve crop quality, give the farmer a better income, maintain, or better improve, soil fertility and should not pollute the environment. Fertilizer advice to the farmer aims to satisfy these conditions. This discussion is based on work by the *Austrian Fertilizer Advisory Service (OeDB) [18]*.

A practical and reliable method of obtaining information on crop potash requirements is the field experiment. This gives reliable information for a particular site but results can be extrapolated to other conditions only to a very limited extent. Since it is impossible to carry out an experiment on every field, there must be recourse to other methods – K uptake by the crop, soil and plant analysis – if sound advice is to be given over a wide field.

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Potassium uptake

Uptake is the product of two variables: yield and K concentration in the plant. Both are variable, hence data for K removal show great variation. K concentration in the plant is by no means constant; it may decrease as yield increases while, if the K supply is above the optimum, there may be luxury consumption. Further, supply of other nutrients, especially nitrogen, greatly affects K uptake. The plant can only make efficient use of nitrogen when K supply is sufficient */8, 26, 27/;* the potassium nitrogen interaction is most important.

Approximate values for K uptake can be obtained from tables which give K uptakes for the various crops in relation to yield. Tables giving both K removal in harvested produce (grain, tubers, roots) and in crop residues (straw, leaves) are especially useful */21, 22/.* For the purpose of striking a potash balance we may use either «gross uptake» (K in whole crop) or «net removal» (K in marketed produce). Naturally, much information on removals has been accumulated */15, 19, 24/.*

Because the K content of the straw at the fully ripe stage is only a half of that at the time of maximum crop development */3/,* K removals at harvest do not correctly indicate the total K requirement of the crop.

Because of the great variation in K uptake, it is usual to present data simply for low, medium, high and very high yield levels though this has no strict statistical basis.

Soil K content

The plant obtains its potassium needs from both soil and fertilizer. Soil K content is thus important. Methods of soil analysis used up to now all aim to imitate the plant root and to measure potentially plant available K. The value of soil analysis can only be checked by investigating the connection between soil K value and yield response to K fertilizer. The lower soil K content, the more likely there will be response to K fertilizer. As a result of generous fertilizer treatment in the past, response to K fertilizer is nowadays slight and it has become more difficult to correlate the results of field experiments with soil analysis. Absence of response to K indicates an abundant supply.

The value of soil analysis can be improved by considering also K saturation of the CEC, *i.e.* the ratio of K to other cations, rather than just the absolute value for exchangeable K.

Soil analysis is most valuable in the low range where there is a much closer correlation with K response than is the case at higher levels */4/.* In the higher range it is necessary to consider other factors which affect growth and so adjust values for mg K_2O/ 100 g soil. Such factors are:

- Analytically determined soil factors like clay content, organic matter status, pH, clay mineral composition, content of other nutrients, biological activity,

- Site factors such as soil depth, rooting pattern, soil compaction, water relations and aeration,
- Plant factors like root development or plant-specific K needs.

Analytical results must be considered against the general background if sound fertilizer advice is to be the result. Much more promising than the investigation of new methods for extracting soil K is taking into account of other soil properties. The goal must be integrated soil investigation.

The Dutch */17/* set a lower value for 0.1 *N* HCl soluble K for specific soil types with increasing organic matter content and increasing pH in somewhat the manner indicated below, expressing the result as «K number»: critical K values differ greatly between soil types.

In Switzerland */25/* as in the GDR */12/* critical values change with soil group. In Austria and in Bavaria */1/*, 5 levels from very low to very high differ as between, light, medium and heavy soils (Table 1).

The K recommendations for different crops for categories of soil K are given in Table 2. Soil K content is the most important factor in determining K fertilizer requirement. As time went on it became necessary to introduce further categories, *e.g.* category D (high) and category E (very high). It would appear that at very high soil K levels, K fertilizer could be omitted in the short term without incurring yield loss.

Table 1. Critical K values (CAL or DL) as related to soil texture for arable and grassland soils.

K content	mg K_2O/100 g fine soil Arable incl. vegetables			Permanent grass
	light	medium	heavy	
A very low	<6	<8	<10	<6
B low	6-10	8-14	10-16	6-10
C sufficient	11-25	15-28	17-32	11-25
D high	26-40	29-40	33-45	26-40
E very high	>40	>40	>45	>40

Table 2. K recommendations for various crops at varying soil K levels.

Crop	kg/ha K_2O Soil K category				
	A	B	C	D	E
Cereals	130	110	90	50	–
Grain maize	250	220	180	90	–
Sugar beet	420	360	300	150	–
Potatoes	250	220	180	90	–
Grass (cut)	250	230	210	110	–
Vineyard	100	80	70	40	–

As in the Netherlands, K recommendations differ as between crop groups.

The more favourable the environment the better soil potash is translated into yield. Deep well-structured soils promote rooting and thus favour K uptake. Compacted soils with poor water relations and poor aeration hinder K uptake and crop yield. K recommendations are generally increased in dry areas on account of reduced K availability.

The effect of environmental factors on potash recommendations cannot yet be quantified in this country, but a series of fertilizer trials on over 50 sites should give the required information in the near future. Further, soil mapping should be completed at the same time. For the time being, site factors are brought into account in a somewhat general and rather complex fashion. K recommendations are generally higher for sites of high yield potential.

Site factors affecting yield level are taken into account using the standards in Table 3.

Table 3. Adjustment of recommendations for site potential.

A. Definition of potential yield levels as related to site.

Yield t/ha						Yield class
Cereals	Maize	Sugarbeet	Potatoes	Meadow	Vineyard	
3.0	5	40	20	7	7	Low
4.5	7	50	30	8.5	10	Medium
6.0	9	60	40	10	13	High
7.5	11	70	50	11.5	17	Very high

B. K recommendations for different crops as related to yield class with soil category C.

Yield class	kg/ha K_2O					
	Cereals	Maize	Sugarbeet	Potatoes	Meadow	Vineyard
Low	70	150	270	150	150	50
Medium	90	180	300	180	210	70
High	110	210	330	210	270	90
Very high	130	240	360	240	330	110

Plant factors

In this regard, specific crop needs (root development and potential yield) are taken into account. A particular case is the difference in K requirement between arable and grassland *[11]*. To obtain full yield, K rates must be increased above indicated crop requirement especially on K fixing soils on arable land, while on grassland the required yield level is obtained with normal applications. Similarly the monocotyledons have a lower K requirement than the dicotyledons.

Leaf analysis

Leaf analysis with due attention to position and timing of sampling can be used in place of or as an adjunct to soil analysis *[2,20]*. This is applicable especially for K where there have been good correlations between plant K content and response to K fertilizer. The value of leaf analysis lies in the following order for different crop groups: forest trees > fruit trees > vineyard > grassland > arable. An advantage of leaf analysis is that it shows up the effects of antagonisms on the plant. Used in connection with soil analysis it can be a valuable indicator of fertilizer needs.

With cereals, the connection between K content of the plant and increased growth in response to K fertilizer is marked *[14]* and plant analysis can better reflect the K supply of a site than soil analysis. The critical value is 2 to 2.2% K_2O in dry matter over the period from shooting to full ear emergence *[16]*. On light soils leaf analysis is particularly useful soil analysis is a better indicator on heavier soils *[23]*. Our own experiments *[9]* with N applied at 0, 100 and 200 kg/ha to grassland showed a better correlation of yield with plant K content than with soil analysis (Table 4).

Table 4. Correlation between yield of grass and plant K content or soil K content at differing N levels.

		r	
	N0	N100	N200
Soil K (CAL) 1970-1973	0.42	0.58	0.59
K content of grass 1971	0.18	0.66	0.81
K content of grass 1972	0.81	0.81	0.81

Fertilizer experiments

Experiments with increasing rates of potash should also include variable nitrogen treatments in order to yield full information. We cannot here recapitulate the results of numberless potash fertilizer experiments. We emphasise that these experiments should be of sufficient duration if the information obtained is to be reliable. The use of results from experiments of short duration has led to mistaken fertilizer advice. Farming is a long-term occupation (over generations); the experimental approach should be similarly long term.

Referring to Table 5, on the basis of the first year's results alone K, would have been recommended only at 200 kg/ha N. On the basis of the first two years, K also increased yield at the lower rates of N but K manuring would hardly have been profitable at NO. It was only in the longer term that the true value of K fertilizer became apparent. Shortterm potash experiments can give misleading information *[13]*.

When the soil K content is already high, it is quite usual for there to be little or no effect of K fertilizer in the early years. In such cases, the investigator has to exercise some patience in awaiting the effects of run-down in soil K. One of the few published results of long-term investigation was given at the *11th IPI Congress in Bern [6]* and is shown in Figure 1. In this experiment with vines, the effect of K fertilizer became apparent only from the 6th year.

Table 5. Yield increase (K_{150}-K_0) in kg dry matter per kg K_2O at increasing N levels on grassland–Giesshübl

Period	N0	N100	N200
1st Year	−2.9	−1.2	+3.4
Year 1- 2	+5.3	+1.5	+9.3
Year 1- 5	+10.3	+7.2	+17.1
Year 1-10	+11.4	+11.8	+24.9
Year 1-15	+12.0	+12.7	+27.9

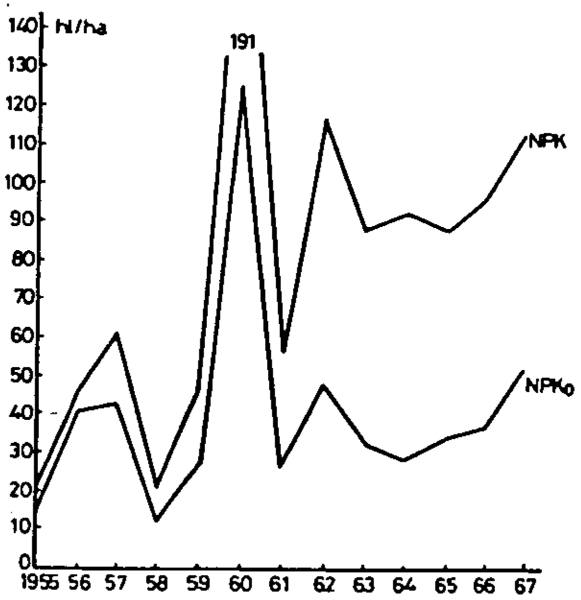

Fig. 1. Effect of potassium on vines at Targon [6].

Surveys

These are practical, but cannot give sufficiently full information. They can only give indications, and apparent findings need to be confirmed in proper experiments.

Crop price / potash price ratios

The K response curve relating yield to rate of K is only half the story. The farmer is more concerned about the economic return and for this the ratio between value of crop increase and cost of fertilizer needed to produce that increase must be taken into account. The ratio unit price of wheat to unit price of potash in Austria has changed as follows:

1960	0.73
1970	0.90
1980	1.39
1985	1.47

In terms of wheat grain, the cost of potash to the farmer is twice as much as it was in 1960. Such facts must be taken into account in giving fertilizer advise.

Economic targets

Early advisory effort emphasised the effect on yield without due regard to the cost of treatment. In the simplest terms, the highest return per unit of fertilizer is obtained in the lower range of yield and at modest rate of fertilizer, but the aim of fertilization is to achieve maximum profit which is attained at the point on the response curve where marginal fertilizer cost is balanced by the marginal value of yield increase */9/*. If marginal cost exceeds marginal return there is a loss unless credit is given for effects on soil fertility (residual effects on following crops). This apart, the identification of maximum profitability should be a simple matter */10/*. In practice, however, this is not so simple because crop yield and fertilizer response are subject to considerable uncertainty showing variation with soil conditions, weather, crop and crop variety.

The response curves illustrated in Figure 2 show that as fertilizer rate increases (×) response (y) decreases. The optimum fertilizer rate depends upon the price/cost ratio. If this is 0.75 we need a yield increase of 112.5 kg grain to cover the cost of 150 kg K_2O; if it is 1.5, we need 225 kg grain. In this theoretical example, the economically optimum K rate decreases from about 135 to 110 kg/ha K_2O.

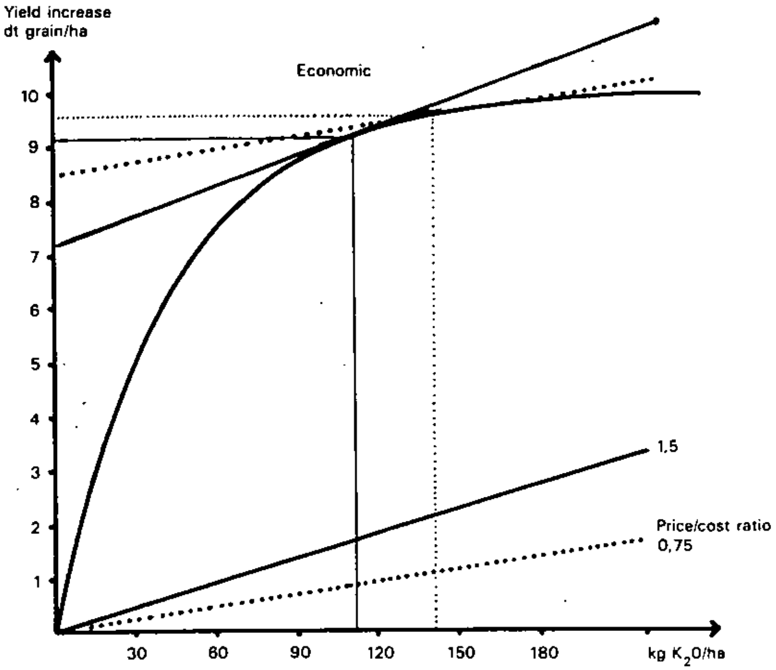

Fig. 2. Relation between optimum K fertilizer rate and price/cost ratio.

Potash balance

Striking a balance between potash application and potash removal is helpful. When soil potash is abundant, maintenance of the K balance may be the only guide. It is usually desirable to confirm or complete the indications from the balance by soil analysis. Either gross or net balance can be used.

Gross	*Net*
Total K removal	Removal in grain, tubers, roots
+ Leaching	+ Leaching
— K from weathering	— K from weathering
— K in residues	
= Total fall in K	= Total fall in K

Using the net balance involves less work and is less subject to error as the return in crop residues, estimation of which is subject to error, does not have to be included. Even the net balance is subject to error because leaching at about 10-30 kg/ha/yr and mineralisation are not precisely known.

The dressing needed to maintain a desirable level of soil K may be less than K removal on high K soils. In contrast, on low K soils and where there is a tendency to leaching or fixation it will be considerably higher. K recommendations could be based solely on the K balance if soil conditions and their effects on K dynamics could be ignored.

Potash fertilization – investment in soil fertility

Applying K fertilizer at a rate above the economic optimum is not futile because the result is an increase in soil fertility. It is an investment and should be valued as such. Even if the invested K does not bring an immediate increase in yield a return in the future is to be expected.

The increase in potash price between 1960 and 1985 (Table 6) means that expenditure to bring about an increase in soil K stock in 1960 has yielded a return of about 4%. The effect of potash fertilization in Austria on soil K status is indicated by the results of routine soil testing (Table 7).

Since the start of soil testing, the proportion of soil insufficiently supplied with K (A+B) has declined from 70 to 34%.

Table 6. Change in cost of potash fertilizer in Austria.

	Cost of potash S/kg K_2O	Relative
1960	1.85	100
1970	2.17	117
1980	3.61	195
1985	4.83	261

Table 7. Change in soil K status as indicated by routine soil testing.

	No of tests	% in K content class				
		A	B	C	D	E
1953/54-1971/72	1 859 731	32	38	30	–	–
1978/79-1985/86	579 496	8	26	42	17	7

Fertilization system

Recommendations for specific crops are to be found in many books and these are valuable though one is not compelled to follow them to the letter. Alternative policies are to apply to each individual crop its own requirement or to treat the rotation as a whole. In the latter case, the requirements of the individual crops are totalled over the rotation and the average annual requirement is applied each year regardless of crop. This requires that the potassium status should be reasonably uniform over the whole area and that each part of the arable area should carry substantially the same succession of crops. Manuring the rotation offers some economy in cost and labour and it is easier to calculate the return of nutrient in organic manures and crop residues. Rotational manuring can be related to the whole farm or to a part of it.

When soil K status is high or very high, it is permissible to apply the total potash requirement to the potash-demanding crops, relying on residues to supply the needs of the cereals which themeselves receive none. The requirement for cereals is added to the calculated needs of the potash-demanding crops. It remains to mention supplementary fertilisation for deep-rooted and long-term crops where, on establishment, ploughing in to depth more than the average annual requirement of fertilizer should be considered.

Cost of investigation

The costs of experimental and advisory work have to be set against the gain to be expected from good advice. This is decisive in the decision to establish a research and advisory service. As soil fertility increases the return by way of crop increase decreases and then the research and advisory costs loom proportionally greater.

The client

An important point in fertilizer advisory work is of a psychlogical nature. Advice given must be definite. The best advice is useless if the farmer finds it unacceptable. It must be clear and easy to follow. Advice may be affected by the socioeconomic status of the farmer. For hobby farms and rented farms and farms without security of tenure, economic return on the current crop is the prime consideration while for those who can be more assured of the future, the building up of soil K status assumes greater importance.

Aspects other than yield

Though it is difficult to quantify, the effect of potash on crop quality may dictate upward or downward revision of the recommendation. If winter-hardiness and standing power are in question, increased potash dressings may be a corrective.

The advice given must take account of the K content of farm manures and crop residues, and this has the same value as fertilizer K *[5]*.

While fertilizer advice is only a help to the farmer in taking decisions, by Austrian law it must be based on the latest scientific information. The advisory organisation is responsible for the correctness of its advice. This is a considerable responsability.

Making advice effective

Advice is only effective when its recommendations are correctly followed. There must be mutual trust between the farmer and his advisor if results are to be fruitful *[7]*. Computerisation can assist with information and accounting support but this cannot replace scientific knowledge though it can support it. It is noticeable that many farmers are particularly impressed by a computerised service.

Along with other factors, the carrying out of over 3 million soil analyses and the phosphate and potash recommendations resulting therefrom has made Austria over 100% self-sufficient in food. This is impressive economic progress achieved which is however not reflected in the level of farm income. This and notably the large inter-regional differences in soil K status, are sufficient reasons for further improvement in methods of fertilizer advice. There is a demand for further scientific investigation and advice.

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Closing Remarks

The Need for Potassium in Relation to Supplies of Major Plant Nutrients

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Fertilizer usage has contributed much to the increase in crop yield in recent years. However, we have now arrived in the industrialised countries in a situation of agricultural surpluses and some governments are thinking in terms of lower yield and restricted fertilizer consumption. In such a situation, it is more than ever important for the farmer to control fertilizer usage in such a way as to maintain profitability.

Papers presented at the colloquium have discussed matters against the background of this general problem. It is more than ever important to understand the function of potassium in building crop yield and to appreciate the importance of correct quantitative relationships between potassium and the other major and minor nutrient elements. We are concerned with the «harmonic» inter-relationship between the major nutrients. In achieving this aim we need to be able to define the desirable nutrient status of the soil and to take steps to achieve and maintain such a condition.

Experimental techniques are required which will accurately determine the nutrient inter-relationships which are needed to achieve optimum crop yield and quality. In this connection solution culture is a useful technique. An experiment compared nutrient uptake and yield formation using six nutrient solutions the compositions of which are compared in Table 1. These solutions show extreme variation as regards both nutrient ratio and total concentration.

Yields and nutrient uptake by tomatoes were measured in both static (concentration reducing throughout growth) and flowing (nutrient concentration kept constant) solution culture *(Kopetz and Steineck [1962]; Steineck [1962]).* The results are shown in Figure 1 for yield and Figure 2 for nutrient uptake *(Bergauer [1976]).*

Table 1. Composition of different nutrient solutions.

Solution type	Ion concentration (milligram atom/l)					
	N	K	P	Ca	S	Mg
Gericke (1940)	12.0	10.0	2.0	2.0	1.0	1.0
Knop (1860)	8.4	2.5	1.1	3.5	1.2	1.2
Institut (1970)	2.7	2.7	2.7	2.7	2.7	2.7
Shive (1915)	10.4	18.0	18.0	5.2	15.0	15.0
Hoagland (1939)	15.0	6.0	1.0	5.0	1.0	1.0
Lundegård (1932)	3.0	10.4.	7.4	4.6	7.1	7.1

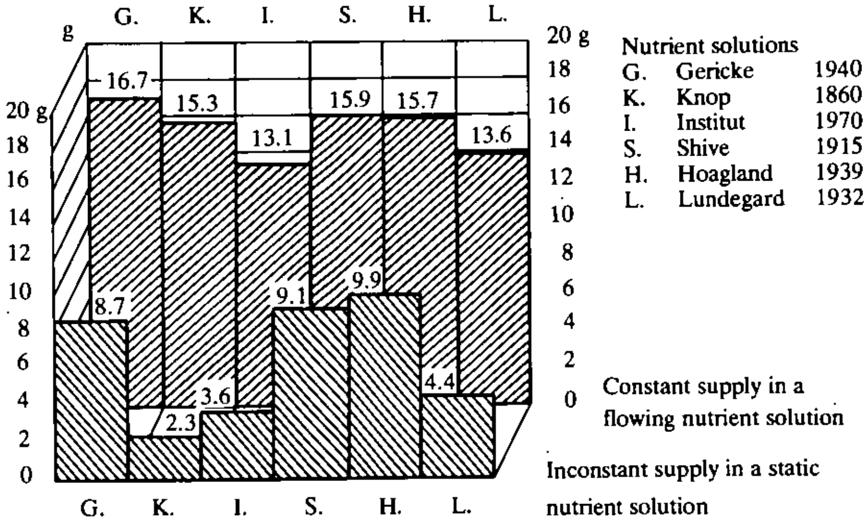

Fig. 1 Dry matter weight per plant in dependance of the nutrient solution with inconstant supply in a static nutrient solution and with constant supply of 6 major elements in a flowing nutrient solution.

In static culture, when the solution concentrations decrease as a result of plant uptake, there are great differences in total dry matter yield between the different solutions. The *Gericke, Shive* and *Hoagland solutions* give good results. It appears that these three are of suitable composition to supply the plant's needs over an extended period whereas the other three are not. In the case of *Shive's* solution this seems more a result of relatively high concentration rather than of ionic balance. The *Gericke* and *Hoagland* solutions produce a high yield with a relatively low total nutrient concentration but the *Knop, «Institut»* and *Lundegård* solutions do not, because they are not of the appropriate nutrient ratio. Indeed there were symptoms of potassium deficiency in plants grown on *Knop's* solution which is too low in K.

In contrast, in flowing solution culture, there is relatively little difference in dry matter yield between the six tested solutions and the nutrient ratio seems to be of minor importance. This indicates that when nutrients are supplied in excess of the plant's requirements over a period, nutrient uptake is an expression of the plant's actual requirements. Excess over the plant requirement remains in the solution. There is an extreme difference in nutrient ratio between *Gericke's* and *Shive's* solutions but the yield is substantially the same under either treatment.

Translating this into conditions as they are in the soil, it would appear that, as abundant supplies of each major nutrient are present, the ratio between nutrient ions is scarcely of significance. It is also clear that when ratios between nitrogen, potassium, phosphorus, calcium, sulphur and magnesium vary greatly, as countless examples of soil analysis show them to do, so long as the amount of each nutrient is above a threshold value indicating sufficiency, yield will be unaffected by fertilizer treatment.

The objective for today and the future for any given set of conditions must be accurately to determine fertilizer needs from both physiological and economic standpoints. In this connection the question arises as to what is the best way to proceed. At the Institute we have used flowing solution culture in which the nutrients are held constant at a 1:1:1:1:1:1 ionic ratio and at 3 strenghts: 0.1, 0.8 and 2.7 mg atom/l. The assumption is that the three major nutrients are present in sufficient quantity and the same availability and that then nutrient uptake is an expression of the plant's selectivity in uptake.

It follows that a first experiment should demonstrate the required inter-nutrient ratio and, having this knowledge we can refine the method in a further experiment in which the nutrients are offered in this ratio. From such an experiment we obtain the results illustrated in Figure 2. Here, the results from the series with the nutrients in equal concentration (dotted line) are compared with those from the series where nutrients are supplied in accordance with indications from the former. In the former series, uptake is in the order N somewhat greater than K and both these elements very much greater than those of the rest with Ca and S appreciably higher than P and Mg. Increasing the solution concentration by a factor of 3 increases the uptake only of N and K.

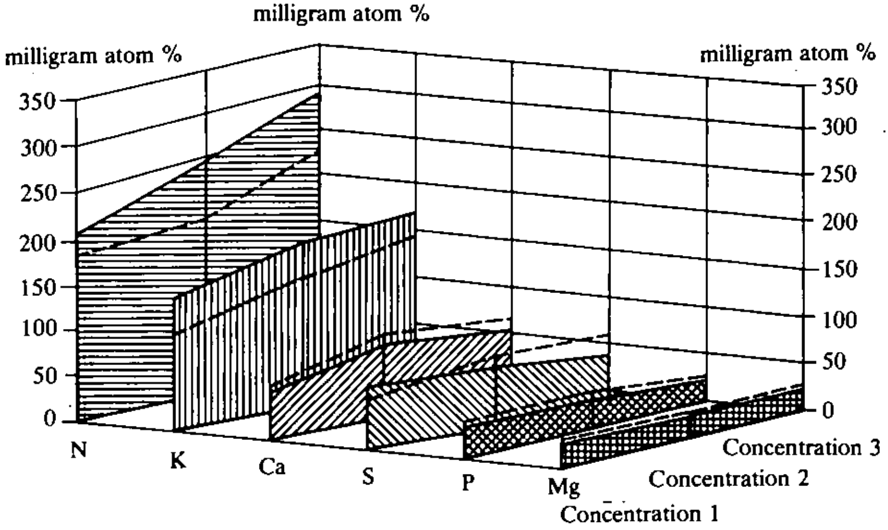

Fig. 2 Nutrient content in dry matter of a tomato leaf in milligram atom %. Dotted line = offer in equal ion concentrations. Straight line = offer in relation to uptake.

In the second series, uptakes of N and K are increased while those of Ca, S, P and Mg are reduced (solid lines). Furthermore, higher yields were obtained in this experiment, indicating the importance of nutrient ratio. Similar experiments were done with other crops such as potato, sugar beet and cereals, and from the results, «harmonic» internutrient ratios can be determined.

Further precision can be obtained by considering nutrient concentrations in individual plant parts and the results for tomato are illustrated in Figure 3. The stem contains much N and K in the ratio 1:1; content of the other elements is small. The fruit has a much higher N content relative to K and content of the other elements is minimal. The root shows a much wider N:K ratio and its content of Ca, S, Mg and P is much higher than in the shoot. Concentrations of all elements except P are highest in the leaf.

As the site of synthesis, the leaf is the most important organ and it is reasonable to assume that leaf analysis would be the best indicator of the desirable nutrient ratio for yield formation. Table 2 translates the findings in terms of milligram atom percent into practical fertilizer terms.

In practical terms, the required nutrient ratio is 1:2.2:0.5 ($N:K_2O:P_2O_5$)

So far as fertilization is concerned we should aim at soil conditions which will ensure a constant supply of nutrients in the desired ratio. This also makes economic sense since the crop will only take up elements in the quantities which it needs for optimum yield.

Table 2. Indicated nutrient ratio for tomato.

Content in leaf dry matter	nitrogen	phosphate	potash
milligram atom %	259	25	167
ratio	1	0.097	0.640
mg element	3626	775	6513
ratio	1	0.21	1.74
mg oxide	3626	1775	7849
ratio	1	0.490	2.164

The aim of this colloquium has been to find research methods which will indicate how to determine the crop's demand for potassium in relation to the other major nutrients on physiological grounds in order to optimise economic return and protection of the environment.

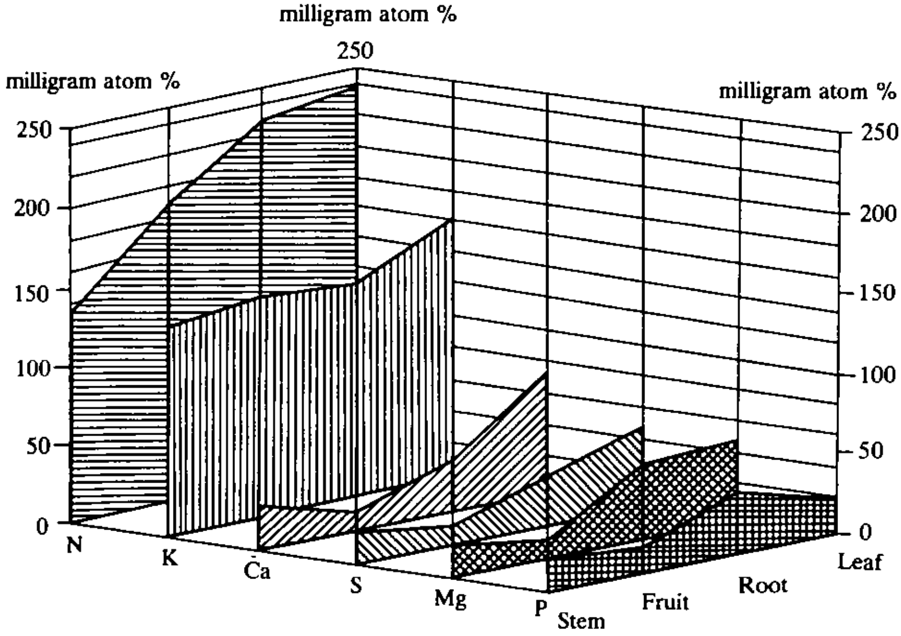

Fig. 3 Content of 6 major nutrients in the dry matter of stem, fruit, root and leaf of tomato in milligram atom %.

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