Potassium in Soil

International Potash Institute 1972

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Proceedings of the 9th Colloquium
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Contents

1st Working Session: **Mineralogy of Soil Potassium**

2nd Working Session: **Ion Exchange System of the Soil**

3rd Working Session: **Ion Transport System in the Soil**

High Patronage: Dr. J. ERTL, Minister of Agriculture of the Federal Republic of Germany

Chairman of the Colloquium: Prof. Dr. D. SCHROEDER, Director of the Institute for Plant Nutrition and Soil Science, Christian-Albrechts-University, Kiel/Federal Republic of Germany; Member of the Scientific Board of the International Potash Institute

Discours d'ouverture

P. CHAUDET, Ancien Président de la Confédération hélvétique, Président de l'Institut International de la Potasse

Herr Ministerialrat,
Herr Dekan der Landwirtschaftlichen Fakultät der Technischen Universität München,
Herr Professor Schröder,
Meine Herren Vertreter der bundesdeutschen und bayerischen landwirtschaftlichen Forschung,
Meine Herren Mitglieder des Wissenschaftlichen Beirates,
Meine Herren Referenten,
Herr Direktor der Fachhochschule Schönbrunn,
Meine Damen und Herren,
Mesdames, Messieurs,
Ladies and Gentlemen,

Es ist mir eine große Ehre, das 9. Wissenschaftliche Kolloquium des Internationalen Kali-Instituts in Landshut eröffnen zu dürfen. Meines Wissens ist es das erste Mal, daß ein offizieller Anlaß des Internationalen Kali-Instituts in der Bundesrepublik Deutschland durchgeführt wird. Um so mehr freue ich mich, daß gerade die traditionsreiche Stadt Landshut im Freistaat und Bundesland Bayern als Durchführungsort gewählt wurde.

Die landwirtschaftliche Forschung Deutschlands nimmt auf internationaler Ebene eine Spitzenposition ein. Wichtige Etappen des Fortschritts in der landwirtschaftlichen Produktion sind durch deutsche Forschungsarbeit geprägt. Es war darum ein Anliegen des Wissenschaftlichen Beirats des I.K.I., daß im Rahmen des gegenwärtig laufenden Arbeitszyklus des Instituts über Grundlagenprobleme des Pflanzennährstoffs Kalium, das wichtige Kapitel des *Kaliums im Boden* in diesem Lande behandelt wird, wo die Bodenkunde seit jeher intensiv gefördert wird.

Ich möchte Herrn Prof. *Schröder*, Kiel, herzlich danken für seine Bereitschaft, den wissenschaftlichen Teil dieses Kolloquiums zu gestalten.

Mein Dank geht ebenfalls an die Herren Professoren *Schuffelen* und *Bach* sowie an die Herren Professor *Mengel* und Direktor *de Tarragon*, die den Vorsitzenden des Kolloquiums in seiner Vorbereitungsarbeit wirkungsvoll unterstützt haben.

Die Gesamtkonzeption des laufenden Arbeitszyklus des Instituts ist vom *Wissenschaftlichen Beirat* erarbeitet worden, dem ich hiefür meine Anerkennung aussprechen möchte.

Ganz besonderen Dank schulden wir Herrn Prof. *Haber*, Dekan der Landwirtschaftlichen Fakultät der Technischen Universität München, den Herren Professoren *Amberger* und *Schwertmann* sowie den Herren Professoren *Schmidt* und *Rumpler*, die es ermöglichten, daß wir das Kolloquium hier in Schönbrunn sowie in Weihenstephan durchführen können, oder welche sich in kompetenter Weise um die Organisation unserer technischen Exkursionen bemühten.

Ihnen allen, meine Damen und Herren, wünsche ich einen erfolgreichen Verlauf des Kolloquiums.

Ich bin Herrn Bundesminister Doktor *Josef Ertl* sehr dankbar, daß er das Patronat über unsere Veranstaltung übernommen hat. Leider hat er sich in Ausübung seiner Pflichten einen kleinen Unfall zugezogen. Er hat mir in einem Schreiben sein Bedauern über seine Abwesenheit ausgedrückt. Wir wünschen Herrn Bundesminister *Ertl* baldige Genesung.

Il n'est pas nécessaire, je pense, de rappeler longuement ici les buts et les travaux de l'Institut International de la Potasse. Sa création a répondu d'une part au besoin qui se manifestait depuis longtemps déjà de pousser à la spécialisation des chercheurs appelés à faire face à la complexité grandissante des problèmes agronomiques. Nous ne sommes plus à l'époque où, dans ce domaine comme dans beaucoup d'autres, la fertilisation des sols peut être recherchée selon des méthodes empiriques. L'augmentation considérable de la consommation mondiale des engrais appelle la mise au point de programmes scientifiquement éprouvés. Mais l'Institut s'est efforcé de répondre encore à une autre préoccupation, à savoir celle de la nécessité économique dans laquelle se trouvent les agriculteurs de tirer le bénéfice maximum de l'application des engrais.

Ces deux axes des activités de l'Institut prennent une importance grandissante dans les pays dits industrialisés, où le problème de la production agricole s'insère dans un contexte extrêmement serré d'intérêts divergents, sinon contradictoires. L'harmonisation de ces intérêts, les points d'intersection à trouver de manière à maintenir une agriculture viable et toujours adaptée au maximum aux possibilités des marchés impliquent la pratique d'une discipline rigoureuse. Et cela autant en matière de recherche fondamentale que d'application dans les conditions économiques et agrologiques si diverses des pays concernés.

En ce qui concerne le Tiers-Monde, nous savons combien les régions en voie de développement trouvent avantage à bénéficier des expériences acquises dans les zones à développement plus avancé. Nous n'avons pas le droit – économiquement et politiquement – d'induire en erreur ou de laisser dans le doute ceux de nos semblables qui attendent de notre part des directives dont ils puissent s'inspirer à coup sûr. Le problème est d'une grande importance, ne serait-ce que considéré sous son angle psychologique, sans négliger pour autant toutes les autres conséquences d'avis qui seraient donnés sans garantie suffisante.

A cet égard, il est heureux que les travaux du Conseil scientifique, les congrès tenus dès 1954 en Suisse, en Italie, en Grande-Bretagne, en Autriche, en Espagne, en Hollande, en Grèce, en Belgique et en France, les colloques d'Irlande, de Suisse, du Portugal, de Yougoslavie, de Finlande, d'Italie, d'Israël et de Suède aient permis l'étude d'un certain nombre de thèmes que nous reprenons périodiquement à un stade plus avancé de la connaissance. La diffusion des résultats de nos travaux par une Revue adressée à plus de 8000 abonnés dans le monde entier, la publication en volumes de plus de 400 conférences et communications scientifiques établissent un lien nécessaire entre Instituts de recherche et hommes de science.

Les missions qui agissent dans le cadre de la coopération technique internationale contribuent aussi à faire de l'Institut un élément propulseur de progrès de même que la collaboration avec d'autres organisations. Je songe surtout à la FAO et au programme alimentaire mondial pour souligner le rôle important que nous avons à jouer à une époque qui appelle impérieusement non seulement l'application, dans tous les domaines, de technologies nouvelles, mais également la coordination générale des efforts.

Curiosité scientifique et mobilité d'esprit constituent les exigences de toute carrière de chercheur. Les liens qui s'établissent entre vous découlent de la nature de problèmes spécifiques sur lesquels ne peuvent influer aucune tendance d'un autre ordre, qu'elles soient nationalistes, idéologiques, anarchiques, c'est-à-dire propres à dévier des lois fondamentales de la nature et de la vie. Je ne me lasse pas de le souligner, à l'heure où le problème majeur qui doit être résolu est celui de l'assujetissement de la technique à l'humain. Partant de cette base de rigueur et d'objectivité scientifique, la recherche trouve sa justification au plan où elle contribue à développer une société orientée vers une conception élevée de sa destinée. C'est un privilège que d'agir sur un terrain solide, sur des données concrètes que ne peuvent fausser les facteurs avec lesquels les hommes doivent par ailleurs compter lorsqu'ils sont engagés dans les actions politiques ou sociales de n'importe quel pays. Leur vraie rencontre ne se fait effectivement que sur des dénominateurs communs, qu'il s'agisse des objectifs à définir, des programmes d'action ou des méthodes de travail.

Dans le désordre des esprits et le rythme des événements contemporains, cette unité de fait a dominé et facilité les travaux de vos colloques et de vos congrès. Elle en explique la réussite. Je souhaite aujourd'hui que nous puisssions clore le colloque de Landshut sur des constats aussi positifs que ceux qui ont caractérisé les conclusions tirées l'an dernier à Uppsala.

C'est dans cet espoir que je vous souhaite, Mesdames et Messieurs, des séances fructueuses, agrémentées au surplus de la qualité de l'accueil dont nous serons cette semaine les bénéficiaires. La Bavière qui nous reçoit fut de tous temps un pays convoité pour sa position stratégique et sa richesse agricole. Son histoire, dont témoignent tant de monuments et d'œuvres d'art, a été marquée de mouvements, d'impulsions souvent déterminantes sur le cours d'événements au plan international. Les structures du pays ont présenté et présentent encore des particularités où le représentant de la Suisse pourrait trouver quelque analogie avec les institutions qui la régissent, notamment dans la constante du courant fédéraliste et de sa confrontation avec l'emprise centralisatrice. Disons pour le moins que passé et présent de la Bavière nous placent dans un climat d'action résolue, dans une ambiance propre à poser les problèmes d'avenir. Nous savons combien ce dernier doit être préparé à la fois par un examen serré des expériences vécues et par une interrogation constante quant aux voies nouvelles où il convient de s'engager.

Je déclare ouvert le Colloque de Landshut.

Introductory Address

Prof. Dr. D. SCHROEDER, Director of the Institute for Plant Nutrition and Soil Science, Christian-Albrechts-Universität Kiel, Federal Republic of Germany; Member of the Scientific Board of the International Potash Institute; Chairman of the Colloquium

Mr. President, Ladies and Gentlemen!

As chairmen of this 9th Colloquium of the International Potash Institute and on behalf of my German colleagues, I bid you a warm welcome here in Landshut-Schönbrunn. We are very glad to have such an IPI-Colloquium for the first time here in Germany.

The general theme of this Colloquium – *Potassium in Soil* – was decided during the last main congress in Antibes in 1970 and the *Scientific Board* of the Institute and the *Preparatory Committee* had only to work out the final programme.

The Board discussed several possible ways of subdividing the general topic so that it could be treated in distinct working sessions, each of which would contribute to the general theme.

One possibility was to divide the subject *Potassium in Soil* according to different types of binding, that is to say: K in the crystal lattice of minerals, K in the organic matter, K in the exchange complex and K in soil solution; all these in relation to the different degrees of K availability.

Another way would have been to subdivide according to the processes of mobilization and immobilization as well as exchange and transport processes, again in relation to problems of availability.

However, we found that this rather theoretical way of handling the static and kinetic aspects of soil potassium did not result in suitable subtitles for the working sessions, so we decided on a more pragmatic approach and subdivided the subject under the three headings:

Potassium in Soil Minerals, Potassium in the Exchange System, and Potassium in the Transport System.

We hope that, in this manner, the broad field of the general theme may be sufficiently covered and that the static and kinetic aspects of potassium in soil are also considered.

With regard to the schedule of the programme we have followed the procedure which proved successful last year in Sweden.

Each working session will be opened with a main lecture, in which a review is given of the present state of knowledge in the special field of the session. We are glad to have found such outstanding scientists as Dr. *Rich*, Prof. *Schuffelen* and Dr. *Tinker* to read these papers.

The main lectures are followed by four to five short communications, in which the results of special investigations, concerning the subject of the working session, are dealt with.

When planning the programme, we assumed that – according to the character of these colloquia – information about *basic knowledge* should predominate and applied aspects should be less emphasized. The applied and practical problems will be emphasized at the main congresses, which are held every four years.

But applied questions will not be entirely neglected during this Colloquium. As you will notice, several papers are presented in the course of the sessions, in which questions of major practical importance are dealt with. In addition, in the closing session Prof. *Mengel* will speak about the implications and conclusions of recent findings concerning potassium in soil in relation to the potassium-nutrition of plants. For half a day we will have an excursion to field experiments, where practical problems of K-fixation are demonstrated. This was – by the way – one reason for chosing Landshut as the place for our Colloquium.

That is briefly, what I wanted to say at the beginning of this Colloquium. My best wishes to all of you for some fine and successful days here in Landshut-Schönbrunn and in Weihenstephan.

1st Working Session:

Mineralogy of Soil Potassium

Chairman of the Session:

Prof. Dr. R. Bach,
Institute of Agricultural Chemistry, Federal Institute of Technology (ETH), Zurich/Switzerland; Member of the Scientific Board of the International Potash Institute

Potassium in Soil Minerals

C.I. Rich, Ph.D., Agronomy Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia /USA

Summary

The crystal structure and morphology of soil minerals affect the release, selection from solution, and fixation of potassium. Recent information from single crystal analyses of the micas and of potassium feldspars, and new studies of the micromorphology and chemistry of individual particles of soil minerals are providing insight into the specific reactions of potassium with minerals in soils. The marked differences in potassium release from micas can be related to the orientation of the OH group and to the configuration of the O atoms surrounding the K atom. Significant differences in release of K from feldspars are attributed to differences in Si-Al ordering and to the morphology, size of unit crystals, twinning, and perthitic structure.

The paradoxes of slow K release from clay-size mica particles, compared to those of silt size, and the release of K on drying of some soils are discussed in terms of crystal structure and micromorphology. 'Wedge shaped' interlayers in weathered micas and in vermiculites and smectites containing mica-like zones appear to be responsible for selection of hydrated cations of different size. Hydroxy-Al interlayers in vermiculites and smectites increase K-selectivity and reduce K-fixation as well as reduce the cation exchange capacity. The interlayer hydroxy-Al also is related to the decrease in the ratio of adsorbed K to Ca with increase in temperature.

1. *Introduction*

The availability of potassium to plants is related in many ways to the structure and morphology of soil minerals. In this paper, the relationship between potassium and crystal structure and morphology will be emphasized. The large amount of potassium in soil minerals, fixation of applied potassium, and varied ion selectivity have led research workers to study the relationships between potassium uptake by plants and soil mineralogy for many years. Most of the available information pertains to weathering sequences, potassium release rates and fixation capacity measurements. Comprehensive reviews on these subjects are available [1, 31, 55]. More information is needed that relates potassium chemistry in soils directly to mineralogical properties of the soils. Although the complexity of soil minerals discourages a direct study, such an approach seems necessary to an adequate understanding of soil mineral-potassium relationships. Recent advances in instrumentation such as the scanning electron microscope, the electron microprobe, and in thermal, infrared, and x-ray diffraction instruments seem promising in studying the soil minerals. We can also utilize the knowledge that has been obtained through the study of single crystals and specimen type minerals. An important use of this information is in developing theories to explain the behavior of minerals in soils. Eventually, of course, these theories will have to be confirmed, modified, or rejected by studies directly with soil minerals. The present difficulty of a direct approach is partly related to the general presence in soils of several minerals that affect potassium chemistry. Furthermore, each of these minerals varies in particle size, in individual properties and in degree of weathering. Another difficulty in relating single crystal studies to soil minerals is that the latter are usually different from specimen minerals because of differences in formation and because of weathering and alteration, such as the addition of oxides on external as well as internal surfaces. These difficulties also give reason for continued research on the development of chemical methods with whole soil material that estimate long and short term potassium release, selectivity and fixation. Studies of specimen and soil minerals can, however, contribute to the development and interpretation of these chemical methods. In seeking the full understanding of soil potassium-mineral relationships, it will be necessary to consider the field soil at least to the depth of rooting in the case of soil fertility relationships and often deeper in the case of soil genesis studies.

The following discussion will be concerned with the two major groups of K-bearing minerals in soils, the micas and the K-feldspars. In addition, illites, weathered micas, vermiculites and smectites that may contain exchangeable K and non-exchangeable K, perhaps in mica like zones, will be considered. Other K-bearing minerals are present in soils but because of lack of information and limited occurrence, they will not be discussed. Studies of weathering rate [*27, 31*] and availability to crops [*55, 58*] suggest that the micas are more important than K-feldspars in supplying K to plants. But because of the abundance of K-feldspars in the earth's crust and the evidence that the weathering rate of feldspars and micas varies markedly, the importance of feldspars is probably frequently greater than is often indicated. Weathered micas exert a marked influence on ion selectivity and fixation, whereas the cation exchange reactions of weathered feldspars is quite limited [*46*].

2. *Potassium in micas*

2.1 *General structure of micas*

The micas are 2:1 layer-structured silicates that are composed of a sheet of octahedra between two sheets of tetrahedra. Each tetrahedron is composed of a Si or an Al atom coordinated with four O atoms. The two sheets of tetrahedra are arranged so that the apical oxygens of the tetrahedra of each sheet point toward the center of the layer and are shared with the central octahedral sheet. Two hydroxy groups and four apical oxygens coordinate about each octahedral cation position. In some case F substitutes for OH. In trioctahedral micas, all three octahedral positions are filled, whereas in dioctahedral micas only two out of three octahedral cation postions are filled. The K resides between the silicate layers, that is, in the interlayer positions. The bonding in the silicate layer apparently is largely covalent [*9, 19*] but is partly ionic.

2.2 *Effect of structure on potassium release*

2.2.1 Potassium – oxygen coordination

Assuming some degree of ionic bonding, it is concluded that interlayer cations of 2:1 layer silicates are held in place largely by the negative charge of the silicate layer itself. This

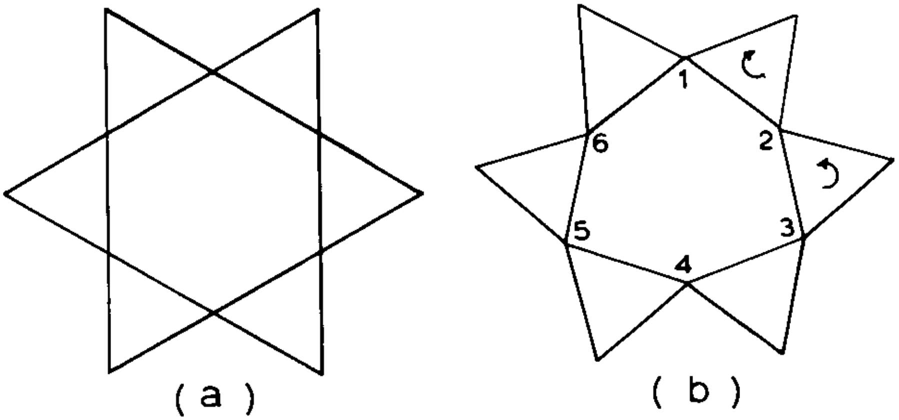

Figure 1. Ideal hexagonal arrangement (a) of tetrahedra in layer silicates and actual (b) ditrigonal arrangement. The degree of tetrahedral rotation varies and generally is greater for dioctahedral than for trioctahedral layer silicates. (After Rich, 'Mineralogy of soil potassium' in 'The Role of Potassium in Agriculture, American Society of Agronomy' [*58*]).

negative charge arises from lack of sufficient positive charge from cations in the tetrahedral or octahedral layers to balance the negative charge of the anions O^{2-}, OH^-, and F^-. The electrostatic deficiency of charge in the surficial oxygens of micas is caused by the proxying of a trivalent Al^{3+} and sometimes Fe^{3+} for quadrivalent Si^{4+}. In the ideal hexagonal arrangement of basal oxygens, the potassium would be in 12 coordination with six oxygens above and six oxygens below. The K-O distance for such an arrangement would be 3.04A. The effective ionic radius a cation in such an configuration would be 1.68A, which is very much larger than the effective radius (1.38A) of K^+ (*Güven* [*26*]). Single crystal analyses of muscovite [*26*, *50*] and other micas show that the interlayer potassium is close to six basal oxygens, three above and three below. The other six oxygens are at a greater distance from the potassium. This arrangement is caused by the ditrigonal configuration of the basal oxygens in each mica layer (Figure 1). The two unrestrained tetrahedral sheets are too large for the unrestrained octahedral sheet in micas and in order that meshing of the three sheets can take place, the two tetrahedral sheets shrink by rotation of the tetrahedra to give a ditrigonal structure [*67*] and the octahedral layer is also stretched. The coordination number of oxygen about K caused by the ditrigonal arrangement is, thus, reduced from 12 to 6 and the K-O bond is shortened and strengthened. The amount of tetrahedral rotation is controlled largely by the population of octahedral cations. A large rotation is found in a dioctahedral structure with two Al atoms and one vacancy in a group of three octahedral cation positions. For example, in muscovite the rotation from an ideal hexagonal position is 13.7°, whereas the rotation is several degrees less in trioctahedral micas such as biotites (*Radoslovich* and *Norrish* [*51*]). Increases in tetrahedral rotation cause shorter K-O bond lengths and a more pronounced six coordination. Thus, the bonding of K is stronger in dioctahedral micas than in trioctahedral varieties of this mineral group.

The mutual repulsion of cations in the octahedral layer causes shortening of octahedral anion edges between cations. This causes the differential motion of apical oxygens of the tetrahedra and makes the tetrahedra tilt such that the surface oxygens are no longer in the same plane.

Tilting of tetrahedra along rows produces corrugations, which may or may not mesh from one layer to the next depending on the stacking sequence of 10A layers. The diffusion path and diffusion rate of interlayer cations may then be influenced by the relations of corrugations in one layer to the next. In trioctahedral mica, there is less tilting of tetrahedra, and corrugations are not nearly as pronounced.

2.2.2 Site of negative charge

One would expect that because of the short distance from the site of the charge deficiency to the K ion the deficiency of negative charge caused by Al^{3+} for Si^{4+} substitution in the tetrahedral layer would be more effective in holding the interlayer cation than would a similar imbalance of charge produced in the octahedral layer. Studies of K fixation by smectites, however, showed that there was no apparent relationship between location of negative charge and K fixation. Increase in negative charge was related to increase in fixation *(Weir* [*74*]*)*. The charge relationship in micas is confounded with other structural changes so it is difficult to determine the effect of charge location.

2.2.3 Orientation of OH groups

Infrared studies of clay minerals show that the dipole moment of the OH vibration is perpendicular to the basal planes in trioctahedral minerals in which the octahedral population is identical (e.g. 3 Mg). In dioctahedral minerals, the dipole moment at an angle that approaches the plane of the silicate sheets. *Bassett* [*7*] proposed that the stability of potassium in the micas is related to the orientation of the OH bond. When the OH is perpendicular to the sheet plane as in phlogopite (octahedral population is 3 Mg), the potassium is repelled by the OH. In muscovite, the OH is not directed toward the K and, thus, K stability is greater.

Infrared studies [*21, 69, 70, 76*] show that various populations of octahedral cations give different OH-stretching frequencies and directions. Within one particle, apparently different octahedral populations (including some vacancies) occur. Thus, one could expect degrees of OH-K repulsion within one particle.

The octahedral population can also be affected during weathering. Oxidation of iron can lead to its ejection from the octahedral position [*22*]. Conversion of trioctahedral to a dioctahedral variety of vermiculite can be done in the laboratory and apparently takes place in nature. Thus, oxidation of iron in weathering micas may reduce the rate of potassium release. If Fe^{2+} is oxidized in place, for instance in an octahedral grouping such as Fe^{2+}, Mg, Mg the OH direction is made more favorable for K retention because of the asymmetry of the positive charges [*3, 33*] (Figure 2). Oxidation of Fe^{2+} can occur without decrease in the negative charge of the mineral [*2*].

2.2.4 Change in silicate layer dimensions

The major control of the tetrahedral rotation in 2:1 layer silicates is by the octahedral sheet. Its dimension is increased as larger divalent cations replace the small trivalent Al^{3+} in this sheet. However, the interlayer cation has some control of tetrahedral rotation and,

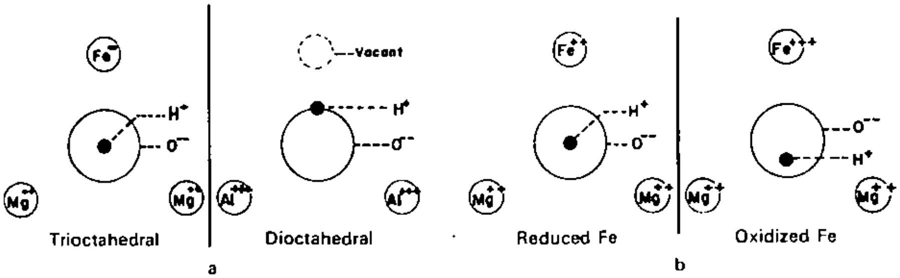

Figure 2. Effect of composition of octahedral layer of micas on OH dipole moment; (a) dioctahedral *vs.* trioctahedral (b) effect of oxidation of Fe^{2+} to Fe^{3+}.

thus, the *a* and *b* dimensions. *McCauley* and *Newnham* [*43*] concluded that the interlayer cation exerted 10% of the control of the tetrahedral rotation. *Leonard* and *Weed* [*37*] and *Burns* and *White* [*12*] found that the *b* dimension of micas changed when the K was replaced with other interlayer cations. *Leonard* and *Weed* [*37*] found that hydrated divalent cations increased the *b* dimension of muscovite, whereas when these cations were dehydrated, the *b* dimension decreased relative to that of the original muscovite. The wrinkles produced in the expanded portion of trioctahedral micas in which K is replaced by hydrated cations [*53*] suggests that stretching of the mica sheets occurs parallel to the basal planes.

2.2.5 Changes in negative charge

Cations in addition to Fe in octahedral positions can be ejected from the structure during weathering processes. The apparent loss in cation exchange capacity may result from protonation of the OH groups [*30, 48*] and subsequent reactions with Al. This reaction may accompany the loss of octahedral cations according to the equation proposed by *Jackson* [*30*]:

$$\text{Layer-OH Al}_{0.33} + H^+ \rightarrow \text{Layer OH}_2 + 0.33\ Al^{3+}.$$

Similar reactions with octahedral Mg and Fe probably take place. Hydrolysis and organization of the interlayer Al^{3+} may produce titrateable but non-exchangeable Al, which can account for the apparent loss in negative charge as measured by CEC determinations.

2.2.6 Chemical Composition

From the discussion on effect of crystal structure and K release it is apparent that the chemical composition profoundly affects K release. The principal control of ditrigonal twist and tilting and the direction of the OH bond is chemical since these factors are related primarily to the composition of the octahedral layer. Trioctahedral micas lose their potassium at a faster rate than dioctahedral micas. This fact has in the past been attributed to oxidation of Fe^{2+} to Fe^{3+}, but phlogopite with very little iron present also loses its K easily.

The replacement of hydroxyl by fluoride would be expected to increase the retention of K by mica since the repulsion of K by the proton of a directed OH group would not occur. This greater K retention by micas containing F has been confirmed experimentally by *Rausell-Colom et al.* [*53*], *Mackintosh* [*42*] and by *Leonard* and *Weed* [*38*].

2.3.1 Effect of particle size

Chute and *Quirk* [*15*] studied the rate of diffusion of K from illite of clay ($<2\mu$) size. The rate of K diffusion from two illites was found to be about 10 orders of magnitude slower than that reported for biotite and phlogopite by *Rausell-Colom et al.* [*53*]. *Chute* and *Quirk* found that over the relatively short times of their experiment that loss of K followed a theoretical diffusion equation. Experiments by other workers show that as K depletion of small particles is approached, the loss of K by illite and other clay-size mica does not follow short term diffusion equations.

If K release from mica were a simple diffusion-controlled process, one would expect that at a particular percentage of K depletion the rate of K release would decrease with particle size. For initial losses of K and for larger particle sizes such as a relationship often holds [*15, 60*] but at later stages of K depletion and for clay size micas this relationship does not hold. The particles of small diameter generally release K at a slower rate than coarser particles. *Reichenbach* and *Rich* [*54*] showed that K could be removed more easily by Ba exchange from the 20–5μ fraction of a muscovite than ranges of finer particles down to 0.08μ. *Scott* [*60*] also found that only 65% of the total K could be removed by sodium tetraphenol boron from a $< 0.2\mu$ fraction of muscovite. *Mortland* and *Lawton* [*44*] also observed higher rates of K-release by NaCl solutions from large biotite particles than from finer particles.

The very slow release of K from clay-size particles of partially K-depleted micas has much importance as regards soil fertility as well as soil genesis relationships since much of the mica in soils is of clay size. The factors regarding K release that may be influenced by particle size are frequency of discontinuities and the degree of bending of the silicate layers.* If large-grained micas are reduced in size by grinding, one would expect that splitting would first occur along planes of discontinuity. Thus, the proportion of these weak planes may be reduced as particle size is reduced.

The silicate layer must bend in order to accommodate the larger hydrated cations that replace K at the edges of the mica layers. Initially, unhydrated exchanging cations may enter the interlayer and then hydrate [*15, 75*]. If in one particle all interlayers begin to lose K at the edges, then the bending is accumulative and the *thicker* the particle the more the bending. Bending would tend to stretch the oxygen sheet on one side of a layer and compress it on the other and effectively loosen the K-O bonds [*54*]. On the other hand, bending tends to assist in splitting of the particles. In small particles, the distance necessary to split a particle all the way through from one side to the other is less than in large particles so the opening of an interlayer in small particles, once initiated, may then continue to completion. If this occurs, the bending is less and K is retained more strongly. *Bassett* [*6*] proposed that if K is removed from one interlayer, the bonding about K in the adjacent interlayers is strengthened. The occurrence of 1 to 1 regular mica-vermiculite interstratification can be explained on this basis. Although regular interstratification is

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* See section of 'Effect of Crystal Imperfections', below.

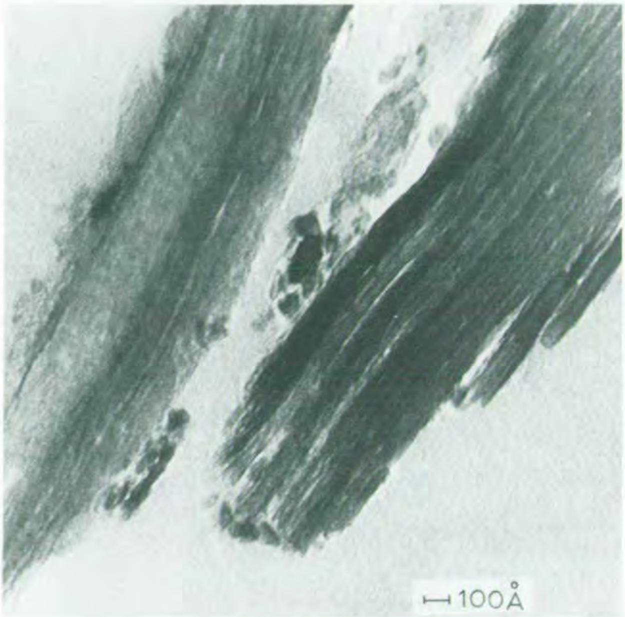

Figure 3. 'Packets' of layers in a weathered mica-vermiculite clay particle from a Nason soil (Virginia) as seen in a transmission electron micrograph of an ultramicrotome section. (Prepared by *J.L. Brown*, Georgia Institute of Technology, Atlanta, Ga.)

often associated with the coarser fractions, its occurrence in the finer fractions apparently is more common than once realized [*56*]. Nevertheless, a 10A component remained in a $<0.08\,\mu$ fraction of muscovite after removal of K had essentially stopped [*54*].

2.3.2 Effect of crystal imperfections

Direct observation of the microstructure of naturally weathered micas by transmission electron microscopy of micas by *Brown* and *Rich* [*10*] revealed that micas are frequently composed of books of 10A basic units. The existence of these books has been by substantiated by scanning electron microscopy by *Reichenbach** and in the author's laboratory. In Figure 3 is seen a transmission electron micrograph of an ultramicrotome cross section of a weathered mica vermiculite clay particle from the Nason soil in Virginia. Packets are evident in this clay size particle.

Artificially altered micas are often separated into packets and *Chute* and *Quirk* [*15*] suggest that a mica crystal can accommodate only a limited number of expanded layers before the strain produced splits the flake all the way through.

These packets may represent, in some cases, units of spiral growth. The observed growth step height in micas has been reported by *Sunagawa* [*66*] as varying from a single 10A unit thickness to many hundred unit cells *(Kretz* [*36*]*)*. Ultramicrotome-electron micro-

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* Personal communication from Prof. *H.G. von Reichenbach.*

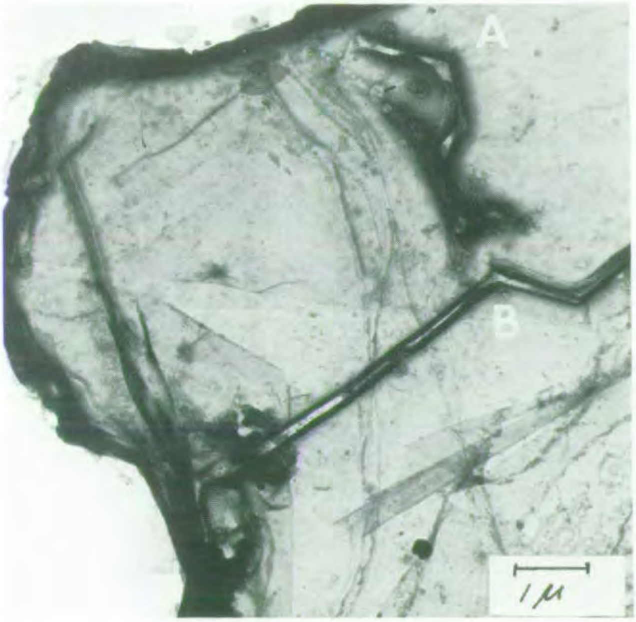

Figure 4. Electron micrograph of a C-Pt replica of a weathered muscovite flake showing scrolling at weathering boundaries of crystals of different orientation (A and B) within one particle. Prepared by *J. le Roux* [*40*].

scope work of *Brown* and *Rich* [*10*] indicated 50 to 15 10A layers. It would be expected that the fewer the number of unit layers in a step the lower the hydration energy necessary for the initiation of expansion of a single interlayer space.

The occurrence of packets is so common that other sources of discontinuity are suspected. *Caslavsky* and *Vedam* [*13, 14*] reported that muscovite frequently has discontinuities along the basal plane. Regardless of their cause, these packets probably cause planes of discontinuity, which are weaker than the normal planes separating the 10A units of mica. Such planes apparently open early in weathering and, in the interlayer space produced, the distance between layers is greater than 4 to 5A expected in vermiculite. Warping of the layers by expansion, when K is replaced in the outer fringes of the normal packets, possibly causes the spreading of the interlayer space between layers.

If it is assumed that bending of mica layers promotes K exchange, these planes of discontinuity may initially increase the weathering rate, but once opened all the way through a particle, the strain due to bending is released and further exchange of K is inhibited.

Raman and *Jackson* [*52*] reported that portions of the basal surfaces of micas show openings into the structure from which the layer roll back and form scrolls. Such entries into the interlayer space should increase the exchange of interlayer ions. Evidence was presented by Raman and Jackson of scrolling of these layers with hydrated cations and flattening of the layers when K ions were returned.

Le Roux and *Rich* [*40*] observed that scrolls apparently formed at borders of crystals of different crystallographic orientation and present in the same particle (Figure 4).

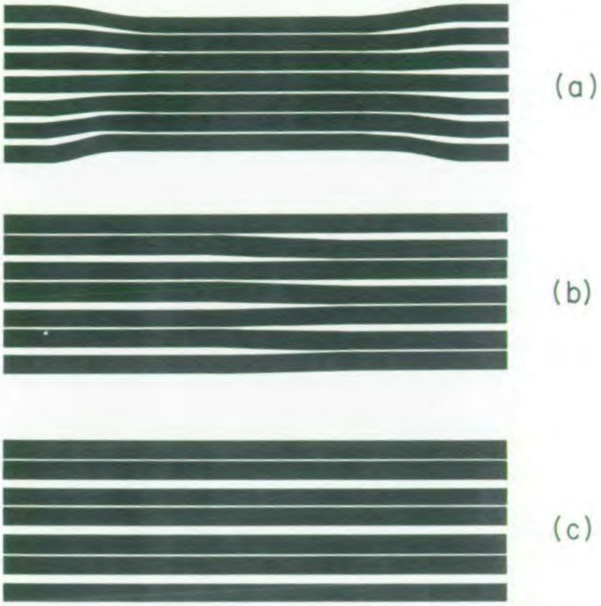

Figure 5. Diagram of a weathered mica particle containing about 50% expanded (vermiculite) layers: (a) 'frayed edge' and mica core, (b) alternate layers opened half way through interlayer, (c) regularly interstratified mica-vermiculite (no 'wedge zones').

3. *Potassium in illites mica-vermiculites and smectites*

3.1 *Effect of structural properties of illites, weathered micas, and smectites containing mica like zones*

Illite: 'The name *illite* was proposed by *Grim, Bray* and *Bradley* in 1937 for the mica-type mineral occurring in argillaceous sediments. It was specifically stated that the term is not proposed as a specific mineral name but as a general term for the clay mineral constituent of argillaceous sediments belonging to the mica group' [*25*]. Illites contain less potassium than well crystallized micas [*73*] and some of them are mixed layer minerals whereas some are not [*25*]. Since many soils are developed from material weathered from sedimentary rocks, illite is a common constituent of soils. Based on C.E.C. and surface measurements, illites inherited by soils probably have some internal surface on expanded or partially expanded interlayers.

The configuration of interlayers in illite as well as weathered micas from igneous rocks is important to ion selectivity. In Figure 5 is a diagram of three 'mica-vermiculite' particles each with about 50% expansible layers. In model (d), the interlayer spaces are either expanded or non-expanded uniformly through each interlayer. In models (a) and (b) the expanded interlayers are not continuous but have internal terminations forming 'wedge zones' [*29, 60*]. *Rich* and *Black* [*60*] and *Rich* [*57*] proposed that such zones are responsible for screening hydrated cations of different size and, thus, selecting the effectively small K, NH_4, and other monovalent cations of similar size, and excluding large hydrated multivalent ions. According to this theory, as more interlayers are partly

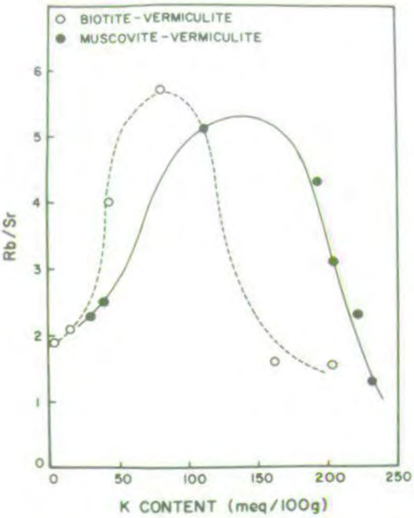

Figure 6. Rb/Sr selectivity of 20–5 μ muscovite and biotite particles depleted of K to varying degrees (after *le Roux* and *Rich*, Soil Sci. Soc. Amer. Proc. *33*, p. 686 [39]).

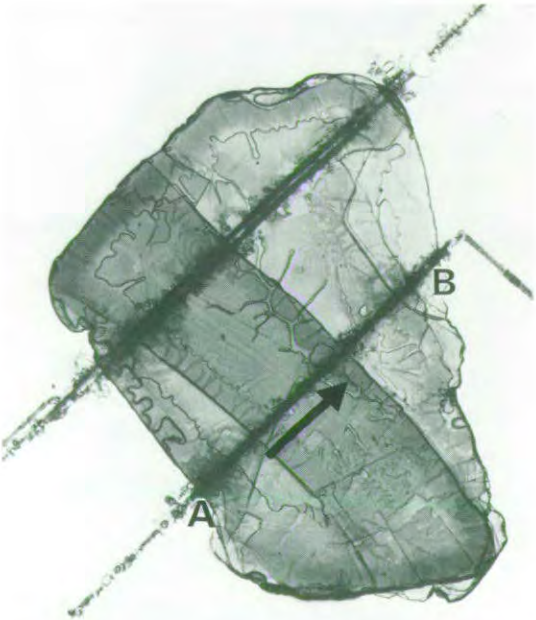

Figure 7. Photomicrograph of a biotite particle after partial K depletion, treatment with a mixed Rb/Sr solution, and scanned with an electron microprobe. Scale = 100 microns (After *le Roux et al.*, Clays and Clay Minerals, *18*, Figure 4 after p. 334 [40].

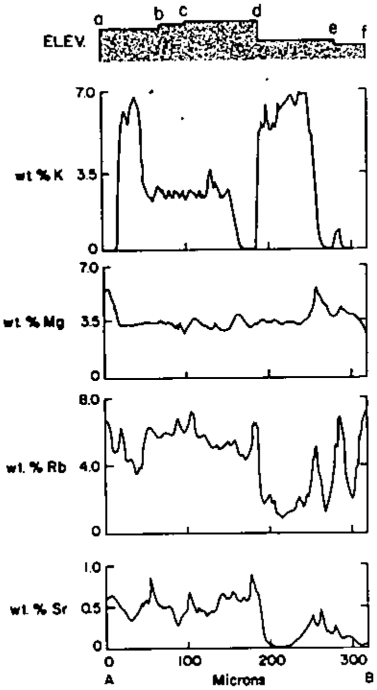

Figure 8. Elemental analysis of biotite flake in Figure 7 along lower path of probe. Upper profile is a traverse of the topography along the electron probe trace. (After *le Roux et al.* Clays and Clay Minerals, *18* p. 335 [40]).

opened, 'wedge' zones increase and then decrease as the interlayers are opened all the way through the particle. Experimental evidence for this is given in Figure 6. Biotite and muscovite particles were depleted of K to varying degrees and then a mixed Rb/Sr solution was added and the relative selectivity of the two ions was measured.

This mechanism of cation selection at wedge zones assumes that the interlayer space of the expanded portion remains open. Should the interlayer space collapse at the particle edges, then the mechanism is limited [*40, 72*]. Charge density, concentration and type of cations in solution, and the presence or absence of hydroxy-Al interlayers affect collapse and, thus, K selectivity and fixation [*45, 58, 59*]. A high charge density, a high concentration of large monovalent ions (e.g. K, NH_4, Rb), and the absence of hydroxy-Al interlayers promote collapse.

Hydroxy-Al interlayer material apparently also has a chemical effect on K/Ca selectivity. *Zelazny* and *Rich* [*77*] found that the K/Ca ratio for adsorbed ions increased as temperature increased in systems containing hydroxy-Al in expansible layer silicates and in a synthetic high-charge cation exchange resins. In the absence of hydroxy-Al but in the presence of a wide range of cations, temperature had little effect on the K/Ca ratio.

Direct evidence for selectivity of Rb at edges and wedge zones of sand size weathered biotite has been obtained with the electron microprobe (Figure 7 and Figure 8). Evidence for retention of Cs at particle edges of clay-size soil vermiculite has been obtained with transmission electron microscopy [*24*].

The K/Ca selectivity of smectites found in many soils exceeds that of specimen type minerals of this group [*60, 63*]. The soil smectites often contain more K than the 'specimen' analogues [*63*] and since no discrete mica is often not indicated in the clay fraction, this K may be in mica-like 'x-ray amorphous' zones in the smectite. *Reynolds* and *Hower* [*56*] point out that a random mixing of mica layers in smectite diminishes the intensity of the glycol-expanded 17A peak of smectite but does not shift its position toward 10A.

Interstratified montmorillonite-micas in soils in the Canadian Prairie Provinces have been studied in detail by *Brydon* and *Kodoma* [*11*]. These clays are generally randomly interstratified but also showed a tendency for zonal segregation of the mica and montmorillonite layers. The authors suggest that the composition of the 2:1 layers varies and is related to the formation of this interstratified system. The composition of the expansible layers indicated that those associated with K-fixation during deposition were more beidellitic (Al for Si substitution in the tetrahedral layer) than the layers which remained expanded. One would expect that the location of positive charge deficiencies in layer silicates would affect retention of interlayer cations. *Weir* [*74*] studied the relationship between K fixation and location of change. A good positive relationship was found between total charge and fixation, but no relationship to charge location was evident.

Brydon and *Kodama* [*11*] and *Kodama et al.* [*35*] proposed that the composition and structure of the mica component layers could vary in different interstratified minerals of similar total chemical composition. The Si/Al ratio within the same mixed layer system can vary. Thus, the average location of charge may not adequately describe a layer silicate in order to relate it to K exchange. Since Si-Al ordering in the tetrahedral layer does not exist [*26*], variation in negative charge about the ditrigonal holes would be expected.

The selectivity and fixation of K in expansible layer silicates depend in a complex manner on the amount of negative charge, the distribution of this charge, the number of wedge zones, the extent of interlayering with hydroxy groups, and the particle size. External cation exchange surfaces would be expected to have low selectivity for K ions, however, allophane-like material with restrictive pore size may have a high selectivity for K.

3.2 *Effect of wetting and drying on K release and fixation*

Drying of a soil may either decrease or increase the amount of K extracted by ammonium acetate. Whether some soils release or fix potassium also depends on the K level [*16*]. Fixation of K on drying of expansible layer silicates is easily rationalized in terms of the reversibility of the release of K by weathering, but the release of K on drying is difficult to explain. That the phenomenon is related to the clay fraction was demonstrated by *Scott* and *Hanway* [*65*]. No discrete mica phase may be apparent by x-ray diffraction analysis but the K may be in small discontinuous mica-like segments. *Bates* and *Scott* [*8*] showed that a soil, which released large amounts of K during drying was inhibited from doing so by alcohols having high boiling temperature and by sucrose. The release mechanism was also partially reversible.

Virginia soils, which contain appreciable K in the mica-vermiculites and also contain hydroxy-Al groups in interlayer position do not release K, on drying.* This fact together

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* Unpublished study of the author.

with the information on the inhibition of K release by non-volatile liquids suggests that K-release is related to collapse of the expansible layer silicate. The hydroxy-Al interlayers and interlayer liquids inhibit collapse. In addition to change in the interlayer space, the rotation of the tetrahedral may change when the soil is dried causing changes in the K-O bond. Dehydration of interlayer cations may permit a redistribution of interlayer cations because Ca could now compete with K for 'wedge' sites. On rehydration there may be a partial return to the original distribution of interlayer cations.

4. *Potassium in feldspars*

General structure

In contrast to the layer silicates, the K-feldspars ($KAlSi_3O_8$) are framework silicates composed of oxygen tetrahedra each containing a Si or Al atom. The Si/Al ratio is 3:1. These tetrahedra are linked together and form a three-dimensional framework. The large K ions are located in interstices between the linked tetrahedra [*4*].

Differences in the order of Si and Al in the crystal cause important structural as well as stability variations in the K feldspars. *Barth* [*4*] gives the following classification of three variants differing with respect to crystal system and to the degree of disorder of the Al/Si distribution.

1. Sanidine, which is disordered monoclinic
2. Orthoclase, which is partly ordered monoclinic
3. Microline, which is fully ordered triclinic

Finney and *Bailey* [*23*] classify the K-feldspars in the following sequence: sanidine, intermediate microline, and maximum microline. In this sequence, the Si/Al order increases.

4.1 *Effect of crystal structure and morphology on K release*

Properties of potassium feldspar crystals that affect their weathering rate are composition, principally the inclusion of Na in the structure, Si/Al order in the crystal structure, crystal and particle size, and the nature of twinning and crystallization of more than one mineral within one particle.

Potassium feldspars formed at high temperature, the granitic type, often contain Na as a substitute for K and there is a considerable lack of order in the position of the Al and Si in the crystal. At lower temperature the disordered phase can invert by a diffusive transformation to an ordering of the Al and Si in small domains *(Finney* and *Bailey* [*23*]*)*.

This results in the familiar cross-hatch twinning of granitic or high temperature microcline. Another consequence of cooling and reorganization is a separation, to some degree, of the Na into small lamellae of pure or nearly pure sodium feldspar. The lamellar structure of potassium of sodium feldspar is given the name 'perthite'. These lamellae can range in size from less than 15A to 1000μ in thickness [*4, 68*]. *MacKenzie* and *Smith* [*41*] studied 150 perthitic feldspars and none showed a maximum microline structure.

Authigentic feldspars are formed at low temperature in sedimentary rocks and are of particular importance to soils. *Jeffries* [*30*] reported authigenic feldspar in Pennsylvania soils. Although authigentic feldspars rarely make up more than a few percent of the total sediment [*5*], there are exceptions in which as much of 70% of a formation is composed of such minerals. Furthermore, on removal of carbonates by weathering one would expect the concentration, particularly of the more resistant K-feldspars to increase. In contrast to the high temperature type, authigentic potassium feldspars rarely contain more than 0.2% Na_2O [5]. They are nonperthitic but the Si/Al ordering varies widely. Monoclinic orthoclase is more common than is triclinic microcline *(Baskin* [5]*)* but even authigenic sanidline has been reported *(Barth* [4]*)*. *Baskin* [5] points out that authigenic feldspar probably has a replacement or epigenetic origin. The rate of growth may have determined the degree of Si-Al ordering, slow growth favoring a high degree of order.

One would expect that the weathering rate would increase with Si/Al disorder and Na content and that a perthitic feldspar would weather more rapidly than a homogeneous particle. In perthitic structures, albite is weathered more rapidly than the K-feldspar. If the lamellae of Na feldspar are removed first, more internal surface is opened and one would expect that the K-feldspar phase would then weather more rapidly than a homogeneous crystal. Weathering is also probably more rapid at the juncture of twins because of disorder at these planes.

Authigenic maximum microline would be expected to be most resistant to weathering because of its order and low Na content but also because of its crystal size and lack of perthitic structure.

Correns [17, 18] and *Huang* and *Keller* [28] found in laboratory studies of low temperature weathering of feldspar particles that residual materials significantly affected the loss of K. During the initial weathering of feldspar grains, K is lost more rapidly than is Si and Al and the oxides of Al and Si form an amorphorus residue layer around the unweathered core. This envelope of residual material slows the diffusion of K. *Correns* [18] calculated that the residue layer on 1μ K-feldspar grains was approximately 300A thick. With weathering the thickness did not increase. In addition, *Correns* [17] observed that naturally weathered feldspar grains were pitted and irregularly weathered, bearing out the non-homogeneous nature of these grains.

In contrast to weathered micas, weathered or unweathered K-feldspars do not have a significant pH-independent cation exchange capacity. *Schachtschabel* [61] and *Nash* and *Marshall* [46] showed that there is preference for NH_4 ions on feldspar surfaces. This suggests that the size of the interstices in feldspar permits ion selection when these interstices are exposed at surfaces. One would expect pH-dependent exchange properties of the residual layer and, thus, an increase in CEC with pH.

5. *Determination of soil potassium mineralogy*

Many of the relationships between potassium and mineralogy discussed in this paper are based on specimen minerals that were not taken from soils. Therefore, many of the proposed relationships are speculative. We need much more information on the specific nature of soil minerals. It is not enough to state that certain soil minerals are K-feldspars and that other minerals are micas. This is not a criticism of past work since the difficulties of making specific determinations are enormous. The difficulty also increases as one considers the finer fractions of soils, the clay and silt, which are assumed to be largely responsible for the mineralogical aspects of potassium fertility.

It is expected that the physical methods of analysis, which have made remarkable progress in recent years, will be improved even more so that the morphology, crystal structure, and chemical composition of the finest soil fractions can be made.

Techniques for concentration of certain soil minerals have been available for many years but emphasis has been given by soil scientists to the heavy minerals. Techniques for the separation and study of feldspars of sand size ($>50\mu$) in sediments are described by *van der Plas* [*68*]. *Kiely* and *Jackson* [*34*] employed sodium pyrosulfate fusion to remove the layer silicates so that the feldspars could be concentrated. Recovery of K-feldspar ranged from 96.5% in the $500-50\mu$ fraction to 64% in the $2-0.2\mu$ fraction. Thus, only partial separation of K-feldspars of clay size is made. Feldspars are usually concentrated in the silt and sand so this may not be a serious problem in many soils.

Studies of thin section of soils with the optical microscope and ultramicrotome sections of soil minerals should continue to reveal morphological and mineral properties related to potassium chemistry.

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Factors of Mica Transformation

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Summary

Recent studies on mica transformation are reviewed with special reference to concomitant processes, that react upon interlayer potassium release. Among these processes, the cooperative interaction between potassium exchange and interlayer expansion supposedly explains the influence of particle morphology upon potassium selectivity in partly altered micas. In addition, layer charge alterations, hitherto regarded merely as secondary and independent reactions, exert some direct influence upon potassium replaceability. Existing exchange models will have to be considerably extended in order to make allowance for these interactions.

Due to the numerous and multiform mineralogical transformations, which have been supposed to occur during weathering in soils, the genesis of most of the common soil clay minerals can theoretically be traced back to mica as the parent material. Notwithstanding the fact that other sources of clay formation are possible or even well established for particular soils, the transformation of micas and its dependence on environmental conditions has thus attracted considerable interest. The ecological aspect of potassium release and of related lattice expansion accompanied by an increase of exchange capacity adds to the importance especially of the initial steps of mica weathering.

The fundamental mechanism of potassium release and layer expansion

It is now generally accepted that the release of interlayer potassium consists of an exchange reaction, which proceeds from the lateral edges to the center of the mica particles. Consequently, exchange takes place at a moving interface separating the potassium depleted and expanded outer region from the central still unaltered mica core. This type of reaction implies a diffusion of exchanged potassium ions from the interface through the expanded lateral zone into solution and an equivalent but reversely directed diffusion of counter ions. Rates of interlayer diffusion, reacting upon exchange rates, are affected by the mutual interaction of counterions, interlayer water, and charged silicate surfaces.

In contrast to exchange processes occuring on external surfaces, exchange of interlayer potassium from micas is thus characterized by the following details:

1. Exchange is inevitably connected with a structural transition of the exchanger.

2. Only part of the total interlayer potassium, consisting of those ions which are exposed at the interface and in expanded interlayers, is contemporaneously involved in the exchange reaction.
3. The expanded region at the edge of the mica particle imposes a buffering action upon the equilibration between solution phase and exchange front, the extent of which is mainly determined by the potassium selectivity and by the relative exchange capacity of that region.
4. A number of parameters affecting equilibria as well as kinetics of potassium exchange undergoes systematic variation, which is correlated to the progress of the exchange reaction. Such variations are: a) decrease of the effective surface of the unaltered mica core, b) increase of the exchange capacity of the expanded portion of the exchanger, c) extension of the diffusion path between exchange front and solution.

The extent of potassium release from micas is determined by the binding forces exerted upon the potassium ions mainly in the exchange front but also in the expanded region. However, the complexity of the exchange mechanism renders the determination of exchange constants almost impossible. That is why relative criteria such as potassium concentration or activity ratios in equilibrium solutions have been used for characterizing exchange equilibria of interlayer potassium.

Considerable differences have been observed by comparing the replaceability of interlayer potassium from different mica species. Muscovite exhibits a much higher potassium selectivity than the trioctahedral counterparts biotite and phlogopite.

Potassium selectivity of micas has been related to the orientation of the O-H bond in octahedral OH groups by *Basset* [2]. In dioctahedral micas the O-H bond is declined from an axis perpendicular to the layer plane into the direction of vacant octahedral sites. The repulsion of potassium ions by hydrogen is thus diminished as compared to trioctahedral micas, where even charge distribution in coordinated octahedral sites leads to a nearly perpendicular orientation of the O-H bond, corresponding with shorter K-H distances. The higher potassium selectivity of trioctahedral micas with heterogeneous charge distribution in the octahedral layer (e.g. lepidolite) as well as the correlation of potassium selectivity and fluor content of micas have to be regarded as confirmation of *Basset*'s theory.

Recent investigations demonstrate that the release of interlayer potassium as a first step of mica transformation can not be fully described in terms of the mechanism outlined above. Additional factors must be considered, which are essentially interrelated with the exchange process. In the following sections two of these interrelations and their significance for mica weathering will be treated in more detail.

Particle morphology and interlayer potassium exchange

The general exchange model outlined above suggests that morphological features, such as shape and size of particles, condition of surfaces, and structural order should exert some influence upon the kinetics of interlayer exchange and expansion.

With decreasing particle size, rates of potassium exchange from interlayer positions are enhanced by shorter diffusion paths as well as by larger specific sectional areas. However, a definite co-ordination between diffusion rate and particle size is prevented by irregularities in particle shape. In addition, structural imperfections enable exchanging cations to penetrate into the interlayers not only through lateral edges but also through fissures and cracks normal to the a-b plane *(Wells* and *Norrish* [*13*]*)*. Such irregular conditions may also be promoted either by partial dissolution as a result of weathering (Figure 1) or by the inclusion of nonmica minerals, which lead to a disturbance of the layer structure during expansion of the mica component (Figure 2). Penetration of solution into openings originated by wrinkling of expanded regions of the particles may contribute to the difficulty of reconciling observed rates of potassium release with simple diffusion models. In any case, the applicability of diffusion models to potassium release from micas depends on the presumption that diffusion gradients are kept constant with time. In soils, this condition is not likely to be fulfilled. Potassium concentrations in soil solutions can rather be expected to approach equilibrium levels. Consequently, exchange coefficients are going to replace diffusion constants as the rate determining factors of potassium exchange, particularily, where precipitation is low or soil permeability is impeded. Thus, the character of interlayer potassium exchange in soils has to be regarded as intermediate between continuous infinitesimal exchange and batch exchange according to the definition given by *Wiklander* and *Nilsson* [*14*].

It is interesting to note that the influence of particle size on potassium release is reversed as the type of exchange passes between these two extreme cases. Laboratory experiments conducted with different mica species reveal that potassium selectivity increases with decreasing particle size *(Reichenbach* and *Rich* [*11*]*)*.

Explanations proposed so far rely on the interaction between cation exchange and layer expansion. As can be concluded from the relation of respective layer spacings, increase of particle thickness in the expanded lateral region by incorporation of hydrated cations into the interlayers amounts to 20 to 30% of the original value. Scanning electron micrographs reveal that the accommodation of the vermiculitic rim to the mica core gives rise to various micromorphological alterations. Wrinkling of the surfaces can be observed extending from the exchange front to the particle edge (Figures 3, 4, and 5). Since silicate layers are bending and shifted from their originally planar position (Figure 4 and Figure 6), particles are caused to split open along preferential weathering planes (Figures 4, 5, and 6). This leads to a disintegration of the particles into 'books' of layers, which in turn are subdivided into packets of smaller dimensions (Figure 6 and Figure 7). X-ray diffraction indicates that random stacking of expanded and contracted interlayers occurs in the transitional zone. Since uptake of hydrated cations into interlayer position forces the silicate layers apart and thus affects the probability of exchange in adjacent interlayers, potassium exchange from micas has to be regarded as a co-operative reaction. Co-operative forces are effective over limited distances. Hence, the balance of the co-operative forces is achieved by an optimal arrangement of layer bending and partial expansion within a transitional zone of definite width.

Several observations seem to indicate that this optimal arrangement within the moving exchange front promotes interlayer potassium exchange. Thus, *Newman* and *Brown* [*10*] were able to show that potassium exchange is initially delayed at undisturbed edges of mica flakes, which are exposed by clean fractures. After the exchange front had been fully developed, further exchange was found to proceed at rates comparable to those observed for less ordered edges. Likewise, when the exchange front approaches the center of the particles at the end of the reaction, reaction rates are generally found to decrease. By treating micas with NaCl solutions, *Newman* [*8*] observed a minimum of potassium concentration in equilibrium solutions after about 10 to 20% of the total potassium was released. This minimum probably results from the fact that, although most of the

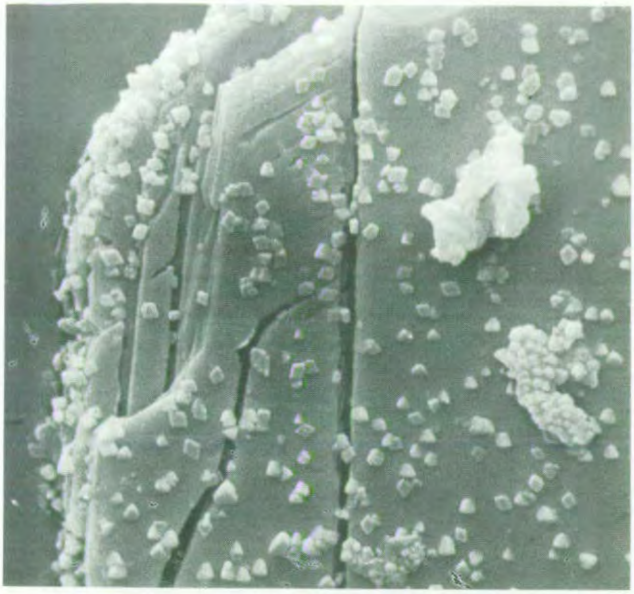

Figure 1. Fissures in a muscovite particle caused by partial dissolution during treatment with 0.1 N $BaCl_2$ solution at 120 °C. Dissolution seems to be enhanced by bending of layers in the lateral region of the particles. Boehmite crystals are formed from dissolved aluminum and deposited on particle surfaces.
(Scanning electron micrograph, magnification 7810 ×)

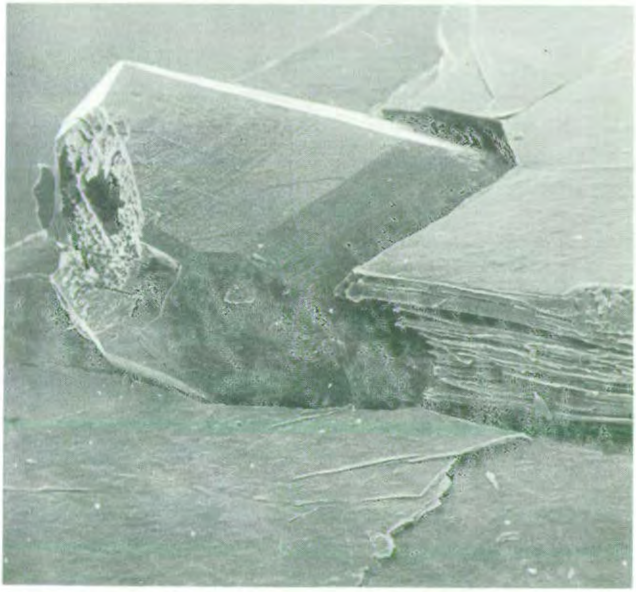

Figure 2. Formation of cracks and openings resulting from inclusions in naturally weathered biotite. The feldspar grain has been squeezed out of its original position by the expansion of mica interlayers.
(Scanning electron micrograph, magnification 6000 ×)

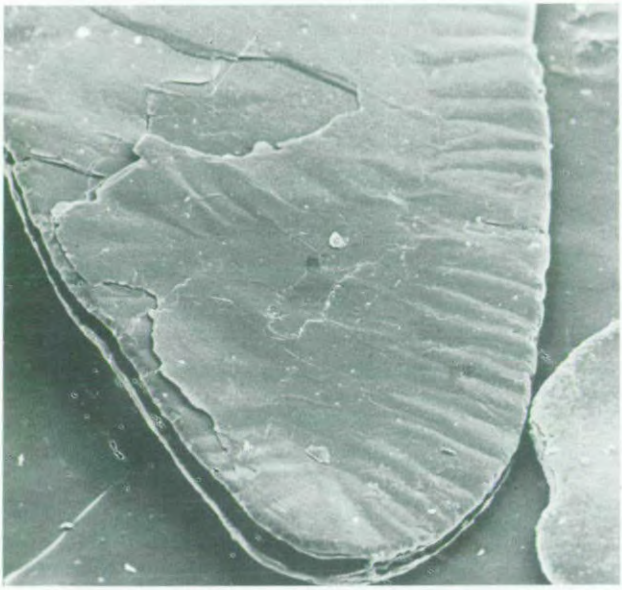

Figure 3. Biotite particle after partial removal of interlayer potassium by barium. The extension of wrinkles in the lateral zone marks the position of the exchange front. Irregular surface morphology on the left hand side of the particle inhibits zonal exchange.
(Scanning electron micrograph, magnification 1090 ×)

Figure 4. Biotite particle after complete removal of interlayer potassium by barium. Bending of layers causes splitting along the layer plane.
(Scanning electron micrograph, magnification 1125 ×)

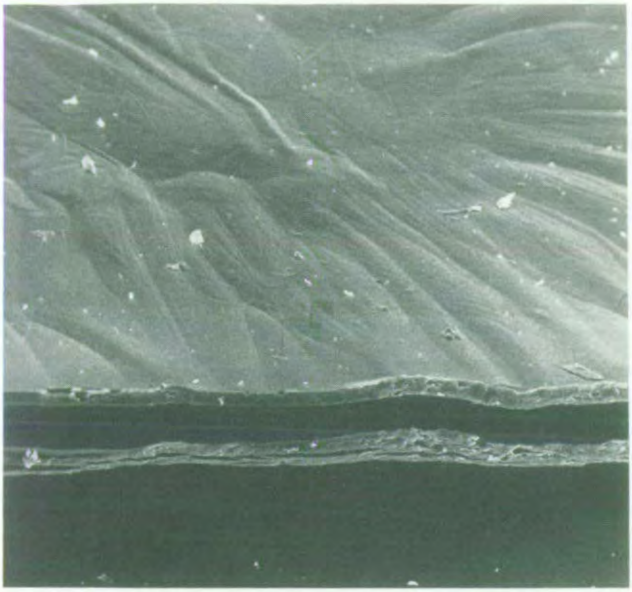

Figure 5. Details of surface morphology in the expanded lateral zone of biotite, exhibiting the superimposition of wrinkles of different dimensions.
(Scanning electron micrograph, magnification 1160 ×)

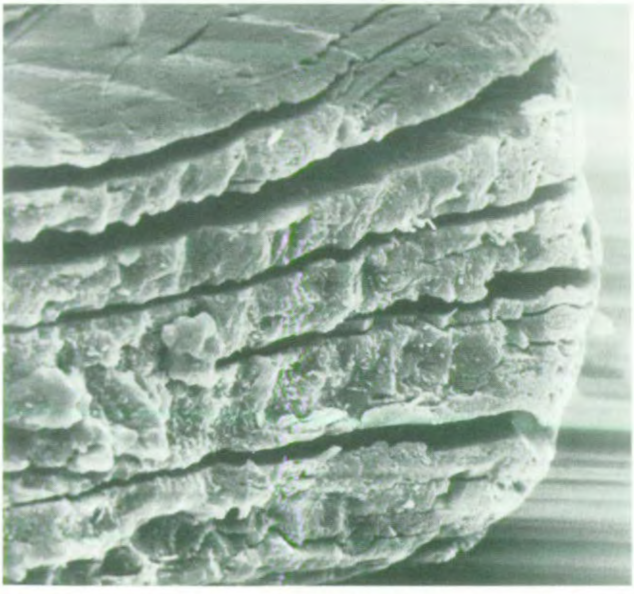

Figure 6. Layer separation and bending at the edge of a biotite particle after removal of interlayer potassium by barium.
(Scanning electron micrograph, magnification 5300 ×)

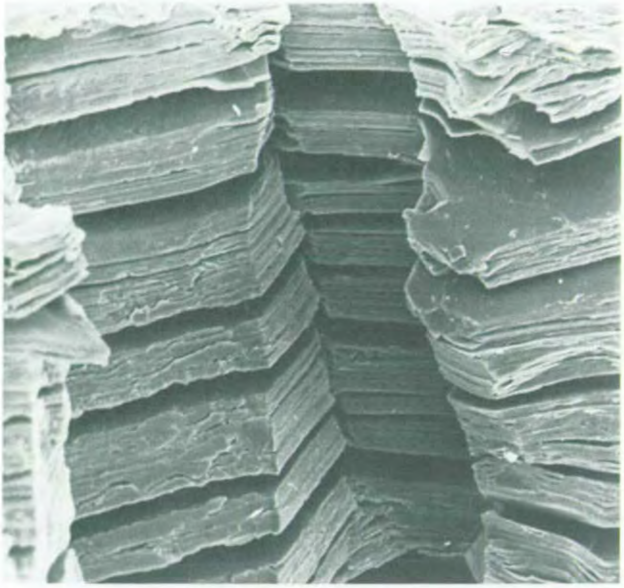

Figure 7. Edge of naturally weathered biotite showing the separation into subdivided 'books' of layers. (Scanning electron micrograph, magnification 10 630 ×)

potassium was already removed from external exchange sites, interlayer potassium exchange was still in its initial phase marked by an incomplete development of the exchange front.

This mechanism also seems to provide a satisfactory explanation for particle size effects upon potassium selectivity. With decreasing particle size, the width of the transitional zone approaches the dimension of particle radius. Thus, even if particle dimensions permit the full development of a stable layer configuration within the exchange front, release of interlayer potassium from small particles is mainly determined by the conditions of edge exchange. On the contrary, in coarser mica fractions most of the potassium is exchanged in a fully developed transitional zone, which moves through the particle.

The above theory, though in accord with several experimental observations, is still rather hypothetical and has to be substantiated by further investigations. Particularly, more information is needed about the physical character of alterations within the exchange front and of the interrelated co-operative mechanism.

Implications of layer charge alterations on mica transformation

According to observations on weathering sequences of soil minerals reduction of layer charge has for long been regarded as an element of mica transformation. Charge reduction of micas has also been obtained in the laboratory by exchanging interlayer potassium with neutral salt solutions. Although micas containing larger amounts of ferrous iron seem to be most susceptible to those alterations, lack of equivalence between iron oxidation and charger reduction points at the fact that other reactions must be involved.

As outlined by *Newman* and *Brown* [9] variation of layer charge has to be seen as the result of various independent reactions. Among these, ferrous iron oxidation is possibly combined with the transformation of structural (OH^-) into structural (O^{2-}). The net charge of the layers would thus remain unaltered, because the increase of positive charge of octahedral iron is balanced by a corresponding reduction of the structural (OH^-)/(O^{2-}) ratio as a result of electron transfer. Loss of net negative charge is proposed to occur either by hydrolysis of newly-formed structural (O^{2-}) groups or by loss of hydroxyls or by both these processes. On the other hand, gain of net negative charge would result from the release of octahedral cations into solution.

Numerous supplementary results which have been achieved by recent investigations substantiate the mechanisms proposed by *Newman* and *Brown*. *Ismail* [5] conducted artificial weathering experiments by adding H_2O_2 to biotite in solutions adjusted to different pH values. Considerable modification of reaction products was obtained depending on the pH of the system. Under alkaline and neutral conditions ferrous iron was released to solution from octahedral position. The release amounted to about 12% of the total ferrous iron content originally present in the untreated material, whereas release of octahedral magnesium was negligible. Ferrous iron oxidation was found to be almost equivalent to the total amount of ions released to solution (including octahedral and interlayer ions).

On the other hand, in the acid environment magnesium was also released to a considerable extent (13% of the total amount). On an equivalent basis ferrous iron oxidation was by far outweighed by the total release of ions to solution. This was attributed to the incorporation of aluminum into octahedral or tetrahedral positions by *Ismail*. However, occupation of interlayer exchange sites by aluminum, incorporation of protons into the structure, and loss of structural hydroxyl seem to remain as alternative and perhaps even more probable explanations.

Whereas large amounts of interlayer potassium were released to solution as a result of the H_2O_2 treatment, such release was not observed by *Ismail* [*6*] after oxidation of ferrous octahedral iron by heating biotites to 450 °C. Evidently, surface charge has been maintained in this case by an electron transfer to structural (OH^-) with subsequent loss of hydrogen from the structure.

Robert [*12*] investigated ferrous iron oxidation as induced by gradual removal of potassium from biotites with NaCl solutions. Oxidation was found to be related to potassium depletion and to reach a maximum value of 56% of the total ferrous iron, when the interlayer potassium was completely removed. Subsequent treatment of potassium depleted samples with H_2O_2 further enhanced oxidation in a way that almost direct correspondence between the oxidized portion of the original ferrous iron content and the exchanged portion of the original interlayer potassium was obtained. As pointed out by *Robert*, it seems obvious from these results that interlayer potassium exerts a blocking effect upon oxidation which, thus, can only occur where interlayers are rendered accessible to oxidizing agents by layer expansion. Oxidation within the intact biotite structure can only be achieved by heating the minerals to about 700 °C. Then, the thermal treatment causes internal charge balance by loss of hydrogen from structural hydroxyl.

Obviously, in view of Basset's theory the mechanisms suggested by *Newman* and *Brown* [*9*] must affect the exchange selectivity of interlayer potassium. Two conclusions can be drawn:

1. Loss of hydrogen from structural (OH^-) should strengthen potassium bonding due to the elimination of potassium – proton repulsion.
2. Heterogeneous charge distribution in the octahedral layer induced during weathering either by ferrous iron oxidation or by the release of octahedral cations should affect the orientation of the O-H dipole and thus also lead to an increase in potassium selectivity.

Recent experimental results confirm these conclusions. *Barshad* and *Kishk* [*1*] obtained a significant reduction of potassium release from biotite, when oxidized samples were treated with $MgCl_2$ solution. This effect was found to be reversible: The replaceability of potassium by magnesium could again be enhanced upon reducing the ferric iron. In vermiculites, potassium fixation was correspondently affected by oxidation or reduction of iron. *Ismail* [*6*] also reported a decrease of potassium concentration in water extracts of heated biotite as compared to natural samples. Application of infrared spectroscopy furnished direct evidence of the influence exerted by iron oxidation upon the orientation of O-H bonds *(Juo* and *White* [*7*]; *Robert* [*12*]).

Although the conclusions drawn above are supported by these findings, the interdependence of potassium replaceability and ferrous iron oxidation in biotites needs further study. If oxidation can only occur in the expanded portion of the mica particle, as suggested by *Robert*, then oxidation would have to be preceded by potassium exchange. Consequently, the proper exchange reaction within the exchange front should remain unaffected by oxidation. Several observations cast some doubt on the temporal as well as local co-ordination of both these processes. Thus *Boettcher* [*3*], by treating biotite with distilled water, through wich O_2 gas was bubbled, achieved complete conversion to vermiculite. According to his suggestion, potassium ions have been expelled from interlayers by ferrous iron oxidation, possibly accompanied by migration of octahedral magnesium ions into interlayer position. Such a mechanism, however, demands that expulsion of potassium and iron oxidation proceeds concomitantly in the reaction zone in order to maintain electroneutrality. As proposed by *Farmer* and *Wilson* [*4*], the formation of regular interstratification in hydrobiotites begins by replacement of potassium round the edge of a surface layer of the biotite and, with bonding of potassium being enhanced in adjacent layers by iron oxidation, proceeds by attack on successive alternate interlayers. This model also rests on the assumption that oxidation acts immediately upon potassium exchange.

Reconsidering what has previously been said about the buffering action of the expanded lateral zone upon the primary exchange reaction, another mechanism of interaction between oxidation and potassium release has to be taken into account. With exchange reactions between micaceous and vermiculitic and between vermiculitic and soluble phase being connected in series, release of interlayer potassium into solution is determined by the product of partial exchange constants of both these reactions. Thus, even if it is assumed that potassium selectivity in the still contracted zone of the particle remains unaffected by the secondary processes of layer charge variations, oxidation would nevertheless exert considerable influence upon the gross replaceability of potassium from micas.

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Potassium in Allophane and in Zeolites

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Summary

Allophane is the primary weathering product when volcanic ash and pumice are thoroughly leached and drainage is unimpeded. Allophane does not mean a distinct mineral species but rather a series of minerals, which are hydrous aluminosilicates of short range order with

$$Al_2O_3 \cdot SiO_2 \cdot 2H_2O \text{ and } Al_2O_3 \cdot 2SiO_2 \cdot 3H_2O$$

as the end members.

Allophanes do not contain an appreciable amount of potassium, but ion exchange experiments indicate, that potassium is preferentially absorbed. Exchange sites as in zeolites are suggested to be responsable for this behaviour.

On hydrolysis volcanic ash and pumice may give rise to the crystallization of zeolites, provided that a high alkali ion to hydrogen ion activity ratio and a high silica activity are preserved. Zeolites are hydrous crystalline aluminosilicates with the general formula

$$(M^{2+}, M^{+}_{2})_{x/2}\,[Al_xSi_yO_{2(x+y)}] \cdot nH_2O.$$

In sedimentary deposits only 6 of the 34 naturally occurring zeolites are commonly found: analcite, chabazite, clinoptilite, erionite, mordenite and phillipsite. The same zeolites may be found in sodic and saline sodic soils. Ion exchange measurements have revealed that these zeolites have a strong selectivity for potassium, rubidium and cesium. They may be used for the removal of potassium (or Cs and Rb) from mixed salt solutions.

There are very few similarities between the structure and properties of allophane and zeolites, but there are genetic relationships which are well established by analytical and experimental procedures as well as by theoretical considerations. Depending on environmental conditions volcanic ashes and pumices may alter into allophane or zeolites. Artificial zeolites are synthesized from amorphous aluminosilicagels which are quite satisfactory models for natural allophanes. In addition soil allophanes may be converted into zeolites by hydrothermal treatment with alkaline solutions.

In the present paper such relationships are treated in some detail with special emphasis on the role played by potassium.

1. *Allophane*

1.1 *Composition and genesis*

The large composition range of natural allophane (table 1) does not allow the designation of allophane as a distinct mineral species. In view of this fact the following tentative definition was proposed at a seminar* on amorphous clay minerals *(van Olphen [26]):*
'Allophanes are members of a series of naturally occurring minerals which are hydrous aluminosilicates of widely varying chemical composition, characterized by short range order, by the presence of Al-O-Si-bonds and by a DTA curve displaying a low temperature endotherm and a high temperature exotherm without an intermediate endotherm.'

The elemental composition of the end members may be expressed in the formulae $SiO_2.Al_2O_3.2H_2O$ and $2SiO_2.Al_2O_3 . 3H_2O$ *(Wada [29]).*

Allophanes are commonly formed during the early stages of weathering of volcanic ashes and pumices when leaching is intense and unimpeded. With continued weathering they may be transformed into crystalline clay minerals, especially halloysite. Allophanes are the main constituents of the clay fraction in ando soils (andepts). *(Aomine* and *Wada [3]).*

1.2 *Morphology and structure*

High magnification electron micrographs, as well as the specific surface area (600 m^2/g) and specific gravity (1,9) indicate that allophane consists of microaggregates built up by 55 Å 'unit particles'. The particles seem to be spherical, surrounded by a monolayer of adsorbed water *(Kitagawa [18]).* In many ando soils derived from volcanic ash and in

Table 1. Chemical composition of some representative allophanes *(Yoshinaga [32])*

	I	II	III	IV
SiO_2	31.72	35.58	36.38	39.92
Al_2O_3	40.89	39.82	37.51	34.78
Fe_2O_3	0.59	0.35	1.12	0.96
TiO_2	0.79	0.45	0.41	1.06
P_2O_5	0.14	0.22	0.19	0.11
CaO	0.11	0.10	0.58	0.16
MgO	0.29	0.17	0.20	0.23
K_2O	0.13	0.16	0.13	0.13
$Na_2O^{+)}$	5.35	5.90	6.12	6.56
$H_2O\,(+)$	19.18	16.67	16.62	15.62
Total	99.19	99.42	99.27	99.53
$\frac{SiO_2}{Al_2O_3}$	1.32	1.52	1.64	1.95

I Kuma, Ehime Pref. Japan (Volcanic ash)
II Aizu, Fukushima Pref. Japan (Pumice)
III Iijima, Nagano Pref. Japan (Pumice)
IV Choyo, Kumamoto Pref. Japan (Pumice)

+) The high Na_2O contents are due to the treatment with sodium salts during sample preparation.

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* United States — Japan Science Cooperation Program.
Seminar on amorphous clay minerals, held at Fukuoka, Japan, Sept. 17—19, 1969.

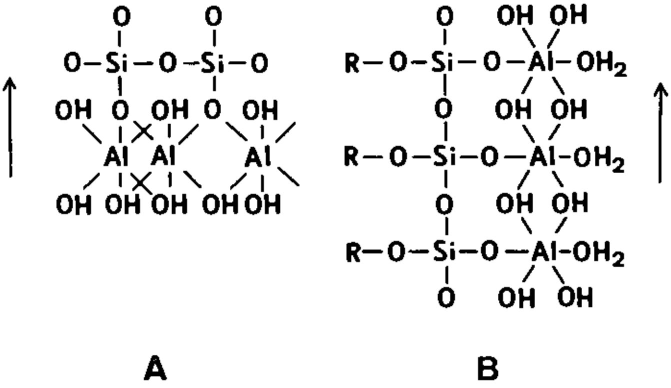

Figure 1. Possible sheet and chain structure of allophane.
A Sheet – like model; ↑ perpendicular to the sheet (Udagawa [25])
B Chain – like model; ↑ direction of the chain (Wada [29])

weathered pumice beds fibrous particles are found beside the common spherical allophane. Since this fibrous species in several respects differs distictly from the coexisting allophane it was designated by a new proper name: imogolite (after Imogo, where it was detected first; *Yoshinaga et al.* [*31*]).

Because of the low molecular order of allophane it is not surprising that the proposed structural schemes diverge extensively. There is no direct method which allows the determination of the exact arrangement of the atoms as with crystalline clay minerals. Moreover many of the methods applied may cause serious changes of the original structure.

From the cation exchange properties of allophane as well as of aluminized clay *De Villiers* and *Jackson* [*28*] deduced that allophane unit particles are built up by a 'permutite core' with an approximate composition $NaSi_3AlO_6(OH)_4$, of which the Na is exchangeable, and a discontinuous shell of hydroxyaluminum units of coordination number 6. The positive hydroxyaluminum edge groups $[Al(OH)_2]^+$ may block some of the tetrahedral negative charges and protonation-deprotonation would result in the observed pH dependent cation exchange capacity.

Working with a cation free artificial system prepared by hydrolysis of aluminumisopropoxide and ethylsilicate, *Cloos et al.* [*13*] suggested a similar model which is also based on a central core built up by a tetrahedral network in which silicon is partially substituted by aluminum and around the core a more or less polymerized hydroxyaluminum coating balancing the negative charge of the core. With increasing Al/(Al + Si) ratio the degree of substitution in the core increases as well as the complexity of the hydroxyaluminum cations in the coating. When the ratio exceeds 0.8 demixing occurs and crystalline pseudoboehmite and bayerite are found in addition to the amorphous aluminosilicate.

From numerous chemical analyses of pure allophanes and from x-ray studies on imogolite *Wada* [*29*] proposed a double-chain-like arrangement composed of a silica tetrahedral chain and an alumina octahedral chain which are linked by common corners (figure 1B). Connexions between the chains may result in the formation of very thin sheets and films.

Udagawa et al. [*25*] extended this basic conception by thermal transformation studies and concluded that allophane has a sheetlike structure (figure 1A) which to some extent would resemble a kaolinite type mineral with clustered defect layer structure (cf. *Brindley* and *Farmer* [*12*]).

It is obvious that there are certain discrepancies between the various model structures. As pointed out by *Lai* and *Swindale* [*19*] there is reason to doubt that synthetic aluminosilica gels can be relied on to depict the structure and properties of natural allophanes. It is well known from zeolite chemistry that the properties of aluminosilicate gels even depend on the sequence of mixing the constituents *(Zhdanov* [*33*]*).*

On the other hand all models offer possible explanations for a great number of experimental observations. Considering the large composition range of the allophanes, one might assume that the different conceptions describe but different members which evolved from different parent material under different environmental conditions.

1.3 *Potassium in allophanes*

Soil allophanes do not contain an appreciable amount of potassium (cf. table 1). Under the conditions leading to the formation of allophane alkali and alkaline earth cations are leached during the first stages of weathering. It seems however that allophane has a definite affinity for potassium. *Wada et al.* [*30*] obtained unusually high C.E.C. values for japanese soil allophanes when determined with potassium salts. They were able to show by comparison with magnesium exchange that potassium is indeed preferentially absorbed. *Van Reeuwijk* and *De Villiers* [*27*] concluded from cation exchange experiments with synthetic aluminosilica gels 'that the fixation of K is sterically controlled and that, as with zeolites of rigid 3-dimensional structure, channels in the gel impose a sieve action on the entry and passage of certain counter ions.' Dried gels showed an increased capacity to fix K. Drying presumably increases the rigidity of the channels in the gel structure which restrict the passage of the larger hydrated cations. Furthermore the K-fixing capacity of the gels increased when the pH, at which K-saturation was performed was raised from 4 to 10. *Van Reeuwijk* and *De Villiers* claimed that fixation takes place at normal exchange sites – even at pH 10 – and no special chemical reaction within the gel is involved.

Again from zeolite chemistry objections may be raised to the last statement of *Van Reeuwijk*. Aluminosilica gels undergo an aging process which essentially consists in a polymerization-depolymerization reaction and in a rearrangement of the gel structure *(Barrer et al.* [*5,6*]*). Sticher* [*23*] showed, that an aged (but still amorphous) potassium aluminosilicate gel of the composition $K_2O.Al_2O_3.2SiO_2.nH_2O$ has other thermal properties than a freshly prepared gel of the same composition.

As pointed out by *van Olphen* [*26*], cation exchange capacity is not a material constant of minerals such as allophanes. Although the above experiments indicate a certain affinity for potassium, it is nevertheless necessary to investigate carefully exchange isotherms and hysteresis effects in order to get a more detailed insight into the exchange and fixation behaviour of the allophanes.

2. *Zeolites*

Zeolites are hydrous aluminosilicates with a framework structure. The structure is made up of (Si, Al)O_4 – tetrahedra in which each oxygen is shared by two tetrahedra. The net negative charge arising from the isomorphous substitution of Al for Si is balanced by

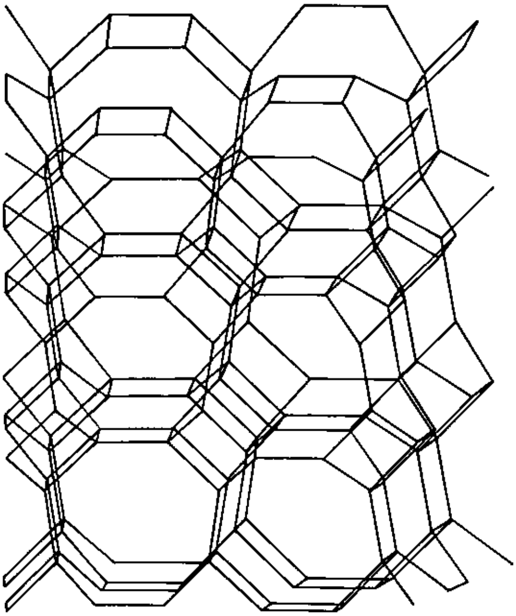

Figure 2. Structure of phillipsite, viewed along [100]
(This figure was kindly supplied by Prof. *W.M. Meier*, Institute for crystallography and petrography, ETH Zurich)

cations, most commonly Ca, Na and K, located in cavities within the aluminosilicate framework. These cavities are interconnected and give rise to a channel system. Water molecules are present in the structural openings.* Figure 2 shows the basic aluminosilicate framework of phillipsite.

2.1 *Occurrence and genesis*

Favorable conditions for the formation of zeolites are:
(1) high alkali ion to hydrogen ion activity ratio and
(2) high silica activity.
Such conditions are encountered in various geological environments. According to *Coombs* [*14*] zeolites are mainly formed:

i. in sediments from deep ocean basins;
ii. as products of diagenesis of nonmarine beds,
    a) products of reaction between glassy tuffs and alkalic ground waters,
    b) products of reaction between highly alkalic lake water and sediments both tuffaceous and nontuffaceous;

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* For further information concerning structure, properties and technical applications, the reader is referred to the excellent reviews by *Barrer* [*7*], *Breck* [*11*], *Grubner et al.* [*16*], and *Meier* and *Olson* [*20*].

iii. in burial metamorphic sequences;
iv. as products of hydrothermal metamorphism in geothermal fields;
v. in volcanic rocks and breccias.

In order to set off the formation of zeolites by contrast with the formation of allophane the following discussion will be restricted mainly to the diagenetic alteration of volcanic ash and tuffaceous parent material.

2.1.1 *Lacustrine deposits*

Falling in the lake waters volcanic ash settles to the bottom. Due to hydrolysis of the ash the water in the pores of the deposit becomes alkaline and zeolites are formed by alteration of the ash. Special attention is drawn on to the highly alkaline saline playas and desert lakes where pH value up to 10 may be found.

2.1.2 *Nonlacustrine deposits*

In nonlacustrine deposits (loose or consolidated) alkali and alkaline earth ions are lost from the uppermost horizon by weathering and leaching. To some extent also desilicification takes place and allophane or, probably in a second step, crystalline clay minerals are formed *(Aomine* and *Wada [3])*. Moving downward the subsurface water increases in pH and in concentration of alkalis thereby providing a chemical environment favorable for the formation of zeolites.

A strong correlation exists between the salinity of the water and the mineralogy of the zeolites formed. High salinity correlates with increased reaction rates but also with a decreased activity of water favoring less hydrated phases *(Hay [17])*.

Of the 34 naturally occurring zeolites only 6 commonly occur in volcanic ash deposits: analcite, chabazite, clinoptilite, erionite, mordenite and phillipsite *(Sheppard [22])* (table 2).

In soils zeolites may be formed when impeded drainage and soda accumulation maintain a high alkali ion to hydrogen ion activity ratio, i.e. in sodic and saline-sodic soils. Analcime has been reported from San-Joaquin-Valley, California *(Baldar* and *Whittig [4])*. Chabazite, phillipsite and erionite are found in the Olduvai Gorge and over the adjacent part of the Serengeti plain (Tanzania) *(Hay [17])*.

Table 2. Zeolites in sedimentary rocks

Zeolite	Idealized formula
Analcite	$Na_{16}[Al_{16}Si_{32}O_{96}] \cdot 16H_2O$
Chabazite	$Ca_6[Al_{12}Si_{24}O_{72}] \cdot 40H_2O$
Clinoptilite	$(Mg, Ca, Na_2, K_2)_3[Al_6Si_{30}O_{72}] \cdot 22H_2O$
Erionite	$(Mg, Ca, Na_2, K_2)_{4.5}[Al_9Si_{27}O_{72}] \cdot 27H_2O$
Mordenite	$Na_8[Al_8Si_{40}O_{96}] \cdot 24H_2O$
Phillipsite	$(Na, K)_{10}[Al_{10}Si_{22}O_{64}] \cdot 20H_2O$

The mechanism by which zeolites may have been formed in nature has been extensively investigated by experimental work. Since World War II an immense effort has been done in order to synthesize artificial counterparts of naturally occurring zeolites as well as completely new species with widely diverging properties.

Although some objections still exist it is largely accepted today that zeolites are formed not by alteration of the parent material in the solid state (as e.g. most clay minerals and allophane) but by solution of the parent material and subsequent crystallization from solution (*Deffeyes* [*15*], *Zhdanov* [*33*]). It seems however rather unlikely that single SiO_4^{4-} or AlO_4^{5-} tetrahedral ions are captured by the developing lattice. Therefore *Barrer et al.* [*5*] suggested that after dissolution of the parent material the tetrahedra regroup about hydrated alkali or alkaline earth ions to form basic polyhedral units which by condensation polymerization can produce more complex arrangements.

2.2 *Potassium in zeolites*

It is a remarkable fact that the Na/K ratio of all zeolites found in sedimentary rocks is considerably lower than the ratio encountered in the environmental lake or pore water (*Hay* [*17*]). Ion exchange measurements have shown that these zeolites have a stronger affinity for potassium than for sodium (table 3).

Na-Clinoptilite removes potassium quantitatively from sea water (*Ames* [*2*]). In erionite a part of the potassium ions occupy positions from which they cannot be removed without destroying the crystal lattice (*Peterson et al.* [*21*]). From ion exchange isotherms *Barrer* and *Munday* [*10*] calculated that from bore waters with K fractions between 0.01 and 0.14, as found in Nevada and California, phillipsites with K fractions between 0.06 and 0.30 would result. In fact most phillipsites found in sedimentary rocks in the Western United States fall into this range.

2.3 *Synthetic potassium zeolites*

In recent years a number of artificial potassium, as well as potassium-sodium zeolites, have been synthesized from aluminosilicate gels, kaolinite, metakaolinite and various other starting materials (table 4).

Table 3. Thermodynamic affinity sequences for chabazite, phillipsite and clinoptilite

Zeolite	Sequence	Authors
Chabazite	$K > Rb > NH_4 > Na = Ba > Sr > Ca > Li$	Barrer et al. [9]
Phillipsite	$Cs > K > Rb > Na > Sr > Ca > Li$	Barrer and Munday [10]
Clinoptilite	$Cs > Rb > K > Na > Li$ and $Ba > Sr > Ca > Mg$	Ames [1]

Table 4. Synthetic potassium zeolites

Symbol		SiO_2/Al_2O_3	Zeolite group/remarks
Linde	F	2.0	
Linde	I	2.0	
Linde	M	2.1	(K-F of Barrer)
Linde	Q	2.2	
Barrer	K-G	2.0-4.2	Near-Chabazite
Barrer	K-M	3.0	Near-Phillipsite
Barrer	K-F	2.0	
Barrer	K-F (Cl)	2.0	with incorporated KCl
Barrer	K-Z	2.0	with incorporated KOH
Zhdanov	K-I	2.0	
Union Oil	U J	5.0	

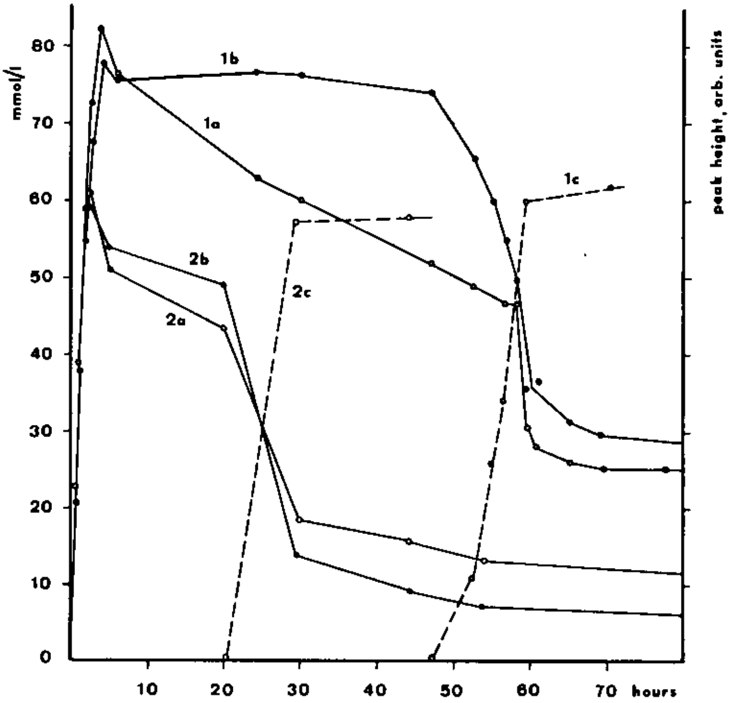

Figure 3. Reaction of kaolinite with 3 molal KOH at 80 °C.
Curve 1: without KCl; a) concentration of Si in solution, b) concentration of Al in solution, c) crystallization of zeolite (as revealed by x-ray analysis).
Curve 2: with one mol KCl per mol KOH; a, b and c as above.

Pure kaolinite with its even and constant silica to alumina ratio of 2.0 proved to be a convenient material for the study of reaction rates and reaction mechanisms of zeolite formation *(Barrer et al. [8], Sticher* and *Bach [24])*. In figure 3 the progress of the reaction of kaolinite with 3 molal KOH at 80 °C is plotted against the same reaction but with additional KCl.

With KOH the reaction product is a mixture of K-G and K-I of which each has a water content of about 17%. With KOH and KCl, K-F is the sole product, with a water content of 11.5%.

As observed in natural environment high salinity strongly reduces the time required for crystallization and favors the formation of less hydrated species *(Sticher [23])*.

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Application of Infrared Spectroscopy to the Study of Minerals Weathering

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Summary

A few examples of application of infrared spectroscopy to the study of modifications undergone by a weathering mica are shortly presented. The principal features of the spectrum of fresh phlogopites and biotites are summarized for the structural OH stretching region. Then it is shown how the possible mechanisms involved in mica alteration modify the initial spectrum, taking into account the attribution of observed bands to particular configurations of the ionic surrounding of hydroxyl groups either in the mica layer or in the interlamellar space.

The study of weathering of micas by infrared spectroscopy has received in the past few years a considerable attention. Two types of informations can be obtained. The first one is the appearance of new bands in the spectrum, which can be ascribed to a new mineral. This is the case for instance of identification of kaolinite in a weathering biotite. Frequently however, the infrared technique is not the only one to yield such an indication, and we shall develop a little more examples showing the characteristic efficiency of the method.

Informations more specific of infrared spectroscopy are obtained when spectral changes which are observed can be attributed to a modification in the structure of the mineral layer or of the interlamellar space. The interpretation of these changes requires a good knowledge of band assignment, and in spite of some uncertainties which are still remaining, it is possible to discuss a weathered mica spectrum.

The most frequently, spectroscopic studies concern the domain of structural OH stretching vibrations. This is due chiefly to two reasons:

– the absorption frequency of OH groups is mainly determined by ions present in their close vicinity, either cations to which they are bound in the layer or interlamellar ionic surrounding.

– an easy distinction is possible between dioctahedral and trioctahedral structures.

Hydroxyls belonging to a dioctahedral structure are inclined on the a b plane with an angle of ~ 16°, whereas hydroxyls belonging to a trioctahedral structure are nearly perpendicular to the a b plane. As the intensity of absorption is proportional to the square cosine of the angle between the electric vector of the radiation and the transition moment of the dipole, it is clear that at normal incidence the absorption of trioctahedral OH will be very faint as compared to the dioctahedral OH absorption. When tilting the sample in the infrared beam, trioctahedral absorption increases rapidly, whereas dioctahedral OH absorption remains nearly constant. This polarization effect is thus very convenient to distinguish the two classes of hydroxyls.

At first sight, in the phlogopite — biotite series, experimental spectra change from one mica to another one. In some cases (phlogopites essentially) resolved maxima appear commonly at similar frequencies; a big deal of work has been done in order to determine frequency and assignment of component bands, either when they are sufficiently resolved or when a numerical resolution procedure is required to separate non resolved overlapping bands as they occur in biotites. In this domain *Vedder* [*6, 7*], *Wilkins* [*8*] and *Farmer* [*3, 4, 5*] have made a remarkable work, and have shown that whatever is the apparent shape of the spectral contour, it is possible to describe any spectrum with a limited number of bands located at given frequencies and corresponding to a given environment. The highest frequency is obtained for trioctahedral OH coordinated to 3 Mg, and this frequency decreases when Mg is substituted for Fe^{2+}, Fe^{3+} or Al.

The case of trioctahedral OH is well summarized by table 1 which gives frequencies and attributions proposed by *Vedder* and *Wilkins*.

For dioctahedral hydroxyls the situation has not been cleared up to the same extent. *Vedder* proposed attributions on the only basis of the charge of the cation. With reference to synthetic celadonite spectra, *Farmer* has shown that the nature of the cation influences notably the absorption frequency. Substitution of a Fe^{2+} ion by a trivalent one decreases the frequency, but the shift due to Fe^{3+} is more important than this due to Al. Table 2 presents some of these attributions.

Table 1 (from ref. 7). Assignments of trioctahedral OH stretching frequencies in phlogopite and biotite

Vibration frequency (cm^{-1})	Occupation of closest three octahedral sites
3712	Mg Mg Mg
3696	Mg Mg Fe^{2+}
3680	Mg Fe^{2+} Fe^{2+}
3664	Fe^{2+} Fe^{2+} Fe^{2+}
3668	R^{3+} Mg Mg
3652	R^{3+} Mg Fe^{2+}
3636	R^{3+} Fe^{2+} Fe^{2+}

R^{3+} = Al or Fe^{3+}

Table 2. Assignments of dioctahedral OH stretching frequencies in various micas

Mineral	Vibration frequency (cm^{-1})	Occupation of closest octahedral sites
Phlogopite	~3625	R^{2+} R^{2+} V
Biotite	~3600	R^{2+} R^{3+} V
(from ref. 7)	~3560	R^{3+} R^{3+} V
	3534	Fe^{2+} Fe^{3+} V
	3557	Mg Fe^{3+} V
Celadonite	3577	Fe^{2+} Al V
(from ref. 3)	3602	Mg Al V
Biotite	3550	Fe^{3+} Fe^{2+} V
(from ref. 3 and 5)	3600	Al Fe^{2+} V
	3620	Mg Al V
R^{2+} = Mg, Fe^{2+}	R^{3+} = Fe^{3+}, Al	V = Vacancy

Anyway, whatever is the elementary mechanism involved in weathering, namely:

a — swelling without any modification of the layer
b — loss of interlayer cation + ferrous iron oxidation
c — loss of hydroxyl proton + ferrous iron oxidation
d — loss of octahedral iron without ferrous iron oxidation
infrared spetroscopy can give a very valuable information.

The simplest phenomenon is swelling without change in layer structure; two different behaviours can be expected according as trioctahedral or dioctahedral OH are concerned. Since trioctahedral OH are nearly perpendicular to the basal plane, they interact with the closest interlamellar species, the K ion. This interaction appears clearly when comparing stretching frequencies of structural OH bound to 3 Mg ions in talc and phlogopite: in the latter case OH absorbs about 36 cm^{-1} higher than in talc which illustrates the influence of the force field originating from K and increasing the frequency of the OH vibrator. When K is expelled from the ditrigonal cavity, the interaction decreases, and we have shown *(Chaussidon [1, 2])* that K — depleted biotites or phlogopites in Na hydrated form show a global shift towards low frequencies in agreement with the preceding remark. This effect is reversible with water content and in the dehydrated samples one tends to restore a force field similar to this of unaltered mica, leading again to an increase of absorption in the high frequency region. As far as no oxidation occurs, we have shown that the total integrated absorbance of OH stretching vibrations was kept constant and that spectra could be described by the overlapping of two systems in equilibrium characterised by the presence of an isosbestic point.

With dioctahedral OH a reverse effect should be expected theoretically. In fact, in our experiments it has never been observed probably because of the strong attraction between K and the free pair of hydroxyl oxygen atom which prevents the expulsion of K facing a dioctahedral OH, at least in the K depletion levels which were reached. However, it has been shown that alteration induces an important accessibility of dioctahedral OH to the interlayer environment, since a few contacts with D_2O vapour at room temperature lead to a strong deuteration of structural hydroxyls.

If one turns now to weathering mechanisms involving points b, c or d, the following modifications of the spectra can be expected schematically:

b — the absorption should increase in frequency domains characteristic of Fe^{3+} and decrease in regions characteristic of Fe^{2+}. The spectrum will shift towards low frequencies, and if one follows *Vedder*'s hypothesis the resolution should decrease because of the increase in half band width when Fe^{2+} is substituted for Fe^{3+}. The total integrated absorbance should not decrease for the OH content remains constant.

c — the same features as above should be observed. However in this case the total integrated absorbance should decrease since it is assumed that OH groups are lost.

d — this mechanism corresponds to the creation of vacancies in the octahedral layer. In these conditions, the ratio of dichroic absorption to non dichroic absorption should decrease.

Practically, all the quantitative aspects quoted above need very careful experiments, in which the orientation of the mica crystal in the infrared beam must be well known. Now, if it is easy to keep intact a flake which has not undergone a too severe alteration, oxidation and loss of protons create very often a physical modification of the sample which breaks and delaminates. One understands then why the spectroscopic study of such mechanisms is difficult.

However, it is possible to observe experimentally each one of these postulated behaviours. Points b and d are evidenced by *Farmer* et al. [*5*]. If oxidation displaces the dichroic bands towards low frequencies, a treatment with hydrazine restores the high frequency absorption which indicates clearly that Fe^{2+} oxidation has the expected effect. Simultaneously, when oxidation is obtained by a strong treatment by H_2O_2 for instance, N_2H_4 does not reduce totally Fe^{3+} and one observes an increase of vacancy bands absorption.

Point c can be illustrated by *Vedder*'s results *(Vedder* [7]*)* who oxidises the mica by thermal treatments. If one assumes that bands due to one or two Fe^{2+} (plus Mg) transform in the corresponding bands with Fe^{3+}, bands remaining after oxidation should be due principally to 3 Mg – OH, 2 Mg Fe^{3+} – OH or Mg 2 Fe^{3+} – OH groupings. Qualitatively, experimental observations are in agreement with theoretical considerations. Quantitatively, *Vedder* could not detect any change in 2 Mg Fe^{3+} – OH absorption, as compared to fresh mica, which indicates very likely that oxidation is going with a decrease of structural OH content.

The loss of dioctahedral OH in oxidation by thermal treatment has been also well observed. *Vedder* has shown that in a fresh mica the vacancy OH absorption is stronger with electric vector of the radiation polarized along a axis of the mineral than with electric vector polarized along b axis. This relative importance is inversed when the crystal has been heated to ~ 600 °C. This phenomenon is attributed to a preferential condensation of two OH groups whose projections on the a b plane are parallel to a axis. As the maxima frequencies with polarization parallel to a or b axis are not the same, it is possible also that this effect is due to a preferential distribution of divalent and trivalent ions in the crystallographic sites of the octahedral layer, which could explain that heating affects first vacancy OH associated to Fe^{2+} *ions.*

It can be remarked that these studies concern generally experimentally altereted micas. The case of naturally weathered minerals is more difficult to study because in addition to the possible simultaneous existence of several elementary mechanisms invoked, it is not easy to control all the parameters required for the obtention of very clear spectra. In spite of interesting works published in this field, one can think that the infrared spectroscopy has still to give numerous new informations.

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Potash in Feldspars

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Summary

In the present short review over potash in feldspars a description of the feldspars composition and structure is followed by a discussion of their physical and chemical weathering under ordinary conditions. The chemical breakdown of the 3-dimensional potash feldspar lattice seems to start by diffusion – and exchange reactions whereby K^+ is substituted by H_3^+O from the solvent. During this stage of incongruent dissolution a protective cower forms. The entrance of H_3^+O presumably weakens the feldspar structure with the result that aluminium and silica is released. The weathering of feldspars is accelerated when the temperature and hydrogen ion activity of the solvent is raised. Nevertheless, potash feldspars will resists boiling with 6 N HCl and in soils they weather very slowly. They are found in some Danish soils deposited about 100000 years ago and microcline generally makes up several per cents of our soils sand- and silt-fractions. It represents a rather useless potash reserve.

1. *Introduction*

Marshall [7] states that 'the predominance of the feldspars among minerals of the lithosphere makes their disappearance by weathering quantitatively the most important chemical reaction since solidification of the earths crust'. In most places this process is far from finished. *Tovborg Jensen* and *Krogh Andersen* [5] found 5–15 per cent of feldspars – mainly potash feldspar – in sand- and silt-fractions of representative Danish soils, and *Rasmussen* and *Tovborg Jensen* [10] found that Danish soils generally contain more than 1 per cent K. This great potash reserve mainly occurs as a constituent of feldspars. Its availability and value therefore depends on the properties of potash feldspars.

2. *The composition and structure of feldspars*

The inertness of feldspars may be explained by their hardness (H = 6) and their composition and structure. These aluminium silicates possess a three-dimensional framework structure, built up of SiO_4 – and AlO_4-tetrahedres. For every 4 tetrahedres – or 8 oxygen atoms – is found 1 extra cation which may be either K^+, Na^+, Ca^{++} or Ba^{++}. Dependent on the charge of this ion the proportion between aluminium and silicon varies between 1:3 and 2:2.

The feldspars structures have been admirably explained by *Taylor* [12]. Their essential feature is rings of 4 tetrahedral groups bound together in parallel zig-zag-formed chains which again are interlinked at regular intervals. The intervening spaces are occupied by the alkali or alkaline earth cations, which in this position coordinate with 7—9 oxygen atoms.

Depending on the size of these metal ions the chains may be more or less contracted and distorted. Feldspars with big ions (K^+ and Ba^{++}) tend to be monocline, Na^+ and Ca^{++} feldspars tricline. With a certain content of the divalent metal ions the c-axis of the crystals unit cell will be doubled.

The feldspars are never the 'pure' minerals indicated by the formulas $KAlSi_3O_8$ for sanidine, orthoclase and microcline, $NaAlSi_3O_8$ for albite, $CaAl_2Si_2O_8$ for anorthite or $BaAl_2Si_2O_8$ for celsian. Besides their characteristic alkali or alkali earth cation they always contain appreciable amounts of one or more of the others. But differences in the ions size and charge may limit the possible ratios of combinations especially if the feldspars crystallized at low temperature i.e. below 500 ° C *(Barth [1])*. Low temperature potash feldspars only contain little Na^+ or Ca^{++} — and vice versa — and in high temperature feldspars a surplus of ions with wrong sizes tend to congregate in zones. Through such exsolution processes new crystals — perthites — may be formed. An example is perthites of $NaAlSi_3O_8$ in sanidine. The plagioclases may be said to represent a complete series of feldspars with the end members albite and anorthite. However, it has been found that this series covers several domains with different feldspar structures.

Low temperature potash feldspar (microcline) also shows a high degree of order in the distribution of AlO_4- and SiO_4-tetrahedres. The high temperature form (sanidine) in this respect is characterized by nearly complete randomness and orthoclase takes up an intermediary position. This kind of disorder will not change to order when the feldspars are cooled down but this is thought to be of only minor importance for the minerals stability since both AlO_4- and SiO_4-tetrahedres may be distorted by the electrostatic forces from the mono- and divalent metal ions.

3. *The processes of feldspar weathering*

The mechanism of feldspar weathering and dissolution is not well known although it has been studied by many scientists. These minerals react slowly at ordinary temperature but long lasting experiments have given good results. More than 40 years ago *Tamm [11]* carried out such experiments. By using the best physico-chemical methods then known he studied the physical disintegration and the chemical weathering and dissolution of feldspar lumps which for some weeks were shaked with water or with diluted acids to keep the suspension within chosen pH-limits. When pure water was used as solvent pH of the suspensions rapidly rose and finally reached values about 11. At the same time K^+-ions went into solution.

Tamm showed that the reactivity of the feldspars under such circumstances varied with the amount and fineness of the clay-size material formed by shaking the coarse feldspar lumps. Thus the initial weathering of feldspar proceeds by surface reactions in which K^+ is displaced by H^+. *Tamm* also demonstrated that in this initial stage will the feldspars dissolve incongruently, the dissolution of silica — and in neutral or alkaline suspensions also aluminium — lagging behind that of potash. In this way the feldspar surface is coated with a protecting layer and the minerals reactivity reduced.

In accordance with this *Rasmussen* and *Tovborg Jensen [10]* found that under prolonged electrodialysis did pulverized microcline only release appreciable amounts of potash in the first part of the dialysis period. During the first 3 days more potash was dissolved than in the 4 weeks to follow and after about 1 week only very small and seemingly constant amounts were daily released.

Experiments which have helped to a better understanding of the weathering processes have been conducted by numerous investigators besides *Tamm*. Only a few may be mentioned here. *Correns* and *v. Engelhardt* [*3*] followed the decomposition of finely ground potash feldspars suspended in solutions with fixed pH-values. The dissolved feldspar components were regularly removed by dialysis or ultra filtration. Their results show that parts of the feldspars go into true solution and confirms that the feldspars dissolve incongruently during the first stages of chemical attack when its breakdown proceeds at its highest rate. The protective layer thereby formed varies in composition according to the systems pH-value. Its molar ratio of SiO_2 to Al_2O_3 was found to have its minimum value in nearly neutral solutions. In agreement with *Tamm, Correns* and *v. Engelhardt* found this minimum value to be 5–6. From a certain stage the feldspars dissolved almost congruently so that it could be concluded that the coating from now on would not grow in thickness or alter in composition.

Later *Huang* and *Keller* [*4*] have shown that the dissolution rates of the different feldspar components will also depend on the complexing properties of the solvent.

The displacement of K^+ by H^+ or H_3O may partly take place through exchange reactions. Already *Tamms* results indicated that for potash feldspars may this process be reversible, and *Nash* and *Marshall* [*8*] found that on fresh feldspar surfaces may exchange reactions between H^+ and metal ions proceed. It seems that only very thin surface layers react in this way. Such exchange reactions which apparently took place in deeper layers might show character of fixation processes since the calculated bonding energies of the metal ions varied according to the feldspars composition and lattice structure.

The substitution of K^+ by H_3O seems to weaken the feldspar lattice. *Bondam* [*2*] found from X-ray measurements that the attack by H_3O was accompanied by a slight expansion of the lattice in feldspar surface layers. He also obtained infra-red absorption lines that might indicate the presence of hydrogen bonds presumably between absorbed H_3O and surrounding lattice-bound oxygen atoms. Thus absorbed H_3O-ions may facilitate and be used in hydrolytic reactions by means of which Al-O-bonds are thought to be ruptured. The aluminium thereby goes from the 4-coordinated to a 5- or 6-coordinated state with the result that it will be expelled from the feldspar lattice structure. At the same time Si-OH-groups are thought to be formed.

Several scientists have stated that during chemical weathering the feldspars tetrahedral framework may not dissolve completely but only be broken down to small bits which after slight alterations may form building stones in the neogenesis of crystalline silicate minerals. This question will not be discussed here. It may be mentioned however, that in most of the weathering experiments carried out at ordinary temperature formation of well crystallized silicate minerals have not been reported. However, precipitates with a more or less ordered, clay-like structure have been reported, e.q. by *Bondam* [*2*] and *Lerz* and *Borchert* [*6*].

4. *The availability of soils feldspar potash*

All experimental evidence shows that the chemical breakdown of feldspars accelerates with raising temperature and hydrogen ion activity of the solvent. The rapid weathering of feldspars reported by *Pedro* [*9*] may be partly explained by the extraction temperature, which was kept at 65 °C. It is also evident that feldspars show a high initial reactivity even in neutral solutions. However, these facts should not lead to optimistic wievs about the availability of potash in feldspars. To illustrate the inertness of these minerals I may mention that in our laboratory we found that pulverized microcline did only lose 2 per cent of its potash when boiled with 20 per cent HCl for 1 hour.

The inertness of feldspar minerals is also borne out by mineralogical studies of soil profiles. Old and thoroughly weathered tropical soils may have lost all their feldspars but under Danish climatic conditions these minerals have persisted in sand- and silt-fractions of soils from glacial drifts even of Riss age. However, they may have begun to diminish and be sorted out. Thus *Tovborg Jensen* and *Krogh Andersen* [*5*] found microcline to be present in much greater quantities than plagioclase and soils formed from Riss glacial drift were relatively poor in feldspars. Surface layers of these old deposits contained almost no plagioclase even if such minerals were found in the deeper strata. In soils formed from drifts of Würm age no such difference between surface and underground was found. However, *Tovborg Jensen* and *Krogh Andersen* calculated that if the young and the old deposits at the time of deposition had the same mineralogical composition, the present difference would only correspond to the weathering of about 1 kg potash feldspar on each hectare annually.

It seems safe to conclude that in our soils the feldspars represent a big but rather useless potash reserve.

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Mineral Reserves of Potassium in Irish Soils and their Release

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Summary

The nature of the K reserves of 26 Irish soils representing the principal mineral soils of the country was determined. Feldspars and micas were the only K-bearing minerals detectable in the soils and the contribution of each in the different size fractions was determined by selective dissolution. The different mineralogical parameters of the soils were related to their ability to supply K to grass after continuous cropping without K fertilisation.

Mica was the principal K bearing mineral in all except the granite derived soils; mica content ranged from 2 to 18 per cent of the soils studied. K feldspars were abundant in granite derived soils and occurred also in significant quantities in some limestone drift derived soils which appear to have some igneous rock influence. Mica edge surface was the only mineralogical parameter which related to the ability of the soils to supply K to grass after 4 years continuous cropping without K fertilisation.

Introduction

Large reserves of potassium occur in soils in mineral form — the average K_2O content of soils is about 1.4 per cent [*Rich, 1968*]. Irish mineral soils contain 0.2 to 3.5 per cent K_2O [*Walsh, 1970*] mainly in the form of micas and feldspars. The weathering of K bearing minerals has been extensively reviewed [*Reitemier et al., 1951; Rich, 1968*]. K feldspars are relatively resistant to weathering; micas weather more readily and sometimes can supply the entire plant needs for potassium. Weathering of micas and feldspars depends on mineral properties and the environment. Release of potassium from micas occurs at the edges of the platelets and a relationship between the edge mica surface of soils and K release seems likely.

The purpose of this study was to assess the nature of the K reserves in Irish soils and to relate them to the ability of the soils to supply K to grass.

Materials and Experimental

Soils from 26 experimental sites representing the principal mineral soil types in Ireland were studied. The soils had a wide range of parent materials and K contents. Some of their properties are presented in Table 1.

Table 1. The soils studied

Site	Parent Material	Texture	Soil Type
A, B, C, D	Old Red Sandstone/Shale	Loam	Acid Brown Earth
E, S	Shale	Clay loam/Loam	Acid Brown Earth
F	Morainic Sand	Sandy Loam	Brown Podzolic
G, H, I, O, P, Z	Limestone Drift	Loam	Grey Brown Podzolic
J, K	Granite	Sandy loam	Brown Podzolic
L	Mica Schist	Loam	Brown Podzolic
M, N, Q, R	Limestone Drift	Sandy loam	Brown Earth
T, U	Silicious Limestone Drift	Clay loam/Loam	Gley
V, W, X	Coal Measure Shale	Loam	Gley
Y	Marine Glacial Drift	Clay loam	Gley

The experiment included treatments of 0, 90, 180, and 310 lbs K per acre annually on grass plots, each treatment being replicated 4 times. Four cuts of grass were taken each year for 4 years and removed from the plots. The K content of each cut was determined. Soil samples from each of the sites were fractionated into two sand-sized, three silt-sized, and two clay-sized fractions after removal of carbonates, organic matter and free iron oxides [*Jackson, 1956*]. Mica and K feldspar content of the fractions were determined by the pyrosulphate fusion method [*Kiely and Jackson, 1964*]. X-ray diffractograms of Mg and K saturated samples of the fractions were obtained using CoK α-radiation. Mica edge surface was calculated based on figures in *Jackson* [*1956*].

Results and Discussion

The K_2O content of the soils ranged from 0.36 to 3.01 per cent (Table 2) with a mean value of 1.35. It was determined largely by parent material. Mica was the dominant K bearing mineral in all except two granite derived soils; it ranged from 2 to 18 per cent of the soils and increased with decrease in size fraction. K feldspar content ranged from 0.4 to 16.1 per cent of the soils; it exceeded 5 per cent only in the granite derived soils. The area of mica edge surface, a measure of the mica content and its size distribution, ranged from 4.8 to 21.8 sq m/100 g in the soils.

In the first year of continuous cropping dry matter yields on plots which received no K fertiliser ranged from 6687 lbs per acre on the heavy textured Gley soils T and U to 8473 lbs per acre on the loam texture limestone drift derived soils (G, H, I, O, P, Z). On the fourth year of continuous cropping yields were lower and ranged from 4292 lbs per acre on the granite derived soils (J, K) to 8323 lbs per acre on the limestone drift derived soils (G, H, I, O, P, Z). The response to added K in the first year ranged from 3 per cent on the Gley soils (T, U) to 24 per cent on the light textured limestone drift derived soils (M, N, Q, R); the per cent response increased markedly in the fourth year of continuous cropping ranging from 21 per cent on sites T, U, Y to 118 per cent on the granite derived soils (J, K). Soil physical properties and available soil moisture appear to have affected dry matter yields significantly; the heavy textured Gley soils and to a lesser extent the sandy loam soils gave lowest dry matter outputs.

Release of K to grass in the 4th year of continuous cropping without K ranged from 26 to 151 lbs per acre. When 310 lbs K per acre were applied 3 of the soils supplied less K to grass than that applied as fertiliser while the remaining soils released between 10 and 168 lbs K in excess of that applied. In general the soils which released highest K where no K was applied also released highest amounts of K where 310 lbs K were applied. Of the three

Table 2. Potassium parameters of the soils studied

Site	K_2O Content per cent	Mica per cent	K feldspar per cent	Mica Edge Surface Sq M/100 g	K released lbs/ac K_0	K310
A	1.26	11	0.5	11.8	136	109
B	1.80	16	0.7	18.2	90	94
C	2.05	18	0.7	21.8	—	—
D	2.07	17	2.3	17.8	41	52
E	2.15	18	3.1	15.3	54	67
F	0.77	5	2.8	7.1	39	–46
G	1.69	12	4.2	20.2	90	124
H	1.04	7	2.6	13.7	93	124
I	1.04	5	4.1	11.5	49	83
J	3.01	10	16.1	9.8	26	33
K	2.63	10	13.8	10.2	44	68
L	2.36	15	5.0	8.5	60	14
M	0.80	6	2.0	12.3	39	10
N	0.58	5	1.5	9.4	90	33
O	0.86	7	2.2	15.1	151	119
P	0.91	7	2.0	18.9	87	34
Q	0.48	2	2.1	4.8	33	58
R	0.69	5	2.1	8.5	33	37
S	1.66	15	1.1	14.3	65	56
T	0.61	5	0.6	8.1	57	60
U	0.36	3	0.5	9.2	51	–92
V	1.21	12	0.4	14.3	106	88
W	1.45	14	0.4	21.3	129	–6
X	1.21	11	1.0	16.1	47	96
Y	1.58	11	4.1	20.5	123	24
Z	0.95	7	2.3	21.4	121	168

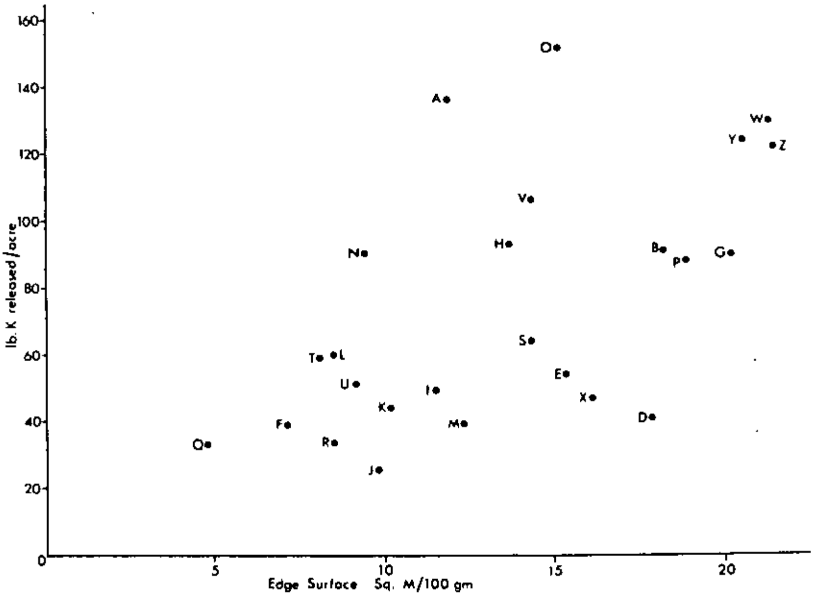

Figure 1. The distribution obtained when mica edge surface was related to K uptake by grass in the 4th year of continuous cropping without K.

soils which apparently fixed K, two had a heavy texture, all three contained vermiculite, and soil F was a sandy soil where leaching of K was likely.

Mica edge surface was the only mineralogical property which related to K uptake by grass. In Figure 1, the K released to grass on the 4th year of continuous cropping without K is related to mica edge surface. The relationship was affected by factors such as species, drainage, and moisture holding capacity which controlled grass yields in some soils and limited K uptake. Differences in growth potential between the sites is reflected in the K removed by grass e.g. sites A and O consistently outyielded the other sites.

K release is significant in most Irish soils even where high K levels are applied. Where no K is applied for 4 years 25 to 150 lbs K per acre is released to grass. Mica edge surface gives some measure of the K supplying power of soils.

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1st Working Session: Some Remarks on the Discussion on Mineralogy of Soil Potassium

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During the past ten years studies about potassium in minerals have been focused on micas and smectites. The most important questions, which are still unsettled, concern potassium fixation, mechanisms of K-depletion and the rate of K-release from micas. The three problems are related to each other.

K-Selectivity

K-selectivity is connected with the geometrical environment of the potassium sites and the energetical situation. External prism faces are not or almost negligibly involved in cation exchange. Since all interlayer sites are assumed to be geometrically equivalent, so far only four different site-types are considered: interlayer sites, sites on edges, on external basal planes, and a series of sites in the wedge-zone of weathered and partially depleted mica particles.

Assuming a pure beidellitic charge type and a random distribution of the excess negative charges onto the oxygens bordering the interlayer region, 10 energetically different interlayer sites have to be distinguished. One of these is equivalent to the sites in micas, another is similar to sites in illites, two further sites correspond to the charge density of K-fixating vermiculites.

Therefore, two main questions arise:

1. is potassium fixation due to sites in the wedge zones only?
2. To what extent do highly charged interlayer sites of smectites and mica-type sites contribute to K-fixation?

Furhter interesting questions seem to me:

a) Dimensions of the wedge zones? Maybe, detailed discussions and statistical treatment of the remarkable pictures of *Graf v. Reichenbach* can give some informations.
b) Determination of the excess charge density and the excess charge distribution. The methods of *Weiss* and *Lagaly* give detailed information about the density and its limits. However, charge distribution and relations to K-fixation need further research.
c) Determination of the ratio of beidellitic and montmorillonitic charges.

The group of Prof. *Henin* is doing excellent work in this field and we do hope that we shall get details in the near future.

K-Depletion

Understanding of the K-depletion of micas is related to the understanding of possible mechanisms. At least four types have to be distinguished:

1. Simple ion exchange reaction, assuming, that the geometrical situation is extremely in favor of potassium ions.
2. Depletion connected with charge reduction via oxidation of octahedral Fe^{2+} to Fe^{3+}. In this case, the depletion should be favored in biotites compared with muscovites. Experimentally, influence of the redox potential E-redox onto the depletion process should be observable.
3. Depletion connected with charge reduction via simultaneous migration of H^+ (or Li^+) into octahedral vacancies.
4. Depletion connected with a temporary charge increase in a transition state, either by reduction of Fe^{3+} to Fe^{2+} in octahedral positions or by extraction of octahedral cations and thereby increase of the number of octahedral vacancies, mainly in trioctahedral micas. Are there any indications of the main factors from experiments at constant pH-value or constant pLi value? Measurements of the activation energy of depletion of di- and trioctahedral micas should elucidate, whether only one mechanism occurs in nature or several mechanisms compete.

Rate of K-Depletion

As far as the reaction rate is concerned, differentiation of chemical and X-ray degree of the reaction is important. Probably both values differ by the contribution of the wedge zone or part of it.

There seems to be no doubt about the unexpected particle size effect due to which the reaction rate decreases with decreasing particle size. Cooperative effects seem to contribute mainly to this influence. Detailed studies on lattice faults are necessary, in order to ensure the particle size effect. New methods for the detection of lattice faults would promote further development.

Mechanistic treatment of the K-depletion points to a strong influence of surface roughness, especially that of the prism faces.

Thus, main questions seem to me:

1. experimental data on differences in the degree of reaction.
   New data would also contribute to the problem of phase definition in transition states of K-depletion.
2. Evaluation of cooperativity factors of the reaction.
3. Demonstration and quantitative determination of lattice faults of micas before, during and after K-depletion.

Report on the 1st Working Session: Mineralogy of Soil Potassium

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1. *Introduction*

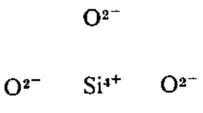
The main lecture and the communications presented an excellent picture of the present knowledge on potassium in minerals.

The release, selection from solution, and fixation of potassium are affected by
- the crystal structure (e.g. three dimensional frameworks, compact or porous, in feldspars and zeolithes; sheets, expandible or not, in micas and certain clay minerals),
- the configuration of the atoms in the crystal lattice (e.g. ditrigonal arrangement of the O atoms around K; orientation of OH groups; site and distribution of charges),
- the morphological properties such as size, shape and surface.

Instead of repeating more details from the reports some *additional informations* may be added especially on
- the chemical bonds in silicates
- the stability of silicates and
- the reactions involved in the chemical weathering of silicates.

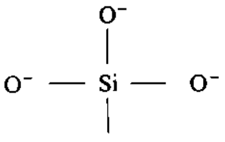
2. *The chemical bonds in silicates*

According to *Pauling* the Si–O bond in the SiO_4 tetrahedron can be described as a resonance bond for which the following structures can be written:



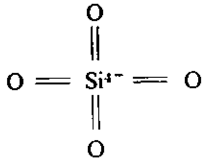
$$\begin{array}{ccc} & O^{2-} & \\ O^{2-} & Si^{4+} & O^{2-} \\ & O^{2-} & \end{array}$$

ionic bond



$$\begin{array}{ccccc} & & O^{-} & & \\ & & | & & \\ O^{-} & - & Si & - & O^{-} \\ & & | & & \\ & & O^{-} & & \end{array}$$

covalent bond
σ-bond

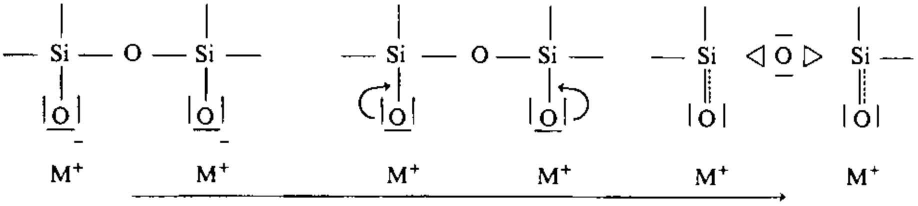


$$\begin{array}{ccccc} & & O & & \\ & & \| & & \\ O & = & Si^{4-} & = & O \\ & & \| & & \\ & & O & & \end{array}$$

double bond
dπ-pπ-bond

From calculations results that the ionic character is about $\frac{1}{2}$ and the double bond character is about $\frac{1}{3}$ for isolated tetrahedra. These values are not constant; they are changed by substituents R surrounding the Si atoms.

If the substituent is an electron donor, the adjacent Si–O bond becomes more polar, if the substituent is an electron acceptor, the adjacent Si–O bond gets more double bond character. Nearly all metal ions (M^+) in the silicate minerals are less electronegative than silicon and behave as electron donors. They consequently cause an increase in ionic character of the Si—O—Si bond and an increase of double-bond character of the adjacent Si—O (—M) bond. This effect is the more considerable the larger the electronegativity difference between silicon and the metal.



decreasing electronegativity of M^+
increasing electron-donating inductive effect of M^+

Since the bond character influences the *bond energy*, substituents also influence the stability of the Si—O—Si linkage. In silicates the Si—O—Si bond is weakend by the electron-donating M^+.

The bond character is also correlated with the *bond length* of the Si—O bond. If the ionic character of the bond is increased, its length is also increased. If the double bond character is increased, the Si—O bond is shortened. While the bond length in quartz (only Si—O—Si linkages) is about 1.60 A, the Si—O distance in silicates varies within the same tetrahedron. The average Si—O distance in many silicates is 1.64 A for the Si—O (—Si) bonds and 1.58 A for the Si—O (—M) bonds.

The electronegativity of the metal ions in the silicates varying within a wide range, the character of the *bonds within the coordination polyhedra of the metal ions*, M—O (—Si) bonds, also varies. It may be more ionic or more covalent.

As the bonds in silicates have only a partly ionic character and as the bond character varies with the chemical composition of the silicates it is certainly not correct to represent the silicates as crystals of ions and to reckon always with the definite ionic radii deduced from really ionic crystals.

3. *The stability of silicates*

In summation of the fundamental chemical facts considered above some principles about the stability of silicate minerals may be stated.

a) The stability increases with increasing degree of condensation of the silicate lattice	↓	orthosilicates chain silicates sheet silicates framework silicates	
b) The stability within a structural group decreases with increasing isomorphous substitution of aluminium for silicon	↓	quartz orthoclase nepheline	SiO_2 $(Si_3AlO_8)K$ $(SiAlO_4)(K, Na)$
c) The stability within a structural group decreases with decreasing electronegativity of the metal ions (increasing electron donating inductive effect)	↓	hypersthene wollastonite	$(SiO_3)_2(Mg, Fe)_2$ $(SiO_3)_3Ca_3$

d) The stability increases also with increasing stability of the metal ion-oxygen polyhedra linking the silicate units.

E.g. Stability increases with increasing M^+-O bond strength ↓

olivine	$SiO_4(Mg, Fe)_2$
zircone	SiO_4Zr

metal	charge	coordination number	M-O bond strength
Mg, Fe	2^+	6	$^1/_3$
Zr	4^+	8	$^1/_2$

In micas, the potassium is surrounded by 12 oxygens. In the actual ditrigonal arrangement of the tetrahedra six oxygens are at a smaller and another six oxygens are at a greater distance from the potassium. The coordination number of potassium versus oxygen is considered to be 6. Therefore, the K—O bond is shorter and stronger as it would be in an ideal hexagonal arrangement of the tetrahedra. The question is open how far the actual charge distribution must be taken into account. Apparently the oxygens in Si—O—Al groups contribute more to the binding of the potassium ions than the oxygens in Si—O—Si groups. However the ditrigonal arrangement would result in a shortening and strengthening of K—O bonds even if only Si—O—Al groups contributed to the binding of K.

Beside charge and coordination number, size and other factors play a role. Their influence may overshadow the differences arising from different structure.

4. *The chemical weathering of silicates*

4.1 *General considerations*

The release of potassium from minerals may be considered as a process of weathering. In weathering there is *seldom one single process* which performs the whole decomposition, but it is possible to distinguish theoretically the reactions involved, e.g. hydration, hydrolysis, oxidation-reduction, chelation.

The *primary chemical attack* may be followed by a rearrangement in the remaining crystal lattice conducing to a new stable mineral.

Products formed by primary weathering processes may react further with one another or with other reactants, at the original site of degradation or elsewhere. In this *secondary weathering,* also different processes may be involved: hydration, condensation, precipitation, adsorption, ion exchange, oxidation-reduction, chelation. Thereby new minerals may be formed.

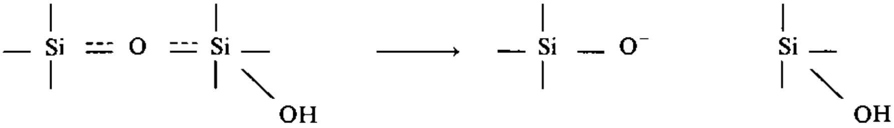
Like other chemical reactions chemical weathering is subject to the *laws of chemical equilibrium.* Thus, agents must be added and products must be removed to avoid equilibrium which would stop any further degradation. In weathering water is the most important transport medium but it is also important as a solvent and agent.

4.2 *Cleavage of Si—*O—M and Si—O—Si bonds

The release of potassium in the weathering of silicates is often connected with a destruction of the mineral lattice. Thereby Si–O–M and Si–O–Si linkages must be broken. The cleavage is performed mainly by hydrolysis or chelation.

In the *acid hydrolysis* a proton is coordinated to the O of Si—O—M linkages (M = Fe, Mg, Al). The M—O bond is split, a Si—OH group is formed and the metal ion immediately reacts with OH or the anion of the acid. The Si—O—Si bonds are more ore less stable against acid hydrolysis. Since the oxygen lone-pair p electrons are partly engaged in bonding with the silicon, they are scarcely available for the coordination of the proton.

The Si—O—Si linkage is split rather by the coordination of a hydroxyl ion to the silicon atom and the subsequent cleavage of the Si—O bond *(base catalysed hydrolysis).*



The coordination of hydroxyl increases the coordination number of the silicon in an intermediate state. The silicon may exhibit a coordination number greater than 4 with respect to OH^-, since the OH^- is similar to the F^- which forms a very stable SiF_6^{2-} complex ion. The formation of such compounds requires the use of the d-orbitals of silicon. Since, however, never more than two such orbitals may be used, the double-bond character of the Si—O—Si bond is decreased. For stabilization, either the OH^- is removed or the Si—O—Si bond is broken.

Powerful agents in the degradation of the silicates are the *chelating compounds*. Oxygen is the most important donor atom (beside F), able to combine with any metal ion having a charge more than one. The others, including S and to some extent N, are coordinated only to B metal cations (having 18 outer electrons). Since the most abundant cations in silicates are A metals (with noble gas electronic structure), e.g. Al, Mg, Ca, the chelative dissolution of silicates may primarily be achieved by oxygen-donor chelating agents with ligand groups such as phenols, aliphatic or aromatic acids and ketones, for example tartaric acid, citric acid, ketogluconic acid, pyrocatechol, salicylaldehyde, salicylic acid.

Chelating agents of this kind are abundant in soil organic matter. Such compounds are excreted directly by plants and microorganisms; to a great extent, however, they are formed by the conversion of the dead organic matter in soil.

Particularly efficient chelating agents in the decomposition of silicates are the o-diphenols (o-dihydroxybenzene derivatives). They not only form stable chelates with many polyvalent cations such as Al, Fe, Ti, but also with Si. Whereas the o-diphenols chelate Si only in an alcaline medium, tropolones (compounds with a pseudoaromatic and planar seven-membered unsaturated carboxylic ring) with an O and an OH group in o-position at the tropolone ring form stable chelates with Si in an acid medium (pers. comm. by Prof. A. Weiss). Such a tropolone is for instance puberulic acid, a mold metabolite.

4.3 *Energetical conditions*

As has been stated before different reactions contribute to the chemical weathering of minerals. These reactions may go on all at the same time, but in a given microsituation there is a sequence of reaction determined by the *energetical conditions*.

5. *Conclusion*

In conclusion it may be stated that the study of potassium in minerals has been more and more diversified and refined but the today's detailed picture was obtained only by the combination of chemical, physico-chemical, crystallographical and morphological methods.

Now a lot of work remains to be done to make fruitful all these detailed knowledges to agricultural science and practice.

Acknowledgements

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2nd Working Session:

Ion Exchange System of the Soil

Chairman of the Session:

Dr. T. WALSH,
Director of the Agricultural Institute of Ireland, Dublin; Member of the Scientific Board of the International Potash Institute.

The Cation Exchange System of the Soil

Prof. Dr. *A.C. Schuffelen*, Laboratorium voor Landbouwscheikunde, Wageningen/The Netherlands

Summary

Originally the opinion was held that the adsorbing material of soil consisted of amorphous compounds. These compounds would attract a layer of potential determining ions (OH^-), which in turn would adsorb a layer of counter ions. Subsequently it appeared that most of the inorganic soil colloids (clay minerals) had a crystalline structure. They owe then negative charge to isomorphic substitutions. Humus is amorphous, it owes its negative charge to the dissociation of the cations. The layer of counterions has a diffuse character. The earliest studies on the equilibrium between the solution and the adsorbing material limited themselves to drawing up empirical formulas. Wherein always only one type of ions is considered. Later formulations, with a thermodynamical background, are based on exchange processes. Here, at least two different kinds of ions are involved.
In recent years special attention was drawn to equilibria in systems, whereby ions of different valence were included. Herefore the formula of *Gapon-Bolt* is often used. For the adsorption of potassium ions strong specific forces occur besides the electrostatic forces. In the case of illite it was possible to distinguish three kinds of adsorbed potassium ions viz potassium on the planar surfaces, on the edges and inter lattice potassium with an increasing force of binding in the same sequence. The not constant relationship between the composition of the soil solution (intensity factor) and the adsorbed amount (capacity factor) makes it very difficult to assign an agricultural interpretation on these values.

Introduction

For good growth, a crop requires a certain amount of nutrient elements. Although the inorganic compounds supplying these elements have to be absorbed from the soil in rather large quantities, they should not be present in too high concentrations, because these might lead to salt damage.
Fortunately a number of buffer-systems is available in the soil to regulate the concentration of nutrient ions in the soil solutions.
The nitrate, sulphate and partly also phosphate anions for instance are buffered by the dead and living soil organic matter or the so-called anion buffer. By formation and decomposition of various organic compounds the concentration of these anions in the soil solution is maintained within certain limits. Phosphate ions however are mainly buffered via a system of non-soluble phosphates. By dissolving and precipitating these compounds (constant solubility product) a certain and in principle constant concentration of phosphate ions is maintained in the soil solution.
Finally the cations, including potassium ion, are buffered mainly by a system of exchange reactions. These reactions control the equilibrium between the solid and the liquid phases of the soil and so reduce the fluctuations in the concentration of cations in the soil solution.
These three buffer-systems are of great importance to elimination of high concentrations, immediately after application of fertilizers and to supplying ions to an exhausted soil solution.

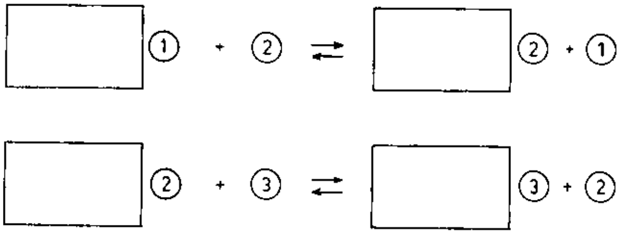


Fig. 1

In this paper only the last mentioned system of ion exchange will be discussed in detail. The phenomenon of adsorption of cations – now also rightly called cation exchange – was discovered in the last century. In the middle of that century it was described in detail by *Way*.

When a soil sample is shaken with a salt solutions it appears that the concentration of the anion of this salt remains practically unchanged or changes only to a slight degree. On the contrary, the concentration of the salt cation drops considerably. This decrease in the concentration of the cation runs parallel with an increased concentration of another cation which apparently originates from the soil. The described process appears to be reversible (figure 1).

The phenomena of ion exchange still form a subject of intensive studies by soil scientists and chemists with special interest in adsorbents. The research is mainly concentrated on the following problems: the properties and nature of the adsorption material, the nature and location of the charge, the empiric and thermodynamic description of the equilibrium. For this a number of models have been set up, which can be used satisfactorily for practical purposes.

The adsorbing material

Phenomena of adsorption and ion-exchange take place mainly on the surface (either internal or external) of the particles of the solid phase. As per unit of weight small particles have the largest total area, they also have the highest adsorption capacity. Accordingly, the soil scientist soon recognizes the clay fraction ($< 2\mu$) as the inorganic part of the soil adsorption complex. Besides, also the soil organic matter (humus) shows the capacity of ion exchange. Until about 1930 both substances were considered amorphous.

According to this conception, the clay fraction of a soil would consist of a mixture of gels of positively charged iron hydroxyde, aluminum hydroxyde and the negative silica oxyde. These simple gels would occur in mixtures with different proportions, mostly with a surplus of negative charge. The magnitude of this surplus charge must be closely related to the mixing ratio of the gels and so lead to differences in the adsorption capacity of the gel. Amorphous permutites were mainly used by *Wiegner* and his school as models for the study of exchange-reactions, which are important in the soil. It was *Mattson* and his co-workers who have prepared a large number of different gel mixtures. They have extensively studied their properties using them as models for the soil colloids.

In 1928 it was shown by *Hendricks* that the soil colloidal fraction was crystalline. This discovery opened the way for the development of the theory of clay minerals. Beside the fundamental work carried out by *Hendricks, Grimm, Bragg, Hoffmann, Edelman* and *Favejee,* many other scientists have contributed to the development of our knowledge in this field. It appeared that clay minerals occur in many variants viz. in a rather pure form, in a strongly contaminated form and many intermediate forms. From the point of view of plant nutrition all these forms may be reduced to three groups with similar properties. The montmorillonite group containing the clay minerals with a high exchange capacity and the property of swelling. The kaolinite group with a low exchange capacity and the property of not swelling. Finally the group of illite or mica having a moderate exchange capacity, with little tendency to swell and a specific binding force for potassium ions. The clay minerals consist of crystalline plates. The thickness of these plates varies between 10 Å in the case of a well peptised montmorillonite and 2000 Å in a well crystallised kaolinite. The length of the plates varies between 500 Å and 20,000 Å.

The fraction $< 2\ \mu$ consists, beside the clay minerals also of hydroxydes of iron and aluminium and hydrated silicic acid. These compounds are either crystalline or amorphous. Amorphous or at least poorly crystallised mixtures of sesquioxydes and silicic acid such as allophane, can also be found in this fraction.

However, in quantitative sense they only play a part of minor importance in soils used for agriculture.

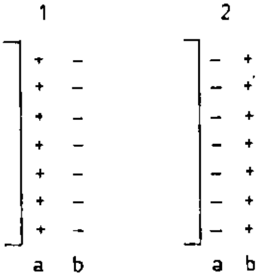
The humus compounds in the soil do not show any distinct crystalline structure. This could indeed hardly be expected, because of the fact that humus must actually be considered as a polymerisate of polyphenols, aminoacids, aldehydes and lignine fragments coupled at random in different quantities and proportions *(Swaby).*

The charge of the particle

Initially studies on the nature of adsorption phenomena were carried out with AgI-sol as an object of study. The field of research was extensively studies by *Kruyt* and other scientists from his school. After thorough investigation, it was found that in the adsorption by AgI-particles, two layers had to be distinguished. There is an inner layer of ions specifically bound at the surface of the particle. These are the potential determining ions, which give to a AgI-particle either a positive charge (when Ag^+-ions are adsorbed) or a negative one (when I^--ions are adsorbed). This inner layer is enclosed by a second layer of ions having a charge opposite in sign – the so-called counterions. This layer neutralises the charge of the particle. The ions of this layer are not specifically bound and may be replaced by other ions (figure 2).

The layer of the potential determining ions and the layer of the counterions form together the double layer. It is mainly the spatial arrangement of the counterions and its consequences, which form the topics which are studied in detail in colloid chemistry. Models such as condensor *(Helmholtz),* as diffuse layer *(Gouy-Chapman)* and a combination of the two *(Stern)* have been used.

Studied of structure amplified by chemical analysis, soon led to the conclusion that there were no reasons to assume the presence of potential determining ions in the adsorption phenomena of clay minerals. An attempt made by *Wiegner* and *Bär* and *Tendeloo* to introduce the OH^--ion as such, met with no response. In fact, a double layer does not exist in the case of clay minerals; there is only a layer of counterions. Nevertheless it is still a



1. positive charged particle, 2. negative charged particle
a. potential determining ions, b. counter ions

Fig. 2

common practice to use the term double layer also for colloids which do not possess a layer of potential determining ions.

The negative charge of clay minerals is caused by two different phenomena. For its major part it is a consequence of isomorphic replacements in the crystal lattice and it is for a minor part caused by the dissociation of acid groups, giving off H^+-ions and so leaving behind a negative surface charge. During the formation of clay minerals a number of lattice sites intended for Si^{++++} become occupied by Al^{+++} and sites destined for Al^{+++} become occupied by Mg^{++}. A consequence of this replacement is a surplus of negative charges (surplus of electrons), manifesting themselves as a surface charge. Through attractions of cations the particle becomes again electrically neutral. The attracted ions form the counterions of the clay mineral. Similar to the counterions in the double layer of a AgI-particle these ions are arranged in a certain order. When isomorphic replacement takes place within the crystal (Al^{+++} by Mg^{++}) the electric charge is contributed in a rather diffuse way, over the surface of the particle. Replacement on the surface of the crystal lattice (Si^{++++} by Al^{+++}) leads to a 'patchy' charge. This opens the possibility of a more specific local binding of the counterions.

The amount of charge of the clay mineral, caused by isomorphic substitution is independant from the pH-value of the medium. This part of the exchange capacity of the soil is constant.

The second type of electric charge is the effect of a dissociation of H^+-ions, from the $\equiv Si-OH$ and possibly also from $= Al-OH$ groups situated on the edges of the clay mineral whereby $\equiv Si-O^-$ and $= Al-O^-$ are formed respectively. This dissociation, comparable to that of the weak acids, only becomes significant in neutral or alcaline range where one has to deal with high values of pK. The adsorption capacity of this part of the clay mineral is thus dependant on the pH value. In general it is of little importance as compared with the total adsorption capacity of well crystallised clay minerals and does not exceed about 5 per cent of its total value. In case of mixed gel compounds like allophanes, it may however, amount to about 50 per cent of the total adsorption capacity.

Adsorption of cations by soil organic matter resembles more the process of salt formation as compared with the above mentioned adsorption phenomena. The non-soluble humus contains, at its internal and external surfaces a certain number of $-COOH$ and $-OH$ groups. By giving off H^+-ions they confer a negative charge to a humus particle which

Table 1.

Adsorbens $< 2\ \mu$	Spec. surface	Charge density	CEC
Kaolinite	1 – 40 m^2/g	2×10^{-7} me/cm^2	0.002 – 0.08 me/g
Illite	50 – 200 m^2/g	3×10^{-7} me/cm^2	0.15 – 0.60 me/g
Montmorillonite	400 – 800 m^2/g	1×10^{-7} me/cm^2	0.40 – 0.80 me/g
Humus	> 800 m^2/g	1–3 $\times 10^{-7}$ me/cm^2	1.0 – 3.0 me/g

attracts counterions or leads to formation of salts with cations. The COOH-groups become active already at pH-values below 6, for the dissociation of OH-groups pH-values above 7 are required. For the soil organic matter the amount of exchangeable cations depends fully on the acidity of the medium. The adsorption capacity increases with the pH-value.

The exchange capacity of clay minerals and the humus is determined by the two following properties: the specific surface area and the charge density of the surface. The product of both these quantities is the cation exchange capacity.

Some data with regard to this capacity is given in table 1.

The exchange capacity of a soil is determined by the amount and nature of both adsorbing components viz the clay minerals and the humus.

In general, a soil with a high exchange capacity will be chemically fertile, often its physical fertility will be poor. Broadly speaking, a soil with a low exchange capacity will have the reverse properties.

Empiric formulations

From the very beginning of the research on the properties of soil colloids attempts have been made to trace the relationship between the amount of adsorbed ions and their concentration in the adjacent solution. Naturally the line one took in the beginning was quite empiric. Experimental research steadily showed that at low concentrations in the solution, the amount of adsorbed ions was approximately proportional to the concentration. At high concentrations of the cation in the solution no relation between the above quantities could be observed. A maximum value seemed to exist for the adsorbed cations, figure 3 illustrates the existing relation.

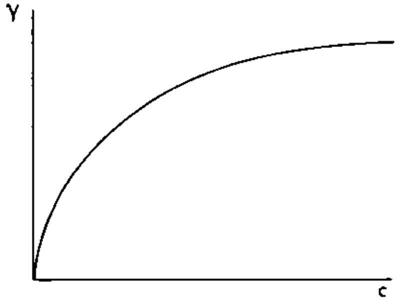


Fig. 3 γ = adsorbed amount pro unit adsorbens
c = concentration in the solution

This adsorption-isotherm may approximately be described by a logarithmic or hyperbolic function. In the 1930-ties the quantitative descriptions of the equilibrium between the adsorbed ions and the ions in solution were based on these functions. ***Freundlich*** formulated the logarithmic function, ***Langmuir*** and also ***Vageler*** made use of a hyperbole. Several variants of these formulations have also been proposed in the hope that they would lead to a better adjustment to the experiment (***Wiegner, Rothmund*** and ***Kornfeld***). In the meantime most of the original formulations belong to the past.

They have played an important part in the calculation of the adsorption capacity of soil as based on a number of equilibrium-experiments. They may be still used for the inference and formulation of qualitative a semi-quantitative relationships; also as an empiric estimate in order to make accessible more complicated calculations.

Modern formulations

The quantiative formulations used at present proceed, in principle, from the thermodynamic equilibrium between the ions in solution and ions in an adsorbed phase. Under equilibrium-conditions the chemical potential μ is the same in both phases.

Table 2 shows a simplified working of this equilibrium. Herein, the monovalent and the bivalent ions are marked as + and ++ respectively, μ is the chemical potential, R the gas constant, T the absolute temperature and K a constant. The subscripts a and o are used for the adsorbed phase and the solution, respectively.

For the correct handling of these considerations, it is necessary to know the activity of the adsorbed ions. As this activity cannot be established by independent measurements, one meets great difficulties. It is therefore necessary to resort to models whereby certain assumptions can be made. A detailed treatment of the problems, which are involved hereby, was given among the others by *Bolt*.

When the general theory is worked out into models, one should, on one hand, consider the necessity to assign a physical interpretation to constants which are introduced, but on the other hand, we must not forget the practical usefulness of the model. It is clear, that concessions are necessary to meet both conditons.

Bolt has classified the models into two groups viz the mono layer models and models with three dimensions. In the first group it is assumed that the counterions adhere to the adsorbent in one layer, a model that fits in with the original ideas of *Helmholtz* about the double layer. In the second group it is assumed that the counterions are diffusely spread over the space. This model adapts itself to the distribution of ions in the double layer as suggested by *Gouy* and *Chapman*.

In figure 4 both cases are represented schematically.

Table 2.

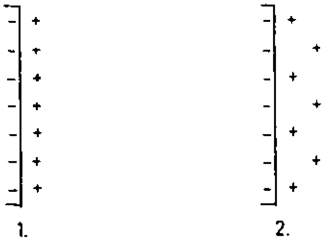
$$\mathrm{exch}(++) + 2\,\mathrm{salt}(+) \rightleftharpoons 2\,\mathrm{exch}(+) + \mathrm{salt}(++)$$

$$(++)_a + 2(+)_o \rightleftharpoons 2(+)_a + (++)_o$$

$$\mu(++)_a + 2\mu(+)_o = 2\mu(+)_a + \mu(++)_o$$

$$\mu = \mu_o + RT \ln a$$

$$\frac{(a^+)_a^2}{(a^{++})_a} = K.\frac{(a^+)_o^2}{(a^{++})_o}$$



1. condenser type of double layer
2. diffuse double layer

Fig. 4

In fact within the practical range three equations result from these models, viz the formulation by *Kerr*, or that by *Vanselow* and the *Gapon* equation. The model according to *Donnan* is quite satisfactory for qualitative purposes but has not sufficient advantages to be recommended for formulating the adsorption of clay minerals. It has been frequently used before *(Mattson, Wiklander, Schuffelen)*, but after the critical treatment by *Schofield* and also by *Klarenberg*, who pointed out its disadvantages when applied on the double layer, its use for study of the ion exchange on clay minerals has been discontinued.

For expressing the relationship between the adsorbed amount and the concentration of the cation in the solution, the formulations of table 3 are used.

It is evident that the empiric formulations always refer to a singl ion, while newly developped formulations are always based on the ratio between different ions. In the latter case the fact that one has to deal with an exchange of ions is clearly expressed.

In the formulations by *Kerr* and *Vanselow* it is assumed that the activity of ions in the adsorbed phase is equal to the mole fraction of the ions. The double layer is therefore actually considered as a solid solution.

Taking the distribution of ions according to *Gouy-Chapman* as a starting point, *Schofield, Errickson* and *Bolt* have shown that the constant in the Gapon formula which is more or less empiric, still has a physical background. It appears to be a function of the charge density at the surface of the colloid. The so calculated constants appear to correspond very well with the values as determined experimentally. According to the

Table 3.

empiric formulae		*model formulae*	
Freundlich	$\gamma = K.c^p$	Kerr	$\frac{\gamma_1^+}{\gamma_2^+} = K\frac{c_1^+}{c_2^+}, \frac{\gamma_1^{++}}{\gamma_2^{++}} = K\frac{c_1^{++}}{c_2^{++}}$
Langmuir	$\gamma = \Gamma . \frac{bc}{1 + bc}$	Vanselow	$\frac{\gamma^+}{\gamma^{++}} = K\left(\frac{c^+}{c^{++}}\right)^p$
Langmuir (ions)	$\gamma_1 = \Gamma . \frac{b_1c_1}{b_1c_1 + b_2c_2}$	Gapon-Bolt	$\frac{\gamma^+}{\gamma^{++}} = K_G \cdot \frac{c^+}{\sqrt{c^{++}}}$
		Donnan	$\frac{(c^+)_i}{\sqrt{(c^{++})_i}} = \frac{(c^+)_o}{\sqrt{(c^{++})_o}}$

γ = adsorbed ions.
c = concentration (activity) ions in solution.
K, p, Γ = constants.

theory given by *Bolt* the value of K in the formula must be near to 1. When the experimentally found value of K shows a considerable deviation it means that besides the electrostatic forces also specific forces are coming into play.

The experimental test of the given formulas has often been repeated and has generally given satisfactory agreement.

The formula derived by *Kerr* refers to ions of the same valence so that the electrostatic forces are equal for all ions. The K-values vary between 1 and 5 following the lyotropic series ($Li < Na < K < Rb < Cs$) and further depend on the differences between the hydration and polarizability of the pair of ions in question. In the case of bivalent ions preference factors are found with values ranging between 1 and 2. The lyotropic series ($Mg < Ca < Si < Ba$) also applies to this case. When using the formula of *Gapon-Bolt* one generally also finds theoretical and experimental preference factors of about 1 or 2. *Schachtschabel* was one of the first to draw attention to the variance in the preference factors depending on the difference in clay minerals.

Specific adsorption

When the behaviour of the potassium ion is considered it appears that the preference factors are not at all constant, especially when it concerns the clay mineral illite. When the adsorption complex has a low saturation with potassium, very high values for the preference factors are found. Table 4 shows some results of measurement of equilibria with potassium ions.

It appears that the preference constant may vary between the values of 2 and 40 in the case of high and low saturation rates respectively. A changing preference constant suggests the occurrance of sites with different binding force. When the sites with the highest energy of binding become occupied first, followed by others with lower energy, the constant will gradually change. Taking into consideration the structure of illite, one can assume that a clay plate will have three different sites of binding viz a surplus of charge on the planar surfaces, on the edges and sides of the crystal and charge sites between the opened up platelets of the crystal lattice. This is schematically represented in figure 5.

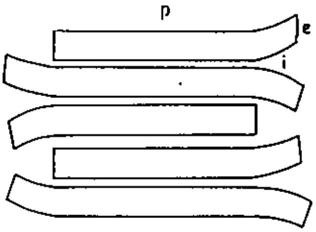
It may be assumed that the preference factor for binding at the planar patches will be normal – that is to say approximately 2; for other sites the factors will have much higher values. It appeared to be possible to verify this assumption by an analysis of the curve representing the relationship between $\gamma_{Ca}\frac{a_K}{\sqrt{a_{ca}}}$ and γ_K (*van Schouwenburg* and *Schuffelen*). This is shown in figure 6.

The results of such a test are given in table 5.

The results are encouraging. There is potassium which is adsorbed with a 'normal' preference constant, there is also potassium adsorbed with a very high preference constant ($K_G = 100$) and there is potassium that is held with even a higher binding energy. It seems

Table 4.

	K_G
Knibbe	4–30
Schwertmann	1–16
Schouwenburg, Schuffelen	2–30



p = planar
e = edge
i = interlattice

Fig. 5

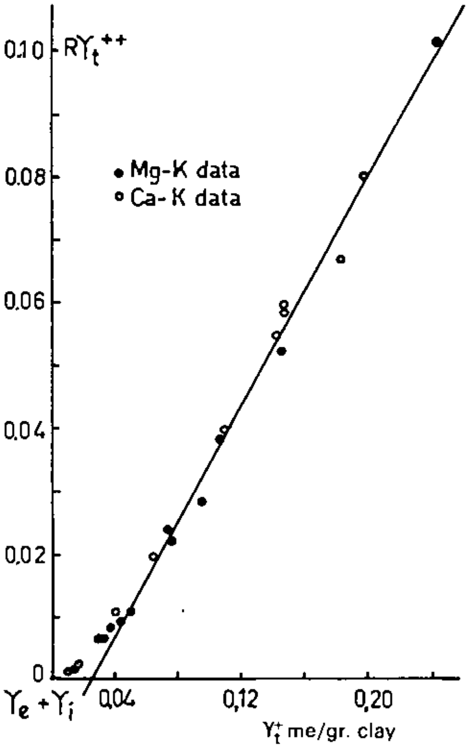


Fig. 6 Relation of adsorbed Y_t^+ and RY_t^{++}

Table 5. Exchange constants and adsorption capacities of the exchange sites of Winsum illite.

K-Mg-exchange	K_G-planar	2.21 ± 0.059
	K_G-edge	102.3 ± 10.3
	K_G-interlattice	~
	CEC-planar	0.426 ± 0.004 me/g clay
	CEC-edge + interlattice	0.025 ± 0.0003 me/g clay
	CEC-interlattice	0.003 ± 0.0003 me/g clay
K-Ca-exchange	K_G-planar	2.12 ± 0.071
	CEC-planar	0.472 ± 0.005 me/g clay
	CEC-edge + interlattice	0.020 ± 0.0008

logical to assume that the latter binding takes place between the elementary platelets so that this fraction is identical with fixed form of potassium. In the mechanism of ion uptake by plants, specific types of binding of potassium are known to occur. This is also the case with illite.

Along the edges of the clay platelets and beside the negative sites with a strong binding energy for potassium, there are also patches with a positive charge. Here a positive adsorption of anions takes place. Usually this positive adsorption is much smaller as compared with the negative adsorption in the double layer. In quantitative sense it is only of importance with regard to the phosphate ions *(de Haan)*. In this paper no attention is paid to this adsorption of anions.

Adsorption of potassium by organic matter

The number of exact measurements in well-defined systems, whereby the adsorbing agent would be the organic matter, is very limited. It is a well known fact that adsorption by humus of bivalent ions Mg and Ca is much stronger than the adsorption of monovalent ions K and Na. This is not surprising because many carboxylates of Ca and Mg are known to be unsoluble or to form either complex compounds or chelates. A quantitative treatment of equilibria, as has been carried out with clay minerals in recent years, is not known to us. Neither is it possible to voice an opinion whether the formulation of *Donnan* or of *Gapon-Bolt* would be the best one to use in the study of the adsorption phenomena of soil organic matter.

Moisture content and ion distribution

It follows from all the formulations either by *Donnan*, by *Vanselow*, or by *Gapon-Bolt*, that changes in the concentration of the soil moisture lead to changes in the ratio between the monovalent and bivalent ions in solution. A lower concentration leads to a relative increase of monovalent ions in solution.

Schuffelen and *Schuffelen* and *Middelburg* have made calculations about this effect based on the Donnan equilibrium. *Jensen* made similar calculations starting from the mass action law which forms a link with the *Vanselow* formula. The formula of *Gapon-Bolt* also lends itself for such calculations since better knowledge has been acquired about the preference factors and their variance. They were made for a range which is of practical interest, viz at a saturation of the adsorbtion complex by K-ions of less than 10 per cent.

Tables 6 and 7 show the results obtained for a clay mineral with properties of montmorillonite and of illite. Both the ratio's K/Ca and the concentration of K in the soil solution are given. In figure 7 the difference between 'montmorillonite' and 'illite' is indicated for one single case.

In soils, the amount of K in the solution is small as compared with the amount adsorbed; therefore, these figures may also be used for dilution, especially when the total concentration of the soil solution is low. Owing to the very preferential adsorption of potassium by illite, its concentration in the soil solution is extremely low. However, when the saturation of the adsorption complex with potassium is increased the differences between illite and montmorillonite tend to become smaller and the average preference factor attains values of the same size.

Table 6. a_K in meq. per liter.

	γ_K	K_G	$c_t = 0.002$ n	$c_t = 0.005$ n	$c_t = 0.01$ n	$c_t = 0.02$ n
Montmorillonite	1%	1.2	0.48	0.71	1.20	1.50
	2%	1.2	0.83	1.42	1.92	3.11
	3%	1.2	1.10	2.00	3.12	4.50
	4%	1.2	1.33	2.51	3.80	5.71
	5%	1.2	1.48	2.84	4.51	6.81
	7%	1.2	1.68	3.63	6.13	9.80
	10%	1.2	1.85	4.03	7.11	11.82
Illite	1%	30	0.02	0.03	0.04	0.07
	2%	18	0.07	0.12	0.18	0.23
	3%	8	0.22	0.30	0.55	0.78
	4%	6	0.40	0.60	1.12	1.11
	5%	5	0.58	1.01	1.50	2.00
	7%	4	0.95	1.65	2.40	3.80
	10%	3	1.30	2.60	4.08	5.82

Table 7. a_K/aca in mg eq.

	γ_K	K_G	$c_t = 0.002$ n	$c_t = 0.005$ n	$c_t = 0.01$ n	$c_t = 0.02$ n
Montmorillonite	1%	1.2	0.31	0.16	0.12	0.08
	2%	1.2	0.79	0.39	0.21	0.19
	3%	1.2	1.12	0.67	0.39	0.29
	4%	1.2	2.05	1.14	0.61	0.38
	5%	1.2	2.86	1.31	0.82	0.52
	7%	1.2	5.25	2.65	1.59	0.97
	10%	1.2	12.33	5.19	2.46	1.29
Illite	1%	30	0.01	0.007	0.004	0.003
	2%	18	0.04	0.024	0.018	0.012
	3%	8	0.13	0.064	0.058	0.040
	4%	6	0.25	0.14	0.12	0.060
	5%	5	0.41	0.25	0.18	0.11
	7%	4	0.82	0.49	0.32	0.23
	10%	3	1.87	1.08	0.69	0.41

Intensity and capacity

Beside the potassium which is located within the mineral lattices and therefore not easily available to plants, soils also contain potassium in exchangeable and soluble forms. In principle, both these forms of potassium are accessible to plant roots. It is true that, under conditions of an equilibrium between the ions in solution and in the double layer, the concentration (activity) of potassium in the double layer is higher as compared to that in solution, but nevertheless the same amount of labour is required to remove one ion from the double layer and from the solution. Therefore, the phenomenon of contact exchange as observed by *Jenny* should not be ascribed to the difference in activity between the solution and the double layer, but most probably to a better diffusion between the double layer and the adjacent wall of the root.

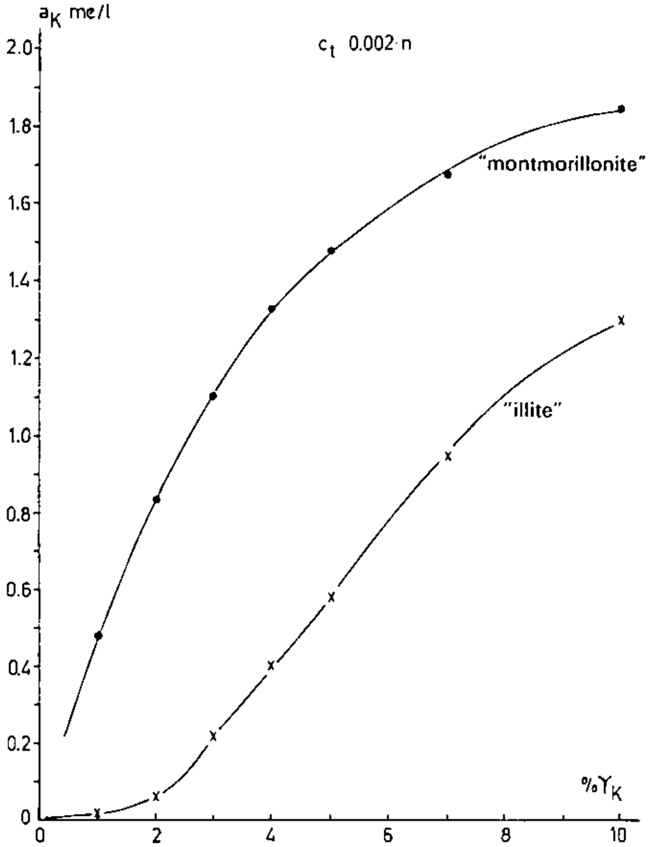


Fig. 7

The actual concentration activity in the double layer cannot be measured. It is therefore quite obvious that the concentration of potassium ions in solution – having the same activity – has been selected as a measure to describe the potassium status of soils. Sometimes not the concentration itself is used but another unit which is connected with it. In the Netherlands the so-called potassium value is used as such. This value indicates the amount of potassium ions present per unit of active material (or in principle surface area). In fact it is a disguised measure for the concentration of the solution.

As potassium is set free from the double layer via an exchange process, a solution of $CaCl_2$ (e.g. 0.01 *n*) is often used, approaching the composition of the soil solution. By means of this solution the equilibrium between the solid and the soluble phases is established and the potassium concentration determined. A number of formulations serving this purpose are described in literature.

Several authors have connected these values with yields and composition of crops. If thereby one limits himself to soil types of similar behaviour, a very good relationship between the two may be found. This makes it possible to make forecasts about the expected response of crops. However, when this relationship is tested on a larger number of different soils, the correlation between the selected units becomes smaller. To overcome this difficulty more properties of the soils have to be included into the correlation by means of correction factors. In principle the plant only reacts on the concentration (activity) of potassium ions in the soil solution. However, this value does not remain constant during the length of the growing season. It was already mentioned above that changes in the moisture content of a soil also lead to changes in the potassium concentration. Whether the variations in the concentration of the soil solution as a result of the ion uptake, are reduced by the buffering capacity of the soil, depends not only on the saturation of the adsorption complex but also on the total amount of this complex present in the soil.

The relationship between the intensity ($a_K/\sqrt{a_{ca}}$) and the capacity (adsorbed potassium) was studied by *Beckett* whose work was followed up by *Arnold* and others. Their data show clearly that the buffering is strongly connected with the soil type although the form of the curve representing this relationship is rather similar for different soils. All this leads to the conclusion that although the a_K or the $a_K/\sqrt{a_{ca}}$ (either or not expressed logarithmically) are the best measures for the activity of potassium to be defined physically, they are by no means the best values to indicate on the availability of soil potassium for the plant.

Correlative research is still necessary where laboratory data are confronted with results of field experiments. It appears that the choice of an intensity factor gives the best results under moist conditions and quick growing crops. The capacity factor ensures better forecasts under dry conditions and slow growing crops. All this refers to the assessment of the soil fertility in regard to the potassium ion as such. When the question of the fertilizer requirement of a certain soil has to be answered usually a capacity factor will prove to be the simplest unit to handle. If an intensity factor is to be used for formulating fertilizer recommendations, it is necessary to know the buffer capacity of the soil. In general it is not an easy task to achieve and forms a great disadvantage for its application in practice.

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Thermodynamics of Cation Exchange in Soils

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Summary

The purpose of the paper is to show the interest of the application of a purely formal thermodynamic reasoning to the exchange reactions in soils.

First, it is the common denominator to which empirical formulation like Gapon's equation can be reduced. Another advantage of the thermodynamic method is its predictive value with respect to ΔF°, ΔH° of an exchange reaction or to the selectivity coefficient, K_c, at any value of the salinity of the soil solution. The validity of the linear relationship that could be expected for the change of ion exchange selectivity with solvent activity has been demonstrated to hold for mono-monovalent exchange reactions. The theoretical basis for calculating the mean activity coefficient in a mixed heterovalent solution is given.

Experimental results do not provide much confidence in the predictive value of the Gapon's equation: there is some evidence that K_G cannot be termed 'exchange constant'. It is contented that the thermodynamic of excess functions not only allows to evaluate the non ideality of a mixing process but could also provide a way of finding an empirical or semi empirical rule for predicting the value of the surface activity coefficient. A first attempt has been made and the approach would be of a considerable interest for a quantitative prediction of exchange behaviour of a given cation pair in a given soil.

The process of cation exchange is one of the most important reactions occuring in soils and, since *Way* in 1850 has stated the qualitative laws of ion exchange in soils, many attempts have been made to formulate the results of ion exchange experiments in terms of quantitative laws. This continuying interest in the study of cation exchange properties of soils is easily understood when one considers the fundamental and the practical importance of this knowledge in the field of plant nutrition.

The main purpose of a practical soil scientist is looking for equations of predictive value. This may explain the widespread use of *Gapon's equation* since this empirical expression predicts a linear relationship between the quantities adsorbed and their concentrations in the equilibrium solution. However when *Gapon's equation* is subjected to direct experimental test there is some evidence *(Krishnamoorthy* and *Overstreet* [*3*], *Van Bladel et al.* [*16*]*)* that the parameter related to the exchange cannot be termed exchange constant, especially in the range of cationic composition of the surface phase where validity of *Gapon's equation* is usually claimed. Still nowadays the subject is a matter of a considerable debate and this emphasizes the interest of the application of a purely formal thermodynamic reasoning to the exchange reaction. Among other reasons for doing so, one can pointed out that these empirical formulations can always be reduced to a thermodynamic expression of the ion exchange equilibria *(Laudelout* [*4*]*)* and further that the thermodynamic method itself has a predictive value since the equilibrium exchange constant between cations A and B could be inferred from any two values of the equilibrium constant pertaining to the exchanges between A and C or B and C. It should be mentioned that any thermodynamic discussion of ion exchange on soils which used the approach based on the equilibrium constant expression requires two fundamental propositions. First the system concerned must have a definite stoichiometry and on the other hand that the analogue of *Henry's law* be obeyed in the trace region for each component. The first requirement is always satisfied insofar as ions are concerned by the condition of electrical neutrality. The second appears to be a law of great generality. An accurate proportionality always exists in the trace regions between fractions of one component in solution and in the exchanger phase although for mono-divalent exchanges *(Van Bladel* and *Menzel [15])* this seems to be restricted to a much lower concentration range than in mono-monovalent exchanges.

Assuming a soil solution system consisting of two discrete phases, an exchanger phase and a solution phase, the process of cation exchange must be represented as follows:

$$2\,\text{Soil K} + \text{Ca}^{2+} \rightleftharpoons \text{Soil Ca} + 2\,\text{K}^{+} \tag{1}$$

$$\text{Soil K} + \text{Na}^{+} \rightleftharpoons \text{Soil Na} + \text{K}^{+} \tag{2}$$

Applying to this heterogeneous system the equations for chemical equilibrium and chemical potential at constant temperature and pressure one derives the standard free energy change as

$$\frac{\Delta F^{\circ}_{(1)}}{RT} = -\ln\frac{\bar{a}_{Ca}\,a^{2}{}_{K}{}^{+}}{\bar{a}^{2}{}_{K}\,a_{Ca}{}^{2+}} = -\ln K_{(1)} \tag{3}$$

$$\text{and}\ \frac{\Delta F^{\circ}_{(2)}}{RT} = -\ln\frac{\bar{a}_{Na}\,a_{K}{}^{+}}{\bar{a}_{K}\,a_{Na}} = -\ln K_{(2)} \tag{4}$$

in which R is the universal gas constant, T the absolute temperature, ā and a represent the activities of the ions denoted in the surface phase and in the equilibrium solution respectively and K is the thermodynamic equilibrium constant.

Equations (3) and (4) can be written more explicitly by splitting the activities at equilibrium to concentrations and activity coefficients

$$K_{(1)} = \frac{N_{Ca}(m_{K})^{2}\,\gamma^{2}_{KCl}\,f_{Ca}}{(N_{K})^{2}\,m_{Ca}\,\gamma_{CaCl_2}\,f^{2}_{K}} = K'_{C}\frac{\gamma^{2}_{KCl}\,f_{Ca}}{\gamma_{CaCl_2}\,f^{2}_{K}} = K_{C}\frac{f_{Ca}}{f^{2}_{K}} \tag{5}$$

$$K_{(2)} = \frac{N_{Na}\,m_{K}\,\gamma_{KCl}\,f_{Na}}{N_{K}\,m_{Na}\,\gamma_{NaCl}\,f_{K}} = K'_{C}\frac{\gamma_{KCl}\,f_{Na}}{\gamma_{NaCl}\,f_{K}} = K_{C}\frac{f_{Na}}{f_{K}} \tag{6}$$

where N refers to the equivalent fractions of the total exchange capacity occupied by the ions specified, m to the concentrations (molalities) of the cations in the equilibrium solutions, γ and f are the activity coefficients in the aqueous phase and in the surface phase, K'_c which contains all the directly measurable quantities is the stoichiometric equilibrium quotient and K_c is the selectivity coefficient of the exchange reaction when quantities in solution are expressed as activities and those in the exchanger phase as equivalent fractions.

Clearly, the value of K (and of ΔF°) is depending upon the standard states chosen for the components, an arbitrary matter up to a certain point. A convenient choice for the exchanger phase is to define the standard state as the monoionic material in partial equilibrium (equilibrium with respect to the solvent only) with an infinetely dilute solution of the salt of the ion in question. For the standard states in the solution the usual ones are chosen which make ion activities approach the corresponding molalities as the solute content approaches zero. In doing so the $\Delta F^{\circ}{}_{(1)}$ is an excess quantity representing the change in free energy when 2 moles of K-exchanger reacted reversibly with one mole of calcium salt, both in their respective standard states. Application of the *Gibbs-Duhem equation* to the exchanger yields the wellknown equations *(Gaines* and *Thomas* [2]*)* for the thermodynamic equilibrium constant, viz.

$$\ln K_{(1)} = -1 + \int_L (\ln K_c dN_k - 2 n_w d\ln a_w) \qquad (7)$$

$$\ln K_{(2)} = \int_L (\ln K_c dN_k - n_w d\ln a_w) \qquad (8)$$

where the term '-1' originates from the fact that a monovalent cation is substituted by a divalent one, n_w is the number of moles of water per equivalent of the exchanger and a_w is the activity of the imbibed water which through the choice of an identical standard state in both phases is equal to the activity of the water in the equilibrating solution. L is an integration path going from a standard initial state of pure homoionic K-soil to a standard final state of pure Ca (or Na) Soil. It involves concentrating the infinetely dilute solution of KCl to a given finite concentration, carrying the exchange at that concentration by increasing the proportion of Ca^{++} (or Na^{+}) ions in the solution and finally diluting the $CaCl_2$ or NaCl solution to zero $CaCl_2$ or NaCl salt concentration.

It may be seen from equations (7) and (8) that at finite concentration of the equilibrium solution the calculation of the thermodynamic constant requires the knowledge of the change in water activity and also to calculate the ratio of activity coefficients in a mixed solution in order to calculate K_c from experimental values of K_c'. On the other hand, the sine qua non condition for applying the thermodynamic method for describing the experimental results is that perfect reversibility exists for the exchange reaction. At finite electrolyte concentration exchange irreversibility is frequently observed but has been shown *(Van Bladel* and *Laudelout* [*14*]*)* to decrease with the ionic strength of the equilibrium solution and to vanish at zero electrolyte concentration. This was to be expected if it is assumed that lack of reversibility is due to inacessibility of the exchange sites, the latter being caused by aggregation of the clay platelets.

Thus, the thermodynamic formulation may only be applied to values obtained from extrapolating the experimental results for ln K_c' to vanishing ionic strength unless the reversibility of the exchange reaction has been demonstrated. Further, this extrapolation procedure not only helps to eliminate errors arising from incomplete attainment of equilibrium but also obviates the need of calculating the activity coefficient ratios and the change in water activity. This procedure was justified experimentally in previous publications *(Van Bladel* and *Laudelout* [*14*]*), Laudelout et al.* [*6*]*)*.

It must be noted that for mono-monovalent exchange reactions there exists a straightforward method to obtain the ΔF° with a very good approximation from experimental data in the region where the analogue of Henry's law is obeyed. Combining the *Gibbs Duhem equation* for the surface phase and making use of the *Margules approximation* for surface phase activity coefficients *(Martin* and *Laudelout* [*10*]*)* one obtains for $N_A = N_B$

$$\ln K = \ln K_c \qquad (9)$$

where N_A is the equivalent ionic fraction of a monovalent cation exchanged against another monovalent cation B. For a pair of salts of singled charged ions at low total concentrations we may identify the stoichiometric quotient with the selectivity coefficient. Provided that K_c' is a slowly varying function, straight lines of unit slope will result when $\log m_B/m_A$ is plotted against $\log N_B/N_A$. This relation has been verified over a considerable range of B/A ratios *(Martin* and *Laudelout [10])* and it has been demonstrated to be also true in the limit region where the analogue of Henry's law is obeyed *(Robeyns, Van Bladel* and *Laudelout [11]).* This was possible using the radioisotopes technique which allows to investigate the trace region with a very high precision in the measurements. Consequently, plots of m_B/m_A vs. N_B/N_A on a log × log scale afford an easy extrapolation procedure at the point where $\log N_B/N_A$ is zero and this gives at once the standard free energy. However, the simplicity of this approach is lost for mixed valence types.

We are aware that practical application of data from experiments on the equilibria on surface regions usually requires the knowledge of water activity in mixed electrolyte solutions. Indeed, if one wishes to know the influence of fairly high total concentration of the soil solution on the selectivity coefficient of a given exchange one needs to correct the stoichiometric quotient K_c' by the activity coefficients of the electrolytes in the mixed solution. The necessary information as to these solution phase activity coefficients can be obtained according to *Harned's rule* viz. that in a mixture of a constant total ionic strength, μ, the logarithm of the activity coefficient of one electrolyte is directly proportional to the ionic strength of the other component.

Briefly, applying the Harned's rule for a mixture of, say, KCl and $CaCl_2$, it may be written:

$$\log \gamma_{\pm KCl} = \log \gamma_{\pm KCl(1)} - \alpha_1 \mu_{CaCl2} \tag{10}$$

$$\log \gamma_{\pm CaCl_2} = \log \gamma_{\pm CaCl_2(1)} - \alpha_2 \mu_{KCl} \tag{11}$$

where $\gamma\pm KCl(1)$ and $\gamma\pm CaCl_2(1)$ represent the mean activity coefficients of KCl and $CaCl_2$ in their pure solution at the same ionic strength μ, α_1 and α_2 are empirical coefficients which depend on the total ionic strength but not on the individual ionic strengths μ_1 and μ_2.

The coefficients α_1 and α_2 can be calculated by making use of *Znadovski's rule* through a calculation method due to *Vdokendo* and *Rjazanov [17]* which is based upon the cross differentiation method of *Mac Kay* and *Perring* [9] (see Appendix).

This method of calculation of the mean activity coefficients in a mixed solution is a tedious procedure. However, it must be emphasized that *Laudelout* and *Thomas [5]* have derived a purely thermodynamic relationship which affords a prediction of the effect of the salinity of the soil solution upon the selectivity coefficient in ion exchange reactions from the change in water content (n_w) of the ion exchanger with composition N_A, viz.

$$\left(\frac{\partial \ln K_c}{\partial \ln a_w}\right)_{N_A} = -Z_A Z_B \left(\frac{\partial n_w}{\partial N_A}\right)_{a_w} \tag{12}$$

where Z_A and Z_B represent the valence of the ions and a_w is the activity of the imbibed water which, through the choice of an identical standard state in both phases, is equal to the activity of the water in the equilibrating solution. It follows that application of this relationship to equations (1) and (2), provided the hydration of the surface phase is a linear function of its cationic composition, yields, upon integration from $a_w = 1$ to a_w

$$\ln K_c^{(1)}{}_{(a_w)} = \ln K_c^{(1)}{}_{(a_w=1)} + 2(n_w^{Ca} - n_w^{K}) \ln a_w \tag{13}$$

$$\ln K_c^{(2)}{}_{(a_w)} = \ln K_c^{(2)}{}_{(a_w=1)} + (n_w^{Na} - n_w^{K}) \ln a_w \tag{14}$$

where n_w^{Na}, n_w^{K}, n_w^{Ca} refer to the number of moles of water per equivalent of pure ionic form of the exchanger.

From these equations, one should expect a linear relationship of $\ln K_c$ with $\ln a_w$. Experimental data from this laboratory on mono-monovalent exchange reactions have already shown that this is indeed observed *(Laudelout, Van Bladel* and *Robeyns [8]).*

It results that the influence of any value of the salinity of the soil solution on the selectivity coefficient may be calculated if it is known or can be predicted in dilute solution provided the difference of hydration numbers is also known. Furthermore, knowing the differences of hydration numbers for two ion pairs A,B and A,C, one may calculate the difference $n_w^C - n_w^B$ which allows to predict the influence of the salinity on the selectivity coefficient for the exchange B,C. The same can be said for the calculation of the standard free energy change and the standard enthalpy change of an exchange reaction knowing those of two other reactions with a common ion. What precedes emphasizes the advantage of the thermodynamic method with respect to its predictive value.

On the other hand it is worthwhile to note that for mono-monovalent exchange reactions, an empirical correlation has been found to hold between the difference in hydration numbers and the polarizability difference of these cations. Such empirical correlations with respect to the polarizability difference were also shown for the $\Delta F°$ and $\Delta H°$ *(Martin* and *Laudelout [10], Van Bladel [13].*

It must be pointed out that a linear correlation with respect to the polarizability for the standard free energy change of an exchange reaction indicates the existence of specific adsorption energies for different ions. With the assumption that the distribution of ions for heterovalent exchange reactions follows the *Gouy-Chapman theory,* one may calculate the primary effect of a Coulombic component resulting from the difference in valence of the exchanging cations aside from the effects related to the size of the ions. This would allow to correlate the magnitude of the non coulombic forces acting for the ionic distribution on colloid surfaces with the polarizability difference of those cations.

An elaborate treatment covering the general case has been presented *(Laudelout et al. [6]).* Lately, it has been shown *(Van Bladel, Gaviria* and *Laudelout [16])* that *Eriksson's equation* in simplified form, as given by *Bolt [1],* is also satisfactory for this purpose especially at low salt level and high surface density of charge of the exchanger.

The advantage of the thermodynamic method with respect to its predictive value has already been mentioned. The same cannot be said for an empirical formulation like *Gapon's equation* and which is of a widespread use for calculating the cationic composition of the exchange complex of the soil from the cationic composition of the irrigation water. For the exchange between K^+ and Ca^{++}, the *Gapon's 'constant'* is related to the selectivity coefficient and the equilibrium constant by *(Laudelout [4]):*

$$K_G = \frac{N_{Ca} a_K}{N_K a_{Ca}^{1/2}} = \sqrt{K_c N_{Ca}} \tag{15}$$

$$\text{and } \ln K = 2\int_0^1 \ln K_G dN_{Ca} \tag{16}$$

From these equations, it is apparent that K_G cannot be treated as a constant throughout the range of cationic composition of the soil exchange complex. Investigation of the deviations of the exchange behaviour of Na^+ by Ca^{++} from the *Gapon's rule* has recently been made over the full range of calcium composition on the exchange complex of a montmorillonite clay and the results have given evidence of the non-constancy of K_G *(Van Bladel, Gaviria* and *Laudelout [16]).*

Equation (5) shows that the thermodynamic equilibrium constant is the product of the selectivity coefficient and the ratio of the surface activity coefficients. It is a simple matter to calculate this ratio at any composition in the surface phase from what has been said on the predictive value of the thermodynamic method with respect to salinity on the selectivity coefficient or to the calculation of the standard free energy change of an exchange reaction. On the other hand, the thermodynamic of excess functions allows to derive the ideal surface activity coefficients which for the general case $A^{Z_A} \rightarrow B^{Z_B}$ can be written *(Thomas [12]):*

$$\frac{f_B^{Z_A}}{f_A^{Z_B}} = \exp(Z_A - Z_B) \tag{17}$$

This defines an ideal exchanger as one for which the ratio of the surface activity coefficients is a constant and for which K_c itself is a constant (at fixed temperature) regardless of surface composition. For the non-ideal case, K_c and the ratio

$$\frac{f_B^{Z_A}}{f_A^{Z_B}}$$

are dependent on surface composition and evaluation of the non ideality of the mixing process is expressed in a plot of

$$\ln \frac{f_B^{Z_A}}{f_A^{Z_B}} - (Z_A - Z_B)$$

vs. surface composition by deviations from a horizontal straight line.

It is obvious that information on the distribution of two cations between the surface phase and the solution phase at various compositions of the latter is a fairly lengthy procedure. For practical purposes it would be of a considerable advantage if, knowing the standard free energy change of a reaction, an empirical or semi-empirical rule is found for predicting the value of the surface activity coefficient. This would allow a quantitative prediction of exchange behaviour of a given cation pair in a given soil. A first attempt in that direction has been made *(Laudelout et al. [7])* using excess thermodynamic functions as it is customary in the thermodynamic of mixtures and the approach seems promising provided the temperature at which the exchange is studied is not too high.

Appendix:

Calculation method of activity coefficients of electrolytes in a mixed solution

Through the cross differentiation method of *MacKay* and *Perring [9]*, the following relationships may be derived for the mean activity coefficients of the electrolytes in a mixed solution of KCl and $CaCl_2$:

$$\gamma_{\pm KCl} = \frac{2m^{\circ}_{KCl}\gamma^{\circ}_{\pm KCl}}{2m_{KCl} + 3m_{CaCl_2}} \qquad \text{(a–1)}$$

$$\gamma_{\pm CaCl_2} = \frac{3m^{\circ}_{CaCl_2}\gamma^{\circ}_{\pm CaCl_2}}{2m_{KCl} + 3m_{CaCl_2}} \qquad \text{(a–2)}$$

This assumes that the different electrolytes obey the *Znadovski's* rule viz. the mixture of two isopiestic salt solutions will give a mixed solution in which water activity is equal to that of the isopiestic solution, or:

$$\frac{m_{KCl}}{m^{\circ}_{KCl}} + \frac{m_{CaCl_2}}{m^{\circ}_{CaCl_2}} = 1 \qquad \text{(a–3)}$$

In the above equations, m is the molality in the mixed solution, m° and $\gamma^{\circ}_{\pm}$ are the molality and the molal activity coefficient of the electrolyte in the single electrolyte solution in isopiestic equilibrium with the mixed solution.

Equation (a–3) may be transformed into:

$$\frac{m^{\circ}_{CaCl_2}}{m^{\circ}_{KCl}} m_{KCl} + m_{CaCl_2} = m^{\circ}_{CaCl_2} \qquad \text{(a–4)}$$

and

$$\frac{m^{\circ}_{KCl}}{m^{\circ}_{CaCl_2}} m_{CaCl_2} + m_{KCl} = m^{\circ}_{KCl} \qquad \text{(a–5)}$$

The ratios $\frac{m^{\circ}_{CaCl_2}}{m^{\circ}_{KCl}}$ and $\frac{m^{\circ}_{KCl}}{m^{\circ}_{CaCl_2}}$ are calculated through the graphical method described by *Vdovenko* and *Rjazanov [17]* and by making use of the tabulated values of the osmotic coefficients Ψ in single salt solution

Briefly, plotting either the products 2 m_{KCl} Ψ_{KCl} and $3m_{CaCl_2}$ Ψ_{CaCl_2} viz. respectively m_{KCl} and m_{CaCl_2} will yield a graph from which the molalities of solution in isopiestic equilibrium correspond to the intersection of any horizontal with the curves that have been plotted. Then, using the calculated values of $\frac{m^{\circ}_{CaCl_2}}{m^{\circ}_{KCl}}$ and $\frac{m^{\circ}_{KCl}}{m^{\circ}_{CaCl_2}}$, the left hand side of equations (a–4) and (a–5) may be plotted against $m^{\circ}_{CaCl_2}$ or m°_{KCl} for any composition of interest of the mixed solutions.

The intersection of the curves with the straight line of unit slope starting from the origin gives the values of $m^{\circ}_{CaCl_2}$ and m°_{KCl} corresponding to the two pure salt solutions in isopiestic equilibrium with a given composition of the mixed solution. The $\gamma^{\circ}_{\pm}$ are found from tables and the mean activity coefficients in the mixed solutions are calculated from equations (a–1) and (a–2). It is then a simple matter to calculate the coefficients α_1 and α_2 of *Harned's relationships.*

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Exchange of Potassium in Soils in Relation to Other Cations

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Summary

Categories of soil potassium and criteria to define their properties and inter-relations, referring specially to the exchange of potassium with other cations are described. Extensive soil properties, such as clay and fine clay content and mineralogical composition are not absolute guides to K exchange and release to crops.
The term *'non-exchangeable* potassium' is a misnomer, and its value in soils to crops is related to the dominant counter-cation in the soil and the characteristics of the crop. Attempts to find a single and simple method of defining the ability and capacity of the soil to release so-called 'non-exchangeable' K to crops seem misguided. Differences between residual K accumulated in soil from K fertilisers, and K that is part of the original mineral matrix, have not been precisely demonstrated. Criteria are suggested that might be used to do so.

1. *Introduction*

Ten years ago, *Cooke* [*1*] wrote:

'Potassium in soils exists in forms ranging from water-soluble K (fully useful to crops) to completely inaccessible K deep within clay particles or fragments of unweathered minerals... *The useful fraction is conventionally measured by the K that is 'exchangeable' with another cation in a neutral salt solution.* But the actual amounts of exchangeable K displaced from soil depend on the cation used and the experimental conditions. Heavy British soils often contain about 1 per cent of total K; *usually only about 1 per cent of this is exchangeable and this fraction can be removed completely by a few good crops.* As exchangeable K is taken up by crops, it is replenished from *stocks of non-exchangeable K held in the outer layers of soil particles;* the size of this reserve determines whether the soil can supply K to crops for many years without potash fertilizers... One reason for such differences' (between soils with good K reserves and those that are quickly exhausted by crops) *'is the proportion of "fine" clay in the soil and its composition. Soils with much fine clay, ..., release more K than those containing coarser clay...* soils which supply small or large amounts of K to crops are usually well separated by their exchangeable K values, but *for soils in the "middle" range such correlations fail, and a rapid and reliable chemical way of assessing their reserves is badly needed.'*

This picture is acceptable *today* in general terms as a basis for discussion. Most aspects can be enlarged upon, but some (those in my *italics*) need revising and new information can be added in the light of recent research.

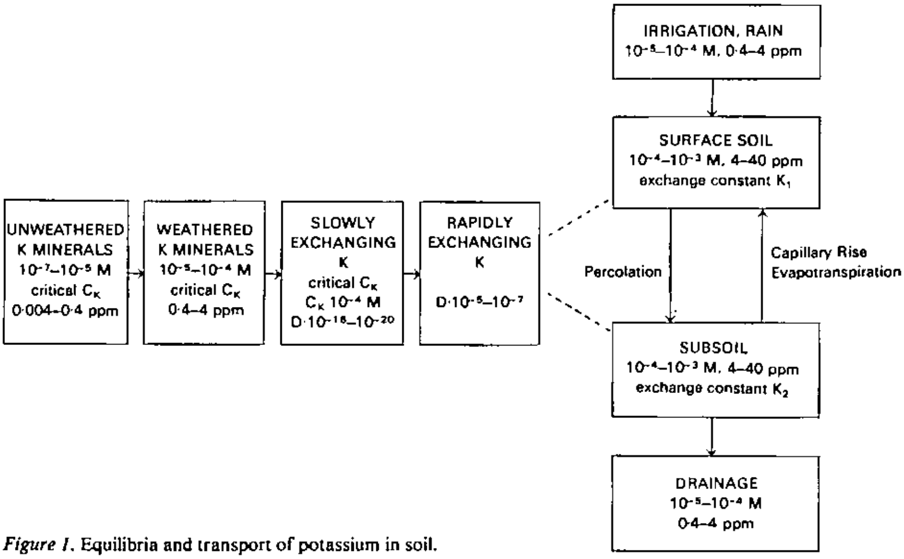

Figure 1. Equilibria and transport of potassium in soil.

The dynamic and static steps in this equilibrium centre on a generally recognised model (figure 1) whose thermodynamic parameters control the short- and long-term behaviour of native and added potassium in the soil towards crops and the environment. This paper attempts, as far as possible, to use these parameters to interpret, explain and predict such behaviour, and in doing so, revises and adds to the picture.

2. *The soil: solution cation-exchange equilibrium*

Theoretical treatments of the relationship between adsorbed cations (compensating negative charges on the soil complex and *accessible to the soil solution*) and cations in solution were discussed earlier [*2, 3*]. An essential condition of the applicability to soil suspensions of equations derived from such treatments, is that experimental results are obtained from a system in equilibrium. To determine the amounts of cations adsorbed on exchange sites in the soil, non-equilibrium desorption methods (using neutral salt solutions, e.g., *M* ammonium acetate or the chlorides of NH_4^+, K^+, or Ca^{2+}) are commonly used. However, the criterion for equilibrium requires that the adsorbed cations be measured under the electro-osmotic conditions prevailing in the chemical equilibrium. This can only be achieved by the now familiar technique of isotopic exchange between adsorbed and solution cations which also enables us to measure changes in the *total* negative charge of the soil with changes in composition of the adsorbed cations. In K:Ca exchange in soils containing hydrous micas and interstratified mica minerals in their clay and silt fractions, increasing proportions of adsorbed K decrease the number of negatively charged sites accessible to solution (cation exchange capacity, CEC; figure 2) until the equivalent K fraction, N_K, in the CEC is between 0.15 and 0.30 in various soils [*4*]. The number of charged sites remain constant at larger N_K values. Experiments with labelled soil suggest that Ca and K ions

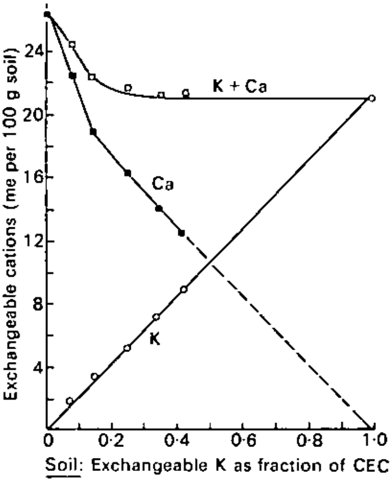

Figure 2. Fractional K saturation, N_K, and exchangeable K and Ca and the cation exchange capacity.

become inaccessible to solution in varying proportions, causing the observed change in CEC.

The ease of exchange of K from soils, clays and resins is governed by the nature of the competing counter-ions in the exchanger. Ca ions dominate the exchange complex in soils of pH > 5.5 (in 0.01 *M* $CaCl_2$ or *M* KCl, equivalent to pH 6.5 in water approximately). Al ions increasingly dominate at soil pH values more acid than 5.5, such that at pH values 4.0 – 4.3, less than a third of the accessible exchange sites are occupied by Ca + Mg ions, and at pH values 3.6 – 3.8, this fraction is about a tenth [*5*]. Also, because soils containing illite-dominated clays strongly prefer Al to Ca ions ($pK_{Ca \rightarrow Al} = 2.3$ to 2.4, in the pH range 2.4 – 4.3; reference *6*), in soils saturated with mixtures of Ca and Al ions, Al ions most likely control the exchange characteristics of K ions. Saline and alkaline soils comprise a third and not uncommon group in which Na ions dominate the soil exchange complex.

3. *Calcium*

K-Ca exchange isotherms in various soils have been most extensively studied by using quantity: intensity relationships between adsorbed K and a derived function of the K concentration in the equilibrium solution (for example, [7]). Such work is a semi-empirical extension of classical concepts used, again extensively, to interpret the exchange properties of montmorillonite for many ion pairs, especially K:Ca (for example [*8*, *9*]). We have, in recent years, attempted to extend these concepts to soils from some English series, covering appreciable areas of arable land, so that a unified picture can be developed of the K:Ca exchange properties of the soil complex in relation to its mineralogical composition, its ability to release K to crops and to predict its potential to release so-called 'non-exchangeable' K [*4*, *10*, *11*, *12*]. We consider that results of practical significance, summarised below, are obtained from this work.

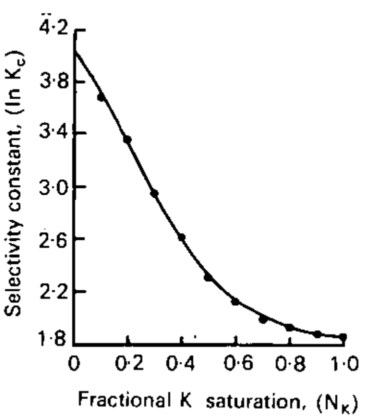

Figure 3. Fractional K saturation, N_k, and the exchange selectivity coefficient, ln K_c, for a Long Load series soil.

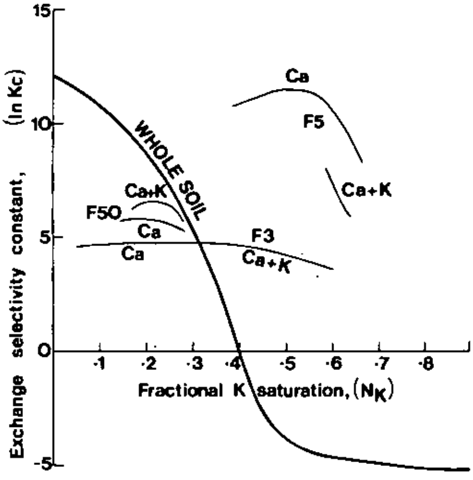

Figure 4. Fractional K saturation, N_k, and the exchange selectivity coefficients, ln K_c, for a Harwell series soil and its particle size fractions (*F3* < 0.3 μ, montmorillonitic, *F5* 0.3—5 μ, zeolitic, *F50* < 50μ, mainly micaceous).

3.1 *Exchange constants*

K:Ca exchange isotherms express the relation between the ion fraction of K^+ in solution and on the soil exchange complex, and can be transformed to selectivity coefficients (K_c, Reference [*4*], equation 1). Qualitatively, the heterogeneity of exchange sites on the soil complex related to *all* its characteristics governing the exchange of K and Ca ions (e.g., mineralogical composition of the exchange complex, interlayer and external surface sites, chelating groups in organic matter, hydration of ions, etc.), is directly reflected by the change in K_c as K ions increasingly displace Ca ions (figure 3). However, the most important parameters derived by applying classical concepts to this change are the thermodynamic equilibrium constant and the resulting standard free energy of exchange (equations (4) and (5), Reference [*4*]). These enable us to compare quantitatively the *intensive* properties of their exchange complexes in K-Ca exchange (table 1), i.e. the forces acting between exchangeable cations and the clay surfaces (dependent on cation

Table 1. Standard free energies for the exchange of K-Na, K-Rb and K-Ca on English soils

	ΔG_0 values for the reaction		
	CaE → KE	RbE → KE	NaE → KE
Bovey Basin	—1245	+377	— 888
Cegin	—1050	+435	— 966
Denchworth	—1770		
Dunkeswick	—1315	+667	—1083
Harwell	—3420	+565	
Long Load	—2120	+474	
Newchurch	—1900	+515	
Sherborne	—2280		
Tedburn	—1370	+447	— 927
Windsor	—1550	+555	—1015

valency and surface charge density) and changes in the microstructure of the clay as the composition of exchangeable cations changes from Ca- to K-saturation. The standard free energy of exchange is independent of *extensive* soil properties, (e.g., clay content, cation exchange capacity, etc.). Table 1 shows that free energy values range from −1050 to −3410 cals./mole expressing a more than three-fold difference in the preference of the soils examined for K ions.

K_c values in the various soils changed considerably with increasing K saturation, invariably demonstrating the heterogeneity of exchange sites (i.e., the mineralogical complexity of the exchange matrix). Similar measurements on particle size fractions of the Harwell soil, obtained to separate and concentrate its principal cation exchanging minerals, showed that K_c for the $< 0.3\mu$ montmorillonite-rich fraction did not change with K saturation (N_k) (figure 4) but the K_c:(N_k) relationships for the illite-and zeolite-rich fractions were complex, and undoubtedly controlled the K:Ca exchange behaviour of the soil.

The standard free energy can also be calculated from the algebraic sum of the electrical work required to move K and Ca ions in opposite directions from the distance of closest approach to the surface of the exchange complex to an infinite distance away from the surface. This requires a precise knowledge of the structural disposition of the cations at the surface and the dielectric constant of adsorbed water and cannot be easily assessed, if at all, in a soil exchange complex. Also, the calculated free energy value is inconclusive about the specific binding of an ion relative to another ion, because the free energy is the algebraic sum of the enthalpy *and* entropy terms on the exchange surface and in solution during exchange.

Ion binding strength is normally defined by the *enthalpy* term alone. The negative enthalpy change for the formation of K-soil from Ca-soil includes the enthalpies of the hydration of ions, their dilution and mixing in moving to and fro from soil to solution, and of exchange. The *entropy* of a system increases as the number of ways in which a system can arrange itself increases. The standard entropy change is the algebraic sum of the entropy changes in the soil and the solution. The probable arrangements of Ca ions in Ca soil are fewer because each ion occupies two adjacent exchange sites on the soil surface simultaneously but K ions position themselves randomly on individual sites. Also in 2:1 layer minerals in K-soil, the interlayer space is smaller, so K ions occupy fewer positions perpendicular to the surface. Thus entropy changes on K-Ca exchange in the solid phase are small and positive for the formation of K soil. In solution, K ions increase entropy by breaking down the structural order of water molecules; by contrast, Ca ions decrease entropy introducing greater order. In dilute solutions the entropy term in K-Ca exchange would be large, causing the observed K-Ca isotherm to show an apparent preference for Ca ions although the standard free energy for K-Ca exchange clearly indicates a strong preference for K ions by the soil.

3.2 *The state of adsorbed potassium*

(i) Activity coefficients. Exchangeable K can be determined by non-equilibrium desorption or by equilibrium isotopic exchange. Both methods are subject to rate-determining steps whose relative speeds require and determine different means of measuring the various forms of exchangeable K. Figure 1 expresses the stages of equilibrium between these different forms. The most easily measured equilibrium is that between 'rapidly exchange-

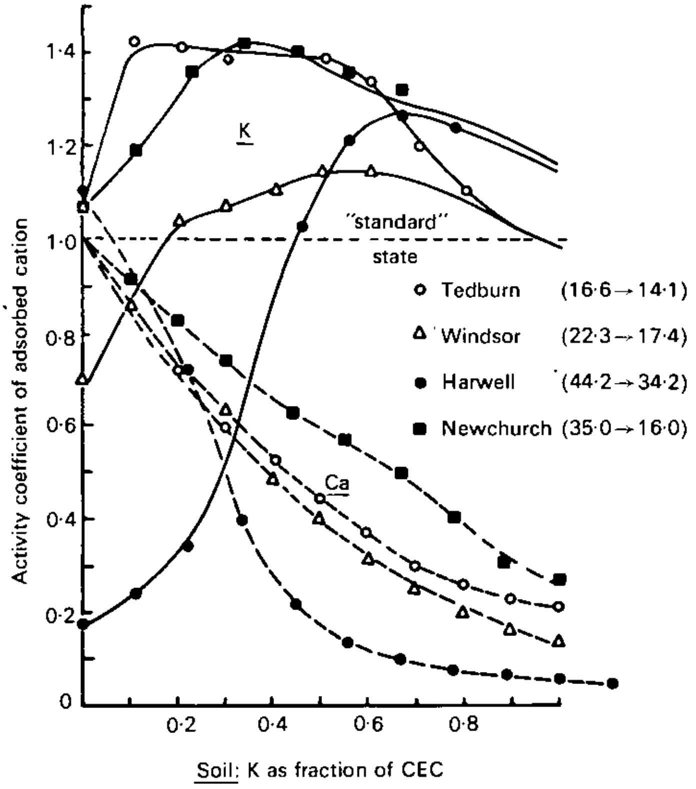

Figure 5. Fractional K saturation, N_K, and the activity coefficients of adsorbed K and Ca in four English soils (results in brackets show the change in CEC from Ca- to K-soil).

Table 2. Approximate mineralogical composition of the clay fractions of English soils and the fractional saturation of adsorbed K, N_K, at which transitions in its activity coefficient, f_K, and the excess enthalpy function, ΔH_e, occur

	Mineralogy of $<2\mu$ clay fraction[1]	N_K-values for f_K-transitions	ΔH_E-transitions
Bovey Basin	—	0.35	—
Cegin	—	0.21, 0.53	—
Denchworth	20%v	0.50	0.3
Dunkeswick	—	0.21	—
Harwell	65% mm, (cli)	0.20, 0.60	0.3, 0.6
Long Load	40% chl-v	0.50	0.1, 0.3, 0.8
Newchurch	35% mm	0.30	0.1, 0.6
Sherborne	35% mm-v	0.50	0.1, 0.7
Tedburn	—	0.11, 0.53	—
Windsor	—	0.21, 0.60	—

[1] mm = montmorillonite, v = vermiculite, chl-v = chloritised vermiculite, cli = clinoptilolite

able' K and K in solution. The properties of 'rapidly exchangeable' K from 0–100% K saturation ($N_K = 0$ to 1) represent the nature of K-specific and non-specific sites readily accessible to ions in solution. Environmental conditions, e.g., the ionic composition and strength of the bathing solution [11], wet-and-dry cycles [13], freeze-and-thaw cycles, etc., influence the speeds at which this readily exchangeable K interacts with K on less accessible sites.

The limiting exchange properties of the more accessible K at small K saturation values ($N_K \to 0$) in the soil complex are similar to those of less accessible K. It is important, therefore, to express these properties quantitatively, referred to a standard state that can be regarded as common to *very different* soil and clay exchange complexes. The standard state assumed for adsorbed K in this classical concept is the fully K saturated form of the soil, and it is explicitly assumed that the free energy status of all exchangers in this form are identical. In agricultural parlance, this implies that the K in all fully K-saturated soils is equally 'available' to plants. This definition allows us to compare rigorously the K status of all soils at various fractional K saturations of the exchange complex.

The activity coefficients, f_K, of adsorbed K in this classical concept, relative to such a standard state, express precisely the detailed behaviour of the soil exchange complex of part or all of the exchange isotherm. The factor that corrects the surface concentration of K ions for specific attractive interactions with the soil surface, f_K, changes with K saturation, N_K, giving maxima and inflexions at different values of N_K (figure 5, table 2). These points of marked change reflect broadly the changeover with increasing N_K from groups of sites with decreasing K preference. The differences between groups of exchange sites in soils depend on three factors: (i) the characteristics of the interlayer space, isomorphous substitution and surface charge density in soil minerals; (ii) the relative degree of chelation of competing cations in soil organic matter; and (iii) on the relative concentrations of competing cations in free solution and adsorbed water.

During exhaustive removal of K from soil in pots by ryegrass [13] and by Ca-saturated exchange resin [11], the K saturation of the soil changes from $N_K = 0.2 \to 0$. A N_K- value of 0 has never been demonstrated experimentally, but the large amounts of K removed by the crops (or resin), and the very small K concentrations in the soil solution during cropping, indicate clearly that some soils must maintain a N_K value $\to 0$ for long periods while much K is removed from sites previously not accessible to M ammonium salt solutions. The activity coefficients of adsorbed K at vanishingly small K saturations, $(f_K)_o$,

Table 3. Release of K from English soils to M ammonium acetate and to ryegrass in pots compared with some soil characteristics

Series	Exchangeable K	K uptake by ryegrass	Uptake of Non-exchangeable K (ppm soil)	$(f_K)_o$	%clay	
					<2μ	<0.2μ
Bovey Basin	102	92	0	0.73	17.1	3.6
Cegin	86	70	0	0.71	12.6	1.6
Denchworth	400	720	320	0.89	42.6	21.9
Dunkeswick	100	800	700	1.43	25.7	10.5
Harwell	2346	2350	4	0.16	37.3	23.8
Long Load	300	180	0	0.82	27.6	11.9
Newchurch	610	1010	400	0.96	41.4	19.0
Sherborne	240	190	0	0.45	29.9	17.3
Tedburn	280	320	40	1.07	24.5	6.0
Windsor	300	160	0	0.71	22.5	10.5

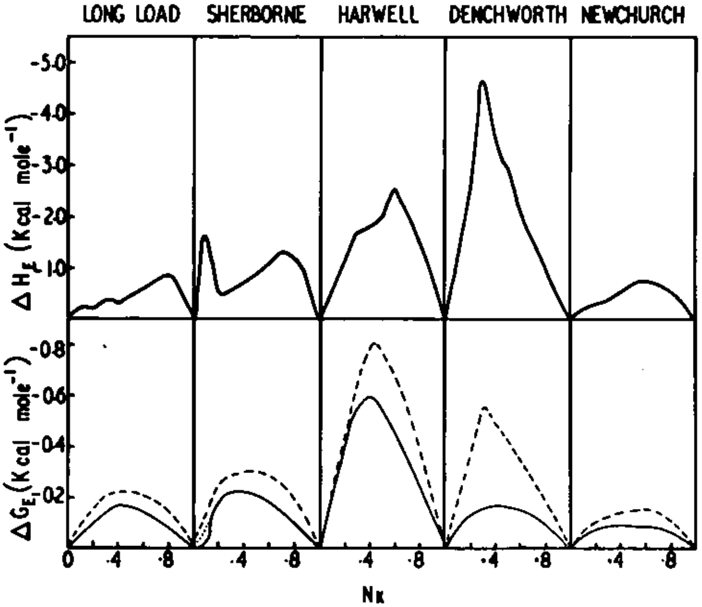

Figure 6. Fractional K saturation, N_K, and excess free energy and enthalpy functions for five English soils.

derived from applying these classical concepts, show that soils with an $(f_K)_o$ value less than about 0.85 do not release K that is not initially exchangeable to *M* NH_4 salts (table 3). Of the ten soils, four with $(f_K)_o > 0.85$, release 40–700 ppm K of 'non-exchangeable' K! These results do not seem obviously related to the 'exchangeable' K value, clay and fine clay content of the soils or the nature of the mica minerals in the clay fraction (table 1). Work now in progress seeks to examine more soil series in this way and to elucidate the way in which fertilizer residues could modify these characteristics of soil K.

(ii) Excess Thermodynamic Functions. In contrast with the activity coefficient of a single adsorbed ion species (referred to its standard state), these functions [*12*] account for the properties of the soil complex in terms of the activity coefficients of *both* adsorbed ions (figure 6).

The change in the *free energy* function with K saturation expresses more precisely the soil property defined by the reciprocal of the K buffering capacity of the soil [*3, 7*], the amount of K per unit weight of soil required to change the K potential of the soil by one unit. Soils in which this function changes least as $N_K \rightarrow 0$, release most K from sites initially not exchangeable to *M* ammonium ions (figure 6).

The *enthalpy function* relationship can be derived from the temperature coefficients of f_K and f_{Ca}, or by calorimetry of the heats of mixing of varying proportions of homoionic soil. This defines the heterogeneity of exchange sites in a soil for K:Ca exchange (figure 6) and comparison with the complete exchange isotherm predicts that, in most soils, the greater part of the cation exchange capacity can be K-saturated only with solutions whose K concentration greatly exceeds their Ca concentration.

The *entropy function*, related to various N_K values, confirms that K adsorption at N_K values corresponding with maxima in the enthalpy relationship leads to an increased order in the arrangements of K and Ca ions and water molecules at exchange sites.

4. *Aluminium*

Aluminium is the second most abundant exchangeable cation in many soils and dominates most strongly-leached tropical soils. Its ionic concentration in the soil solution and on the soil exchange complex is negligible in soils of pH > 5.5 (measured in 0.01 *M* $CaCl_2$ or *M* KCl, when diffuse electrical double layers are confined to the vicinity of charged sites, and pH measurements are reliable and meaningful). This pH is equivalent to about 6.5 in water. Increasing equivalent ion fractions of soluble Al are observed in more acid soils, and on their exchange sites by displacement with *M* NH_4Cl or KCl. (*M* ammonium acetate also extracts part or all of Al ions chelated by soil organic matter [*14*].) An approximate guide to exchangeable Al is taken from our measurements on several soils:

Soil pH in *M* KCl	Approximate N_{Al} in soil
5.5	≤ 0.1
5.0	0.3
4.5	0.5
4.0	0.7
3.5	0.9
3.0	>0.9

Because Al^{3+} is more strongly sorbed than Ca [*6*] and hydrogen [*15*] ions, the exchange of K ions in acid soils must be considered in competition with Al ions. Also, the existence of monomeric and polymeric forms of hydroxy-aluminium ions is well established [*16–20*], the positively charged polymeric forms increase as the soil pH changes from 4 to 6 in 0.01 *M* $CaCl_2$. The progression from $(Al^{3+}) \rightarrow (Al(OH)^{2+}) \rightarrow$ (large polymeric cations of varying size) also causes in increasing preferential sorption of Al (e.g., [*21*]), and eventually the formation of an 'aluminium' chlorite at pH values > 6.

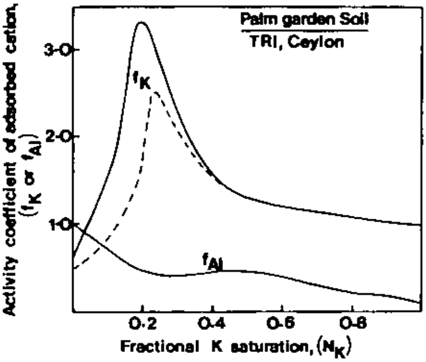

Figure 7. Fractional K saturation, N_K, and the activity coefficients of adsorbed K and Al ions, f_K and f_{Al}, in a Ceylon soil.

This progression of the ionic forms of Al prevents 'fixation' of NH_4^+ (18) and K^+ [*22*] and inhibits interlayer expansion and macro-swelling of expanding 2:1 layer minerals [*23*]. It is relevant, therefore, to consider K exchange in acid soil clays in relation *not only* to protons being incorporated into the lattice and the concomitant loss of net layer charge, *but primarily* to the resultant release of small amounts of Al^{3+} ions displacing K ions from exchange sites. Work reported in the literature hitherto on K release from acidified micas has ignored the role of exchangeable Al and does not contradict the hypothesis that ionic Al is much involved.

We investigated K:Al exchange isotherms on montmorillonite, vermiculite, illite and several soils [*15, 24–26*], but elsewhere, only work on montmorillonite was reported [*27*]. *Coulter* [*24*] showed that in Al → K exchange, montmorillonite slightly preferred Al but vermiculite, illite and two mica-dominant soils selectively adsorbed K (table 4). However, he underestimated this K selectivity by ignoring the initial 5–10% K saturation of the CEC, regarding it as 'difficultly exchangeable' K. This K saturation range includes potassium used by crops, and contributes much to the K selectivity of the soil as measured by the standard free energy value ΔG_0. Singh *and Talibudeen* [*26*] obtained ΔG_0 values from the full isotherm varying between −111 and −2541 cals/equivt (table 5), indicating increasing K selectivity. A lower level of K selectivity or a preference for Al was invariably associated with increasing proportions of chloritic: vermiculitic clay minerals, and higher levels of K selectivity with montmorillonite: illite minerals. An allegedly 'mica-free' soil (CEC 11.0 me/100 g, Soil 6) 'preferred' K most, contradicting the mineralogical analysis of the clay fraction (−2541 cals/equivt). Initially non-exchangeable K was released on exhaustive cropping only by soils containing montmorillonite: illite minerals. Unlike the equilibrium measurements of adsorbed ions by isotopic exchange in K:Ca systems, adsorbed Al was measured by a non-equilibrium desorption method [*14*].

Table 4. Al → K exchange in some English and Ceylon soils and clay minerals

Soil No.	Description	Standard free energy ΔG_0 cal/eqvt	Fractional K saturation N_K	Organic carbon %	$< 2\mu$ clay %	Clay Mineralogy*			Original soil pH (0.01 *M* $CaCl_2$)	$(f_K)_0$	$(f_K)_{0.1}$
						K-M	C-V	mm -I			
1.	Exhaustion Land Rothamsted	—3763	0–1.0	0.8	19	(35)	(— 40	—)	3.9	—	—
2.	Park Grass Rothamsted	— 470	0.1–1.0	2.3	21	75	5	20	4.7	—	—
3.	Deerpark Wexford	— 470	0.1–1.0	2.9	18	75	5	20	4.8	—	—
4.	Vermiculite (Montana)	— 173	0.1–1.0	—	—	20	50	20	—	—	—
5.	Illite (Fithian)	— 173	0.05–1.0	—	—	75	5	20	—	—	—
6.	Montmorillonite (Wyoming)	+ 192	0–1.0	—	—	10	10	80	—	—	—
7.	Eden original	—2895		3.7						0.10	4.0
	TRI, Ceylon		0–1.0		42	Kaolin-rich			3.6		
	oxidised	—3044		0.5						0.20	3.0
8.	Hunuwela original	—3120		2.3						0.10	1.9
	TRI, Ceylon		0–1.0		30	Kaolin-rich			3.8		
	oxidised	—3364		0.3						0.20	1.0
9.	Palmgarden										
	original	—3478		2.8						0.46	1.8
	TRI, Ceylon		0–1.0		23	Kaolin-rich			3.7		
	oxidised	—3763		0.3						0.46	0.9

* Values for Soil 1 are estimated; for soils 2–6, see reference (6)

Table 5. Al → K exchange in and K-uptake by Pueraria from some Malayan soils

Soil No.	Soil Series	Standard free energy ΔG_0 (cal/eqvt.)	Exch. K (ppm)	Uptake of Non-exch. K (ppm)	$< 2\mu$ clay (%)	Clay Mineralogy* K	Clay Mineralogy* C-V	Clay Mineralogy* MM-I	$(f_K)_0$	$(f_K)_{0.1}$
1.	Batu Anam	− 999	70	57	85	25	0	60	0.48	0.75
2.	Chemor	+ 900	24	0	18	80	15	0	0.28	0.35
3.	Kuantan	− 429	39	0	79	75	0	0	—	—
4.	Prang	− 111	39	12	34	75	8	0	0.40	0.85
5.	Rengam	+ 146	55	19	49	80	<5	0	0.15	0.30
6.	Segamat	−2541	63	0	82	75	0	0	—	—
7.	Selangor	−1293	157	140	45	60	0	40	0.23	1.15
8.	Serdang	− 713	42	140	36	60	8	45	0.15	0.80
9.	Ulu Tiram	−1653	24	0	20	80	<5	0	0.62	1.41

* K = kaolinite; C-V = chlorite + vermiculite; MM-I = montmorillonite + illite

Comparing ΔG_0 values obtained from the full isotherms in tables 4 and 5, the strongly leached Malayan soils prefer K much less than those from Ceylon (containing more organic carbon) or from Rothamsted or Wexford, although no general conclusions can be drawn from measurements on a few soils. Removing soil organic matter increased K selectivity (Table 4 and reference [*25*]). Measuring the rate at which K+Al chloride solutions equilibrated with soil showed that 20—24 hours were necessary for true equilibrium [*14, 25*].

These results suggest that the degree of K selectivity of medium to heavy textured 'temperate' acid soils is adequate to maintain their long-term K status. Strongly leached tropical soils, of heavy texture but poor in organic carbon, generally have a much poorer K selectivity. Indeed, when devoid of montmorillonitic or illitic minerals, they preferentially adsorb Al ions. Increasing the organic matter content of soils improves their ability to adsorb and retain K ions by increasing the CEC of the soil and the activity of adsorbed K ions [*25*] (figure 7).

5. *Magnesium*

Direct measurements of Mg:K exchange have not been reported, but Ca:Mg exchange experiments described on soils [*28*] and clays [*29*] enable a qualitative prediction of the characteristics of K exchange in soils as their mineralogical composition and Mg selectivity changes. Increasing vermiculite and Mg content implies greater Mg selectivity [*29*] and predicts an increase in the activity of adsorbed K.

6. *Sodium*

The omission of K-Na exchange experiments on soils would, at first sight, seem strange because saline and alkaline soils are not uncommon in tropical and sub-tropical regions. Our work on Na-K exchange in soils [*4*] shows, however, that the activity coefficient of adsorbed K increases smoothly from about 0.4 to the standard state value of 1.0 as K saturation, N_k, increases from 0 to 1. The ΔG_0 values range from −888 to −1083 cal/mole indicating that soils prefer K ions (table 1), but the activity coefficients show that this K-selectivity is uniformly spread over *all* exchange sites (figure 8). In contrast, these sites show extreme heterogeneity in K-Ca exchange. These results imply that K

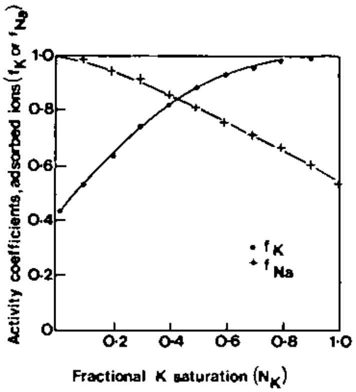

Figure 8. Fractional K saturation, N_K, and the activity coefficients of adsorbed K and Na ions, f_K and f_{Na}, in a Bovey Basin series soil.

release from saline soils containing significant amounts of mica minerals should not be rate limiting.

7. *Rubidium*

Because the ^{42}K isotope decays rapidly (hydrated ion radius ca. 2 Å, anhydrous ion 1.33 Å, half-life 12.4 hours), rubidium-86 (ca. 2 Å, 1.46 Å, 18.6 days) has been used as a tracer in long-term exchange for K, but evidence in the literature suggests that often ^{86}Rb does not 'trace' soil K accurately (e.g. [*30, 31*]). We measured Rb → K exchange isotherms [*4*] on 8 soils and calculated ΔG_0 values ranging from +377 to +667 cal/mole (table 1) indicating a small but significant preference for Rb. The activity coefficients of adsorbed K and Rb, f_K and f_{Rb}, did not change appreciably from the standard state value of 1.0, implying that both ions were equally free to move on soil surfaces. This apparent anomaly was resolved by the discovery that various concentrations of Rb ions added to untreated soils exchanged with Ca ions very rapidly first (in < 0.5 h) and then with K ions, enabling us to calculate small amounts of specifically adsorbed Rb [*32*]. If the Rb:K exchange isotherm is corrected for this 'specific' Rb, ^{86}Rb at known carrier levels can be used as a tracer for soil K. Electron microprobe analysis on weathered micas showed that Rb ions concentrate 'at particle and step edges, at cracks, and in the case of partially K-depleted biotite, at boundaries of vermiculite and mica zones' [*33*]. Recently, our work on soils from a long-term field experiment showed that building up K reserves in a soil increased its specificity for Rb, suggesting that such 'edges, cracks and phase boundaries' were more pronounced, or that because K treatment decreases the CEC, specific Rb sites contribute more to Ca-Rb exchange [*34*]. More organic matter, however, decreases the soil's affinity for Rb.

8. *Organic cations*

Interest in the use of organic cations stems from the possibility that using cations of different sizes and shapes may enable the determination of different categories of soil K and the reserves of non-exchangeable K (e.g., [*35, 36*]). The main difficulties in such work are the purity and stability of the cations, their various degrees of buffering and solubility, and the specific adsorption they show for different minerals. However, these experiments show that the 'displacing powers' of such cations is invariably less than that of inorganic cations such as NH_4^+, Rb^+ and Cs^+, so their use in 'fractionating' soil K does not look very promising.

9. *The nature of 'non-exchangeable' K in soil*

The characteristics of K ions adsorbed on easily accessible negatively charged sites (CEC) were discussed in the previous section. Ample evidence suggests, and sometimes proves, that this potassium is continuously in contact with K ions on less accessible sites, at least in the smaller particle size fractions of the soil (figure 1). The speed with which such equilibria are established depend on (1) environmental factors, such as expansion and contraction caused by 'wet-and-dry' and 'freeze-and thaw' cycles, (2) characteristics of the mineral lattices, e.g., surface charge density, location of negative charges, and the extent of the surface, (3) the nature of the counter-cations in the soil-water complex, (4) the thickness of water films on adsorbing surfaces, i.e. the combination of the average diameter of micropores and the water content of the soil and, probably most important of all, (5) the concentration of K ions relative to other cations in the equilibrating solution.

9.1 *The concentration of potassium in solution*

Several agencies have been used to keep the solution K concentration in contact with the soil at a minimum. Ryegrass was shown to remove significant amounts of 'non-exchangeable' K from soil in pots [*37*] and [*13*] that this K was released at a K concentration of 10^{-4} *M* (4 ppm K) in 10^{-2} *M* $CaCl_2$ from nearly 30 English soils taken from contrasting series. Similar concentrations were measured in subsequent work at Rothamsted [*38*] on soils from Stackyard and Sawyers.

The rate of release of K to crops is governed partly by crop characteristics, including its senescence during which the partial return of K taken up by the crop to the soil through roots prevents decrease in the soil solution concentration, thus slowing and possibly even preventing the further release of non-exchangeable K. Thus, the crop cannot safely be used to measure the rates of release of 'non-exchangeable' K from various sources in soil. Sodium tetraphenyl boron (NaTPB) was used, more often than other agents, to maintain very low and constant concentrations of K ions in solutions bathing soil clays [*39*] and micas [*40,41*] and to measure the rates of release of K. Such experiments invariably show that, given time, K in all micas can be replaced and, qualitatively, the rates of release are in the order: biotites > vermiculites > illites >> muscovites. The exchange of K from soil clays [*39*], up to maximum amounts varying between 20–47% of their total K contents was shown to be semilogarithmically related to time, the remaining truly non-exchangeable K being attributed to feldspars. Extraction with NaTPB involves *in situ* precipitation of the K salt and its subsequent removal as intermediate steps. Thus, the rates of release measured can, at best, be regarded as qualitative expressions of the relative characteristics of various minerals.

Solutions of 0.0033 *M* $CaCl_2$ and 0.25 *M* NaCl at ambient and elevated temperatures

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Exchange of Zn, Mn, Cu and Fe in Relation to Saturation of the Soil Complex

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Summary: see at the end of this paper

1. *Introduction*

Due to the relative low content of trace elements in soils in comparison with the major elements, an important competition from the latter may be expected with regard to the equilibrium reactions in which they take part. Trace elements may be present as free ions in the soil solution, as soluble organo-mineral complexes, in adsorbed form associated with soil surfaces and precipitated or bound in the solid phase. The distinction between surface adsorption and precipitation reactions is however not always clearly distinct *(Hodgson, 1963)*.

The distribution of an element between these forms is the result of several competitive reactions in which major as well as trace elements are involved and the transfer of one form to another depends upon the equilibrium constants governing the different reactions between them. Changes of the equilibrium states will occur in function of the following factors:

- input of elements e.g. by fertilizer application,
- output by leaching or uptake by plants,
- changing water-content (dilution or concentration),
- pH changes.

In fact the pH is one of the dominant parameters influencing the distribution of an element between the above mentioned fractions.

From the analytical point of view the estimation of free ions is quite difficult, because the soil solution also contains the soluble organo-mineral complexes.

In this paper an attempt is described to determine separately these trace element fractions and to observe the equilibrium displacements taking place in function of pH and major element variations.

2. *Analytical methods*

The following analytical procedure for determining the free, complexed and adsorbed ions was used:

a. *the soluble ions* are determined in a 1/5 soil-water extract. In order to separate the free and complexed forms, 50 ml of this extract are treated with 2 g of cation-exchange resin Dowex 50 W (Na-form) and filtered after 1 hour of equilibration. In this way the free ions are removed and further analysis of the filtrate provides the quantities of elements present as organo-mineral complexes.

b. *the exchangeable ions* were estimated after leaching the soil with 1 n NH_4OAc at pH = 7 (*Schollenberger* and *Simon* [*1945*]) at a soil/solution ratio of 1/25. In these percolates the elements Ca, Mg, K, Na, Mn and Zn were determined respectively by flame photometry and atomic absorption.

Since neutral displacement-solutions are not appropriated for the determination of Cu and Fe, due to the lower solubility of their hydroxides (*Jackson, 1958*), these elements were exchanged with 1 n NH_4OAc at pH = 3.

The cation exchange capacity was determined using the NH_4^+ saturated soil from b. After eliminating the excess NH_4^+ with ethanol 95%, the total quantity of adsorbed NH_4^+ was displaced with 1 n KCl and determined by distillation (*Pelloux, 1963*). The calcareous soils (9 and 10) however, were saturated with Ca^{++} by leaching with 1 *n* $CaCl_2$ after which Ca^{++} was displaced with 1 *n* KNO_3 and determined by flame photometry. In order to correct for $CaCO_3$, dissolving during this operation, CO_3^{--} and HCO_3^- are determined in the percolate by titration with H_2SO_4 N/50 (*Pelloux, 1963*). Former research has shown that:

1. even in acid medium the cation exchanger Dowex 50 W fixes completely all free ions in solution.
2. the determination of $CaCO_3$ as described, is in satisfactory agreement with its direct estimation in the soil.

3. *Quantities of exchangeable and soluble elements*

Tables 1 and 2 show the results of the major and trace element analysis in 10 soil samples. The C.E.C. of the soils is significantly correlated with their content of exchangeable Ca, the correlation coefficient between C.E.C. and exchangeable Ca being 0.93^{***}. In case of Mg and K the correlation coefficients are low (respectively 0.59^{*} and $0.525^{(*)}$).

Concerning the trace elements no correlation was observed between their adsorbed forms

Table 1. General soil characterization and major element contents

Sample	C.E.C. in meq/100g of soil	pH H_2O	pH KCl	% C (*Walkley and Black*)	Exchangeable bases in meq/100 g of soil				Total exchange-able bases (milli-eq. per 100 g)	Saturation rate in %	Texture
					Ca	Mg	K	Na			
1. Herentals	7.50	4.85	3.95	2.35	0.70	0.07	0.05	0.09	0.91	12.13	sand
2. Peruwelz	8.30	6.25	5.50	1.30	4.75	0.34	0.16	0.05	5.30	63.85	light sandy loam
3. Wan-Lede	9.40	5.65	4.75	1.54	6.20	0.55	0.60	0.10	7.45	79.25	heavy sandy loam
4. Glabbeek	10.25	6.45	5.25	1.38	2.40	0.70	0.60	0.06	3.76	36.70	light sandy loam
5. Ath	11.25	6.50	5.75	1.42	7.25	0.88	0.48	0.08	8.69	77.25	light loam
6. Merendree	11.55	6.30	5.05	2.23	5.90	1.10	0.20	0.07	7.27	62.90	sandy loam
7. Waarschoot	11.87	5.60	4.60	2.52	4.00	0.35	0.10	0.07	4.52	38.10	loamy sand
8. Proven	15.75	7.75	6.90	0.65	14.40	0.66	0.19	0.08	15.33	97.30	sandy loam – heavy sandy loam
9. Kieldrecht	19.50	7.85	7.20	2.23	14.10	1.37	0.51	0.13	16.11	82.50	heavy sandy loam
10. Pervijze	32.50	7.10	6.65	1.79	11.50	1.03	0.70	0.19	23.42	72.00	heavy clay

Table 2. Soluble (S) and adsorbed (A) quantities of Zn, Mn, Cu and Fe

Samples	In milli-eq. × 10^{-3} per 100 g of soil											
	Zn			Mn			Cu			Fe		
	S_F	S_c	A	S_F	S_c	A	S_F	S_c	A	S_F	S_c	A
1. Herentals	0.46	tr.	6.5	tr.	tr.	tr.	1.01	tr.	4.7	3.60	tr.	80.6
2. Peruwelz	tr.	0.31	11.9	3.57	0.98	59.2	1.10	tr.	7.3	3.10	17.20	141.5
3. Wan-Lede	tr.	0.14	10.7	8.20	tr.	275.7	tr.	0.38	16.5	2.10	4.20	94.0
4. Glabbeek	1.38	tr.	9.6	1.27	tr.	47.4	0.79	tr.	4.7	8.25	27.75	107.5
5. Ath	0.76	tr.	6.5	6.00	tr.	197.6	tr.	0.79	6.3	0.50	6.70	103.0
6. Merendree	0.76	tr.	2.3	1.82	tr.	50.1	1.57	tr.	9.4	18.30	20.20	241.8
7. Waarschoot	0.67	tr.	9.2	0.90	tr.	63.7	3.15	tr.	5.2	1.60	tr.	62.7
8. Proven	tr.	tr.	4.6	tr.	tr.	17.3	tr.	tr.	5.9	2.50	2.90	50.2
9. Kieldrecht	tr.	0.31	6.9	tr.	tr.	29.1	tr.	1.57	14.2	tr.	7.60	394.0
10. Pervijze	tr.	tr.	2.3	tr.	tr.	8.2	tr.	tr.	2.4	tr.	8.10	111.0

S_F: free ions in solution S_c: soluble complexes A: adsorbed ions tr.: trace

and the C.E.C., but the exchangeable quantities were much larger than their water soluble fraction, which was even not detectable in some cases. The amounts of adsorbed Fe ranged between 50.1 and 394.0 micro-equiv. per 100 g of soil.

Exchangeable Mn ranged between traces and 275.6 micro-equiv. per 100 g and in three soils adsorbed Mn was higher than exchangeable Fe. Adsorbed Zn and Cu were of the same order, ranging respectively between 2.3 to 11.9 and 2.4 to 16.5 micro-equiv. per 100 g of soil.

Soluble complexes of Zn, Mn and Cu were only found in a few samples, while most soils contained a relatively large amount of Fe in soluble complexed form.

4. *Mobility of trace-elements in function of pH*

The adsorbed fraction and the mobility of trace elements in soils being strongly influenced by the pH, an experiment was conducted in order to observe the variations in both soluble and adsorbed quantities of Fe, Mn, Zn and Cu under the influence of varying pH-values. Therefore each of these elements was added in increasing quantities to a soil-water suspension at controlled pH.

After equilibration during 30 minutes both the equilibrium solution and the solid phase were analysed in the same way as described before. After filtration the soil was washed with ethanol in order to eliminate the remaining soluble ions.

The soil used for this experiment had a C.E.C. of 11.5, a C-content of 2,23% and a pH-H_2O of 6.30.

The soil/solution ratio was 1/5 and in order to facilitate the observations, the quantities of elements added were varied between 0 and 50 ppm in the solution, while the pH was brought with HNO_3 to values ranging from the original figure down to 0.5.

Due to the so-called suspension-effect the pH of the filtrates did not precisely correspond with the controlled pH of the suspension.

Since percolation of the treated samples was made with a soil/solution ratio of 1/25, the results obtained from analysis of the percolates were multiplied by 5 in order to permit a direct comparison with the corresponding concentrations in the equilibrium solutions (Tables 3–6). Figure 1 representing the solubilization of soil Mn, Zn, Cu and Fe, shows that the solubility of these elements increases rapidly with decreasing pH values.

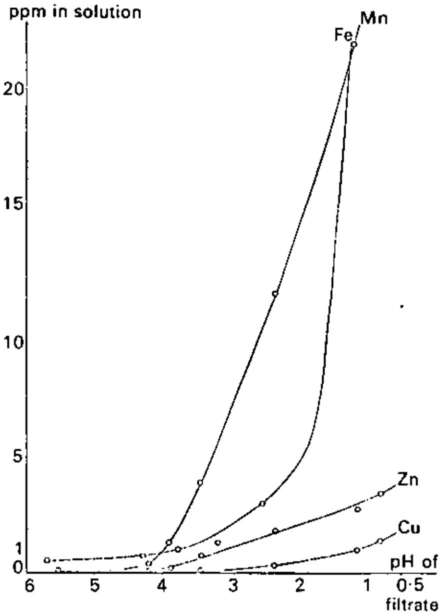

Figure 1. Solubilisation of soil Mn, Zn, Cu and Fe in function of decreasing pH.

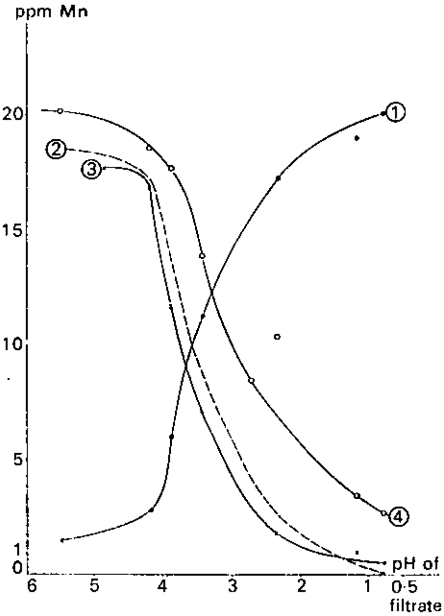

Figure 2. Manganese equilibrium displacement in function of pH(20 ppm Mn added).
curve 1: added Mn remaining in solution
curve 2: added Mn retained by the soil
curve 3: retained Mn as determined by percolation at pH 7
curve 4: retained Mn as determined by percolation at pH 3

4.1. *Manganese*

The results of the experiment with Mn are summarized in table 3.

In this case more than 90% of the added quantities were removed from the equilibrium solution at pH $>$ 5 and up to 50% at pH ± 3.5, while practically the total quantities remained soluble at pH values lower than 2.

Figure 2 shows the Mn-distribution (adsorbed and soluble Mn) in the case when 20 ppm Mn was added to the soil-solution system. Curve 1 represents the quantities of added Mn remaining in solution, while the complementary quantities retained by the soil are represented in curve 2 (theoretical curve).

In order to determine the quantities of adsorbed Mn, percolations were made with 1 *n*-NH_4Ac of pH 7 and 3 (curves 3 and 4).

Curve 3 representing the adsorbed Mn as determined by percolation at pH = 7 corresponds quite truly with the theoretical curve 2, as calculated from the values in table 3. On the other hand percolation at pH 3 provides values which are too high (curve 4).

While the desorption of Mn is quite complete below pH 2, its adsorption strongly increases at higher pH, as might be expected. Since the curves 1 and 3 (figure 1) showing the evolution of soluble and adsorbed Mn are remarkably complementary, it seems that phenomena of precipitation and dissolution did not interfere to an observable extent and that the adsorption of Mn proceeds in a reversible way.

Table 3. Manganese mobility in function of pH

pH	ppm Mn added	pH of the filtrate	ppm Mn in the equilibrium solution	Added Mn remaining in solution (in ppm)	Mn retained by the soil (in ppm)	ppm Mn in the percolates		Mn retained in exchang. form (ppm)	
						pH = 3	pH = 7	pH = 3	pH = 7
6.3 (original)	0	5.50	0.04	—	—	1.47	0.53	—	—
	1	4.95	0.075	0.035	0.965	2.00			
	2.5	5.00	0.075	0.035	2.465	2.20			
	5	5.25	0.20	0.16	4.84	2.65			
	10	5.15	0.47	0.43	9.57	2.84			
	20	5.65	1.52	1.48	18.52	5.10	4.07	18.15	17.70
	50	4.90	6.60	6.56	43.44	14.00			
5	0	4.20	0.40	—	—	1.50	0.48	—	—
	20	4.20	3.20	2.80	17.20	5.10	4.00	18.11	17.60
4	0	3.90	1.36	—	—	1.30	0.92	—	—
	20	3.90	7.44	6.08	13.92	5.35	3.26	20.25	11.70
3	0	3.45	3.96	—	—	1.30	1.00	—	—
	20	3.45	15.10	11.24	8.67	4.08	2.42	13.90	7.10
2	0	2.35	12.20	—	—	0.83	0.60	—	—
	20	2.35	39.50	17.30	2.70	2.96	0.96	10.40	1.80
1	0	1.20	22.00	—	—	1.11	0.15	—	—
	20	1.20	41.00	19.00	1.00	1.81	0.38	3.45	1.15
0.5	0	0.80	24.50	—	—	1.57	0.15	—	—
	20	0.80	44.50	20.00	0	2.12	0.26	2.75	0.55

Table 4. Zinc mobility in function of pH

pH	ppm Zn added	pH of the filtrate	ppm Zn in the equilibrium solution	Added Zn remaining in solution (in ppm)	Added Zn retained by the soil (in ppm)	ppm Zn in the percolates		Zn retained in exchang. form (ppm)	
						pH = 3	pH = 7	pH = 3	pH = 7
6.3 (original)	0	5.50	0.02	—	—	0.34	0	—	—
	1		0.02	—	1.00	0.65		1.55	
	2.5		0.02	—	2.50	1.03		3.45	
	5		0.46	0.44	4.56	1.36		5.10	
	10		0.62	0.60	9.40	2.56		11.10	
	20	5.50	0.97	0.95	19.05	4.70	2.36	21.80	11.80
	50		1.32	1.30	18.70	10.00		48.30	
5	0	4.20	0.06	—	—	0.35	0.05	—	—
	20	4.20	1.78	1.72	18.18	4.55	1.14	22.20	11.70
4	0	3.90	0.27	—	—	0.23	0.06	—	—
	20	3.90	8.80	8.53	11.47	4.10	2.12	19.38	10.30
3	0	3.45	0.87	—	—	0.23	0.05	—	—
	20		16.10	15.23	4.77	2.02	1.18	8.95	5.68
2	0	2.35	1.84	—	—	0.13	0.08	—	—
	20		23.30	20.46	—	1.02	0.25	4.47	0.87
1	0	1.15	2.80	—	—	0.10	0.02	—	—
	20		24.40	21.60	—	0.25	0.10	0.75	0.43
0.5	0	0.80	3.50	—	—	0.16	0.03	—	—
	20		27.40	23.90	—	0.18	0.05	0.10	0.07

Table 5. Copper mobility in function of pH

pH	ppm Cu added	pH of the filtrate	ppm Cu in the equilibrium solution	Added Cu remaining in solution (in ppm)	Added Cu retained by the soil (in ppm)	ppm Cu in percolates		Cu retained in exchang. form (ppm)	
						pH = 3	pH = 7	pH = 3	pH = 7
6.3 (original)	0	5.50	0	—	—	0.11	0	—	—
	1		0.16	0.16	0.84	0.23		0.60	
	2.5		0.16	0.16	2.34	0.60		2.49	
	5		0.36	0.36	4.64	0.88		3.85	
	10		0.20	0.20	9.80	1.95		9.20	
	20	5.70	0.25	0.25	19.75	4.22	0.84	20.55	4.20
	50		0.32	0.32	49.68	6.90		33.90	
5	0	4.20	0.01	—	—	0.15	0	—	—
	20	4.10	0.50	0.49	19.51	3.92	1.10	18.85	5.50
4	0	3.90	0.04	—	—	0.19	0	—	—
	20	3.90	0.55	0.52	19.48	3.92	1.23	18.55	6.15
3	0	3.45	0.04	—	—	0.15	0	—	—
	20	3.35	3.70	3.67	16.34	4.10	0.90	17.75	4.50
2	0	2.35	0.34	—	—	0.19	0	—	—
	20	2.30	15.90	15.46	4.54	2.40	0.62	11.05	3.10
1	0	1.15	1.05	—	—	0.11	0	—	—
	20	0.90	21.40	20.15	—	0.94	0.05	4.15	0.25
0.5	0	0.80	1.40	—	—	0.08	0.09	—	—
	20	0.70	21.80	20.40	—	0.64	0.05	2.82	—

Table 6. Iron mobility in function of pH

pH	ppm Fe added	pH of the filtrate	ppm in solution after equilibration	ppm Fe in percolates with NH_4Ac of pH 3
6.3 (original)	0	5.70	0.55	4.53
	1	5.80	0.20	5.12
	2	5.85	0.27	5.12
	5	5.80	0.20	5.30
	10	5.40	0.10	5.12
	20	5.10	0.20	5.81
	50	4.70	1.15	7.50
5	0	4.30	0.25	4.57
	5	4.90	0.48	4.25
	10	4.00	1.70	6.34
	50	4.35	1.35	5.85
4	0	3.80	1.02	4.50
	5	4.00	0.85	5.05
	10	3.90	1.30	3.80
	50	3.50	1.55	5.75
3	0	3.20	1.32	5.35
	5	3.60	3.65	6.10
	10	3.55	2.35	5.62
	50	3.00	5.25	9.30
2	0	2.55	3.04	6.80
	5	2.70	8.60	9.60
	10	2.90	6.75	8.00
	50	2.20	7.55	8.60
1	0	1.10	42.50	13.00
	5	1.35	35.20	15.20
	10	1.60	26.25	26.25
	50	1.40	73.50	25.75
0.5	0	0.70	216.0	31.50
	5	0.60	275.5	36.00
	10	0.90	217.5	40.50
	50	0.90	212.5	46.25

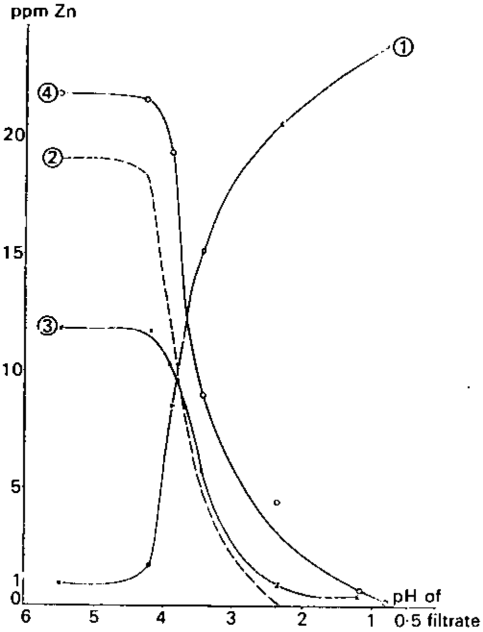

Figure 3. Zinc equilibrium displacement in function of pH (20 ppm Zn added)
curve 1: added Zn remaining in solution
curve 2: added Zn retained by the soil
curve 3: retained Zn as determined by percolation at pH 7
curve 4: retained Zn as determined by percolation at pH 3

4.2 *Zinc*

The equilibrium of soil with Zn-containing solutions at different pH showed that Zn fixation took place in the range between the original soil pH and pH 3.

At lower values the total added quantities remained in solution and a slight dissolution of soil zinc was observed. Table 4 contains some illustrative results and shows also the quantities of this element as determined by percolation of the treated samples with 1 n NH_4OAc at pH 3 and 7. Since it appears that the former percolation method provides values which are higher than those retained by the soil, it can be concluded that the acid displacement solution is not appropriated for the determination of exchangeable zinc. The desorption of this element was practically complete at pH 2.5.

As shown in figure 3 the Zn quantities desorbed at $pH = 7$ (curve 3) were much smaller than the amounts retained by the soil in slightly acid conditions (curve 2). The difference is to be considered as fixed Zn, in accordance with *Elgabaly* [*1950*].

The experiment shows that Zn adsorption was reversible at $pH < 4$ but not at higher pH values.

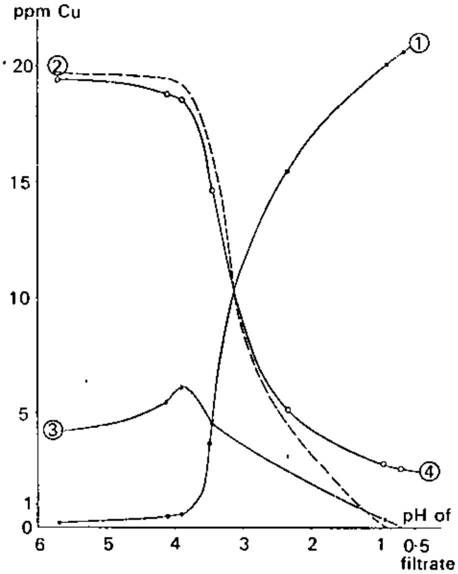

Figure 4. Copper equilibrium displacement in function of pH (20 ppm Cu added).
curve 1: added Cu remaining in solution
curve 2: added Cu retained by the soil
curve 3: retained Cu as determined by percolation at pH 7
curve 4: retained Cu as determined by percolation at pH 3

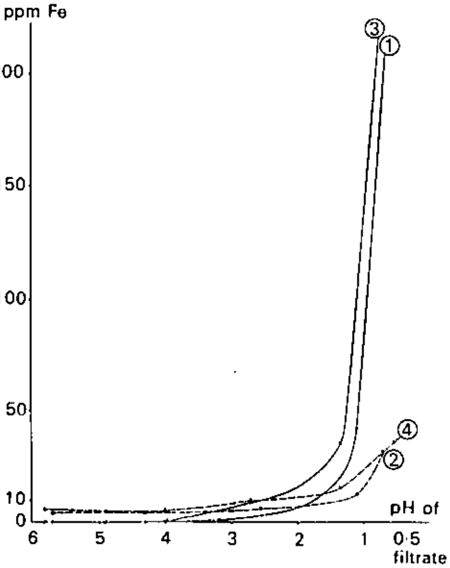

Figure 5. Iron equilibrium displacement in function of pH
curve 1: ppm Fe in equilibrium solution
curve 2: ppm Fe in percolates
curve 3: ppm Fe in equilibrium solution (5 ppm Fe added)
curve 4: ppm Fe in percolates (5 ppm Fe added)

4.3 *Copper*

In contact with Cu containing solutions, the soil continued to fix this element as long as the pH of the equilibrium solution remained higher than 1, at which pH desorption was practically complete. This is confirmed by analysis of the equilibrium solutions as shown in table 5. After separating and washing with alcohol, the remaining soil was once again percolated with 1 *n* NH_4OAc at pH = 3 and 7.

As illustrated in figure 4 the latter method provided only a relative small part of the retained Cu with a maximum at pH values near 4 (curve 3). The decrease observed at higher pH could be attributed to Cu precipiation.

On the other hand nearly the total Cu-quantities retained by the soil during the first phase of the experiment, were removed by percolation at pH = 3 (figure 4, curve 4). The same adsorption and exchange pattern was found for each level of Cu addition between 1 and 50 ppm, as is shown in figure 4 in the case of 20 ppm addition in the equilibrium solution.

4.4 *Iron*

Table 6 shows a summary of the experiments with Fe. As is also illustrated in figure 5, the Fe-content of the equilibrium solution increases very strongly with decreasing pH: at pH-values lower than 2 the added quantities of Fe were fully recovered in the solution and even largely increased by native soil iron. At higher pH a large part of this element is removed from solutions containing more than 2 ppm.

On the other hand the quantities determined as exchangeable Fe by leaching with 1 *n*-NH_4OAc pH = 3, were quite constant in the soil pH-range of 6 to 3 and increased considerably at lower pH. In slightly acid medium precipitation of this element seems to be strongly competitive towards its adsorption.

In this respect Fe behaved completely opposite with the other elements under study. This indicates that the method for determining adsorbed Fe is not valid, at least in strongly acid conditions, while dissolution phenomena predominate in such situations.

These experiments show that only in the case of manganese the amounts retained by the soil were quantitatively exchangeable as determined by leaching with 1 *n*-NH_4Ac of pH 7, zinc being partly fixed at pH > 4 in a non exchangeable way. Copper could be quantitatively exchanged by 1 n NH_4Ac of pH 3. In the case of iron, adsorption was strongly masked by precipitation phenomena, while important native quantities of this element were mobilized at low pH.

5. *Trace-element exchange as influenced by major element additions*

Another experiment was carried out in order to observe the exchange of Zn, Mn, Cu and Fe as influenced by major element additions.

Therefore, three soils with different texture, were treated with Ca, Mg and K, the amounts of which being calculated in order to saturate almost completely their adsorption complex. Therefore the following quantities of these elements were added as neutral nitrates in a soil-water suspension:

Sample	C.E.C. (milli-eq. per 100 g)	original saturation rate	milli-eq. of each Ca, Mg, K added per 100 g of soil
7. (Waarschoot)	11.87	38.10%	7.35
5. (Ath)	11.25	77.25%	5
8. (Proven)	15.75	97.30%	5

After equilibration during 30 minutes the suspensions were filtered in view of the determination of soluble major and trace elements. Furthermore all treated soils were washed with alcohol and percolated with:

- 1*n* NH_4OAc at pH = 7 for the determination of exchangeable Ca, Mg, K, Na, Zn and Mn
- 1*n* NH_4OAc at pH = 3 for the determination of exchangeable Cu and Fe.

The results of these determinations are given in table 7. Comparing the situation reached by the applied treatments, the soluble forms of all the major elements increased quite considerably.

Each individual element added caused an increase of its adsorbed form and a small desorption of the other elements. The equilibrium changes in comparison with the original situation are given in table 8. The Mg treatments caused the largest displacement followed by K and Ca, for which the alteration remained quite low.

The resulting variations with respect to the trace element distribution over soluble and adsorbed forms were practically inexistant for Cu. In the case of Fe no definite trend could

Table 7. Soluble (S) and adsorbed (A) elements in soils enriched with Ca, Mg and K

Soil	Treated with	In meq per 100 g soil Ca								Total exchangeable bases (in milli-eq. per 100 g)	In mg per kg soil (ppm) Zn							
		Ca		Mg		K		Na			Zn		Mn		Cu		Fe	
		S	A	S	A	S	A	S	A		S	A	S	A	S	A	S	A
7. Waarschoot	Ca^{++}	7.50	4.47	0.20	0.12	0.05	0.10	0.06	0.04	4.73	1.50	3.00	7.60	15.30	1.00	1.65	1.00	26.50
	Mg^{++}	2.95	3.17	5.43	1.40	0.05	0.10	0.06	0.04	4.70	2.10	2.75	8.40	16.15	1.00	1.65	1.00	18.95
	K^{+}	1.12	3.00	0.13	0.23	6.20	1.09	0.06	0.04	4.35	0.50	3.25	3.20	17.00	1.00	1.65	2.00	15.15
	orig.	0.20	4.00	0.03	0.35	0.02	0.10	0.04	0.07	4.52	0.22	3.00	0.25	17.50	1.00	1.65	0.45	17.50
5. Ath	Ca^{++}	5.17	7.65	0.26	0.64	0.15	0.46	0.05	0.05	8.80	0.28	1.56	6.80	31.40	0.25	3.32	0.75	25.00
	Mg^{++}	1.90	6.05	2.34	2.93	0.15	0.36	0.06	0.05	9.39	0.28	1.25	5.20	38.40	0.25	1.67	tr.	27.50
	K^{+}	1.52	6.05	0.19	0.69	3.60	1.70	0.05	0.04	8.48	0.22	1.25	3.20	38.40	0.25	3.32	tr.	30.00
	orig.	0.24	7.25	0.05	0.81	0.14	0.48	0.05	0.08	8.68	0.25	2.12	1.65	54.25	0.25	3.32	2.00	28.75
8. Proven	Ca^{++}	3.64	14.62	0.18	0.63	0.08	0.26	0.08	0.05	15.56	0.07	0.63	0.80	5.70	tr.	1.87	1.50	27.50
	Mg^{++}	2.65	12.25	2.14	2.77	0.10	0.29	0.08	0.05	15.56	0.14	0.94	0.80	2.85	tr.	1.87	tr.	20.00
	K^{+}	2.07	14.10	0.12	0.62	3.20	1.73	0.08	0.05	15.50	0.14	0.94	0.40	4.27	tr.	1.87	0.75	25.00
	orig.	0.45	14.40	0.03	0.66	0.03	0.19	0.07	0.08	15.03	tr.	1.50	tr.	4.75	tr.	1.87	1.50	14.00

tr.: traces below detection limit

Table 8. Equilibrium displacements caused by Ca, Mg and K additions

Soil nr.	Treated with	In meq per 100 g soil								In mg per kg soil (ppm)							
		Ca		Mg		K		Na		Zn		Mn		Cu		Fe	
		S	A	S	A	S	A	S	A	S	A	S	A	S	A	S	A
7. Waarschoot	Ca^{++}	+7.30	+0.47	+0.17	—0.23	+0.03	—	+0.02	—0.03	+1.28	—	+7.35	— 2.20	—	—	+0.55	+ 9.00
	Mg^{++}	+1.75	—0.83	+5.31	+1.05	+0.03	—	+0.03	—0.04	+1.88	—0.25	+8.15	— 1.35	—	—	+0.55	+ 1.45
	K^{+}	+0.92	—1.00	+0.10	—0.12	+6.18	+0.99	+0.02	—0.04	+0.28	+0.25	+2.95	— 0.50	—	—	+1.55	— 2.35
5. Ath	Ca^{++}	+4.93	+0.40	+0.21	—0.17	+0.01	—0.02	—	—0.03	+0.03	—0.56	+5.15	—22.85	—	—	—1.25	— 3.75
	Mg^{++}	+1.66	—1.20	+2.29	+2.12	+0.01	—0.12	+0.01	—0.03	+0.03	—0.87	+3.55	—15.85	—	—1.67	—2.00	— 1.25
	K^{+}	+1.28	—1.20	+0.14	—0.12	+3.46	+1.22	—	—0.04	—0.03	—0.87	+1.55	—15.85	—	—	—2.00	+ 1.25
8. Proven	Ca^{++}	+5.19	+0.22	+0.15	—0.03	+0.05	+0.07	+0.02	—0.03	+0.07	—0.87	+0.80	+ 0.95	—	—	—	+13.50
	Mg^{++}	+2.20	—2.15	+2.11	+2.11	+0.07	+0.10	+0.02	—0.03	+0.14	—0.56	+0.80	— 1.90	—	—	—1.50	+ 6.00
	K^{+}	+1.72	—0.30	+0.09	—0.04	+3.18	+1.54	+0.02	—0.03	+0.14	—0.56	+0.40	— 0.48	—	—	—0.75	+11.00

be distinguished and the observed changes were small in comparison with the total amounts present (Table 2). Both Zn and Mn were generally desorbed by the addition of major cations and an increase of their soluble forms took place. The involved quantities were generally small, except in the case of Mn in soil n° 5, originally qualified as being rich in this element.

The increase of soluble Zn and Mn did however not systematically correspond with their desorbed quantities. In neutral and alcaline soil (n° 5 and 8) their recovery was incomplete, apparently due to precipitation, while in acid soil (n° 7) their soluble fraction increased more than expected in accordance with the observed desorption.

6. *Summary and Conclusions*

An analytical method was studied in order to distinguish between adsorbed and soluble free ions as well as complexed elements in the soil.

These fractions were determined in different soil samples with special reference to the equilibrium displacements in function of pH changes and major element additions. The cationic trace elements appeared to be mainly present in exchangeable form.

Adding trace elements to the soil-water equilibrium system resulted in the fixation of Zn, Mn and Cu by the soil at pH values higher than 4. Desorption of these elements was practically complete at pH 2 in the case of Mn, 2.5 in the case of Zn and 1.0 in the case of Cu. Iron behaved in a different way than the former elements, precipitation of this element being strongly competitive towards adsorption.

Reversibility of the adsorption phenomenon was only observed in the case of Mn and Cu, zinc was partly fixed in a non exchangeable way at pH > 4 and iron adsorption was strongly masked by precipitation phenomena.

Major cationic treatments did only displace systematically Zn and Mn, while Cu was not influenced to a measurable extent and no distinct pattern was observable for Fe.

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Changes in K/Ca Exchange Properties of Clay in Loess-derived Soils in Soil Formation.

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Summary

K/Ca exchange curves *(Beckett [3])* have been used to determine changes in K/Ca exchange properties of clays in soil development. The exchange curves must be extended to final activity ratio of 0.4–0.5 (mol/l)½ for determination of clay mineral transformations in Holocene loess-soils so that the immediate Q-I curve becomes linear.

Under these conditions data on K/Ca exchange curves are better suited to determine minor transformations of clay minerals in mixtures of 3-layer-clay minerals than X-ray data or other chemical analyses.

From 52 characteristics analysed the values of the K/Ca exchange curves were the most important for the explanation of transformations of clay minerals in profiles of loess soils. The buffer capacity across ARO (BCKE) has an extremely high sensitivity followed in the second place by the exchange capacity of specific adsorption sites with high affinity for K (CECx). BCKE and CECx decrease with increasing duration of soil formation. Hence, together with the results of the multiple regression analyses, it can be concluded that 18 Å-minerals have changed into 10 Å-minerals during the Holocene period.

Chemical, adsorption and X-ray measurements were made on 31 loess soil profiles from Central Germany and 10 from Lower Bavaria and used to investigate changes in clay minerals. K fertilization was ruled out by the use of limiting values for exchangeable potassium (e.g. 0.46 mg K/g clay for A_1 horizon and 0.55 for A_h horizon) and the processes observed can be explained in terms of K-release and K-fixation by minerals of varying granulation.

K/Ca exchange properties were among those investigated and from changes in these statements can be made about transformations of clay minerals. Exchange properties were determined according to the method of *Beckett* [*3*].

This method had, up to now, been only used for the determination of the K/Ca exchange properties of soils with reference to K-fertilization and K-nutrition of plants. In these cases it can be assumed that the quantities of clay minerals and their composition were equal before the start of the experiment. The object of these investigations was to correlate data from K/Ca exchange curves, which, especially at low AR values, have high precision, with X-ray values which are inaccurate for mixtures of layer-silicates. The parameter derived from the K/Ca exchange isotherm should be related to certain types of minerals and if possible they should be coordinated to the clay mineral types by statistical methods. Thus changes in clay minerals which could not be detected by X-ray analysis could be studied. In this connection it is important that the exchange isotherm should extend to

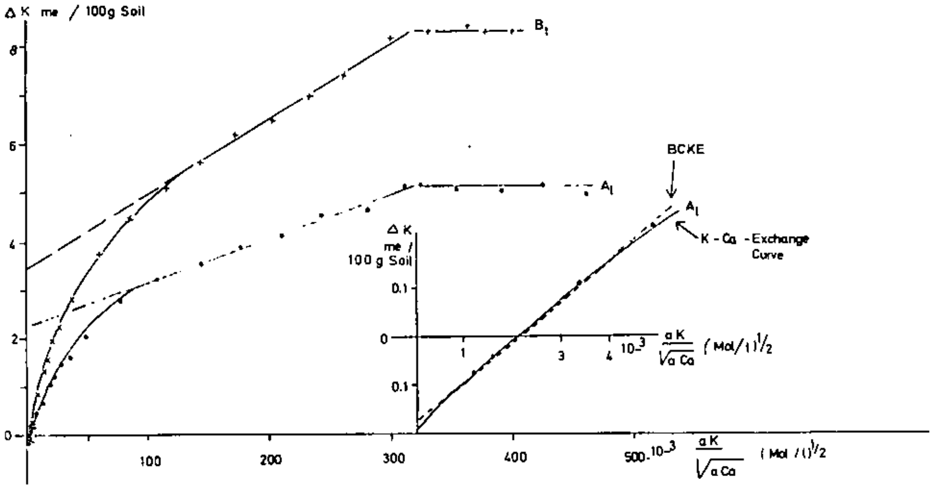

Figure 1. K/Ca exchange curves for two loess soils

include the linear part independent of the clay mineral composition of the soil. In few soils it was not possible to reach the linear part, as reported earlier *(Ehlers et al.* [*8*], *Addiscott* [*1*]*)*. In all the soils studied the curves were extended as far as AR=0.5 (mol/l)½. The form of curve obtained is shown in figure 1 for two soils.

The exchange gradient, PBCK after *Beckett* [*3*] or, briefly, BCK, lies between 0.1 and 0.33 (mol/l)½ and is thus in a higher range than reported until now for other soils *(Beckett* and *Nafady* [*4*], [*5*], [*6*], [*7*], *Acquaye et al.* [*2*], *Zandstra & Mackenzie* [*11*] etc.). The slope is flatter than that found in most other studies. In all soils and sediments analysed the BCK became linear and between 0.3 and 0.4 (mol/l)$^{1/2}$ the exchange curve passed over to a straight line parallel to the x-axis. This is a peculiarity related to the layout of the experiment. In longer periods of exchange (weeks or months) at AR higher than 0.4 (mol/l)$^{1/2}$ more K is absorbed but the slope of BCK did not change to such a degree that the values obtained with a short period of exchange (16 hours) were rendered invalid.

The following values were ascertained from the exchange isotherms for 43 samples (A-, B- and C-horizons) for use in multivariate analysis.

ARO:	activity ratio at the point where the soil solution neither gains nor loses K.
BCK (PBCK):	potential buffering capacity for K
CECx:	exchange capacity of non-planar absorption sites with high affinity for K.
ECK:	maximal sorption capacity for K under the conditions of immediate K/Ca exchange.
BCKE:	buffer capacity for K across ARO, E from equilibrium, measured between 0.3 and 5.10^{-3} (mol/l)$^{1/2}$.

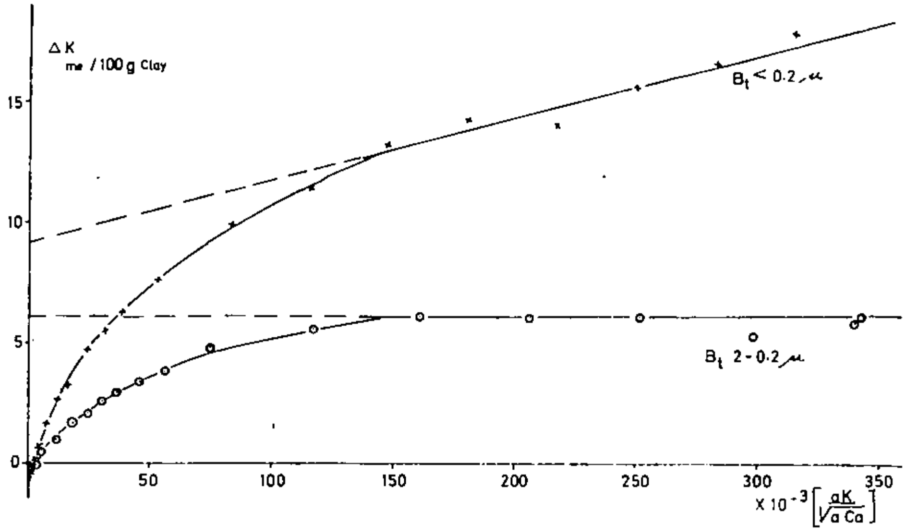

Figure 2. K/Ca exchange curves of 2 clays from a Bt-horizon

Exchange curves of 2 clay fractions from a Bt-horizon are shown in figure 2.

By comparison with figure 1 it can be seen that the K-Ca exchange properties of soils depend to a large extent on the clays $< 0.2\,\mu$. The transition of exchange curves into the straight line parallel to the x-axis starts at AR values > 0.15 (mol/1)½ with the coarse clay. Obviously the transition depends on the level of CECt. The fraction $< 0.2\,\mu$ has a CECt of 74, the fraction 2–0,2 μ of 31 me/100g clay.

The importance of one or several characteristics for the explanation of a problem as a whole, as for example clay mineral transformation in the Late Pleistocene or Holocene period can be estimated by using multiple factor analysis. In doing this, characteristics were combined in independent groups (factors) and ranged in order of their importance. The characteristics found in factor 1 are e.g. the most relevant to the overall relationship. Data from K/Ca exchange curves were also included among 52 characteristics investigated in a larger study *(Niederbudde [9])*. Together with other values as e.g. K-fixation measurements, intensity measurements of X-ray peaks, measurements of areas under the peaks by planimetry, clay contents and other chemical measurements, they were evaluated by factor analysis.

When the data for the loess-soil areas in Central Germany and Bavaria were summarized, the 52 characteristics could be reduced to 19 basic factors, which together explained 99.6% of the total variability of all characteristics. Only the most important, i.e. 1–5, are mentioned here, since they account for about 90%. The following correlation values are expressed as $r^2 \times 100$; they explain formal-mathematical correlation coefficients from a correlation matrix which can be reproduced to factors by calculation rules. They are also called factor-loadings.

The most important characteristic in factor 1 is BCKE, with a factor-loading of 75. There are interrelations to K-fixation and values of 18 Å-peaks. With this BCKE factor 44% of the total variability of all characteristics can be explained. The highest factor-loading of the 2nd factor is achieved by CECx-values at 86. This factor explains 16% of the total variability.

In factor 3 CECt appears with a loading of 92. This characteristic has no relation with data of K/Ca exchange curves. With 12% of the total variability this factor is comparatively unimportant compared to BCKE. In factor 4 ARO was determined with a factor loading of 76. This factor comprises also the values of the exchangeable potassium (contribution to the total variability is 9%).

In factor 5 PBCK (or BCK) dominates with a factor loading of 85 and ECK with 67. The contribution of this factor to the total variability of all characteristics amounts to 5% only. So far, 89% of the total variability of all characteristics has been accounted for.

It is obvious from this description that all data of the K/Ca exchange curves are relatively more important than other characteristics in describing transformations of clay minerals in mixtures of layersilicates. The X-ray values are not important in any particular factor; they are distributed relatively evenly between the factors 1—13 and are much less relevant than data from the K/Ca exchange curves.

It can be assumed that slight transformations of clay minerals in Holocene soils can be better determined by changes in the K/Ca exchange properties than by X-ray research.

Table 1 shows two typical soil profiles demonstrating changes of K/Ca exchange properties by soil formation in Holocene period.

Table 1. Changes of K/Ca exchange properties of clays ($<2\ \mu$) in two loess soil profiles

loc. name	horizon	1 ARo	2 K1	3 CECx	4 (P)BCK	5 BCKE
Adlkofen	A_1	0.75	0.35	8.4	60.9	.469
	B_t	0.85	0.68	9.0	65.8	789
	C	1.07	1.64	17.8	115.0	1409
Neufahrn	A_1	1.14	0.50	11.3	30.9	391
	B_t	0.70	1.67	16.4	50.9	1925
	C	0.93	3.07	20.6	49.8	3131

Dimensions: ARo × 10^3 $(mol/l)^{1/2}$, column 2 and 3: me/100 g clay, column 4 and 5: me/100 g clay per $(mol/l)^{1/2}$

K1 = labile K

BCKE clearly decreases with time during soil formation and CECx has the same tendency. PBCK is less clearly related.

Since there is a positive relation between BCKE and 18 Å-minerals and a negative relation between BCKE and 10 Å-minerals, as was shown by multiple regression analysis *(Niederbudde* [9]*)*, results in Table 1 can be explained in that with increasing time of soil formation from 18 Å-minerals (=beidellite) illites are formed by the exchange of potassium.

This is in accordance with findings on numerous profiles from loess areas in Central Germany and Bavaria in which potassium is enriched in the clay of the solum at pH 5—7 compared to sediments. The sources of K are minerals of silt size. The greater the quantitites and the higher the K-selectivity of the first mentioned minerals the further the transformation of beidellites to illites during the same (Holocene) period. This can be concluded from a comparison of soil profiles of both loess-soil areas.

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The Effect of Illite Content in Soils on the Potassium Supply to Plants*

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Summary

The potassium supplying power of a sandy loam and a clay soil containing different amounts of illite in the clay fraction and clay minerals was studied for ten years under field conditions. The potassium supply of four soils was measured in a growth chamber for 6 months, by intensive cropping cycles of 4 or 7 weeks.

The rate of release of potassium from illite is sufficient to maintain relatively small loads exerted on the soil by several crops. When the plant's demand for potassium is high (e.g. cotton), the rate of K release from non-exchangeable sites is not sufficient.

Introduction

Montmorillonite is the dominant clay fraction in soils of the semiarid regions *(Yaalon [26]).* The illite content in such soils ranges between 0 and 50% of the clay fraction *(Rezak* and *Amer [19]).* The illite in such soils is of a dioctahedral lattice arrangement which may release appreciable amounts of K to the exchange sites, but the rate of release may not be sufficient to maintain the level of exchangeable potassium required by the plant *(Thomas* and *Hipp [22]).* The most commonly used methods to predict potassium demands by plants are based on soil measurements under equilibrium conditions *(Woodruff [23, 24], Beckett [6], Barrow [3]),* and even a recently suggested improved method is based on equilibrium conditions *(Baker [1]).*

In order to calibrate such soil-testing methods many field studies are needed to correlate the soil test value with crop response to fertilizers *(Feigenbaum* and *Golub [9], Hagin* and *Koyumdjisky [11], Halevy [12]).*

The movement of potassium to the plant roots is mainly by diffusion *(Barber [2]).* The plant takes up large quantities of potassium; thus a very rapid depletion of the zone around the root is expected.

The rate of recharge of K in the root zone is the important soil characteristic and the active root surface area and its transfer properties are the most important plant parameters, for determining plant response to potassium fertilization.

The objectives of the experiments reported here were to measure the effect of intensive cropping on the K release characteristic of several soils and the equilibrium parameters of soil potassium; and to determine the release rate that may hinder plant growth.

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Materials and Methods

Five soils from Israel were selected to provide a range of properties with different potassium contents. Particle-size distribution and chemical and mineralogical properties of the soils were characterized.

The particle size analysis was determined by the modified *Sudan method* [*17*], $CaCO_3$ by the gasometric method [*14*], the pH of a soil paste – with a glass electrode, and total K by decomposition in decomposition vessels according to the method of *Bernas* [*7*]. Clay mineralogy was assessed by: X-ray diffraction, DTA, dithionite citrate extraction and total analysis *(Barshad* [*4*], *Jackson* [*13,14*], *Gal* [*10*]*)*.

Available K determinations: Exchangeable potassium was determined according to the method of *Bower et al.* [*8*]. In addition, the cation exchange capacity was measured, and the percentage of K in the total exchange capacity was then calculated. The change in free energy, Δ F, was calculated according to *Woodruff* [*24*]. The concentration of K in a soil extract with 0.01 M $CaCl_2$ using a 1:7 (w/v) soil: solution ratio was measured according to the method of *Woodruff* and *McIntosh* [*25*].

Field Experiments

1. *Citrus*

Samples of soil and leaves were taken annually for nine years, from control plots of a long-term fertilization experiment in commercial citrus orchards at Zrifin. The soil characteristics are summarized in table 1. The orchard was planted in 1957, and the fertilization experiment was started in 1961. The yields and soil and leaf analysis are summarized in table 2.

In the soil, available potassium was determined using the methods mentioned previously. In the leaves, percent K was determined by *Cotton's* method of wet combustion *(Snell* and

Table 1. Some characteristics of the experimental soils

Soil type and location	pH	$CaCO_3$ %	C.E.C. me/100 g soil	Texture	Mechanical Composition			Clay Minerals			Illite in soil %	Total K me/100 g soil
					Sand %	Silt %	Clay %	Montmoril. %	Kaolin. %	Illite %		
1. Sandy regosol (Ze'elim)	7.9	13.2	9.5	Sandy loam to sand	76.0	15.5	8.5	26	10	51	4.3	5.57
2. Brown Hamra (non-calcic brown) (Zrifin)	7.4	–	13.6	Sandy loam	78.8	6.9	14.3	43	25	25	3.6	4.75
3. Grumusolic dark brown soil (Hazor)	7.8	15.5	42.0	Clay loam to silty loam	11.9	42.0	46.1	53	16	13	6.0	10.90
4. Calcareous grumusol (Nir Dawid)	7.9	42.4	32.9	Silty loam	14.0	39.0	47.0	32	9	22	10.0	17.30
5. Alluvial grumusol (Bet Dagan)	7.8	10.0	49.5	Clay	10.4	40.9	48.5	90	—	10	5.1	8.56

Table 2. Orange yields* and plant and soil indices of potassium during 10 years of cropping (Zrifin)

	Years										
Plant data	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	Average
Fruit yield kg/ha	14,200	14,000	16,680	29,720	33,080	33,920	23,920	34,400	33,840	33,280	26,700
K in leaves (% of dry matter)	—	0.94	0.64	0.71	0.56	0.64	0.73	0.63	0.72	0.92	0.72
Soil analysis											
$-\Delta F$ cal/mol	3050	3000	—	2960	2980	3160	2900	2890	3090	3100	3014
C.R. mol/$l^{1/2}$ $\times 10^{-3}$	6.12	6.65	—	7.11	6.88	5.09	7.86	7.99	5.72	5.62	6.56
K exchange me/100 g soil	0.73	0.63	—	0.68	0.70	0.60	0.75	0.78	0.70	0.65	0.69
% K exchange	5.37	4.63	—	5.00	5.15	4.41	5.51	5.73	5.15	4.78	5.08

* Results from the non-fertilized treatment plots in citrus field experiment in Zrifin.

Snell [*21*]). The fruit yield was recorded and the total K removed from the soil was calculated.

2. *Field Crops*

Soil samples were taken annually for seven years, from control plots of the permanent plots experiment of the *Volcani Center* at Bet Dagan [*16*]. The field experiment contained the 225 possible combinations of five levels of N, five levels of P and three levels of K, each on three organic manure levels. The soil characteristics are summarized in table 1. Irrigated field crops were grown in succession, as summarized in table 3. The potassium equilibrium parameters were measured and reported here for the K_0 plots on the highest nitrogen and phosphorus treatments (table 3). The total K content in the upper 20-cm layer of the soil was 8.25 me/100 g in 1963 and dropped to 7.56 me/100 g in 1968.

Growth Chamber Experiments

Continuous cropping of wheat (var. *Florence Aurore)* was conducted. The plants were grown in a growth chamber under conditions of constant temperature (20—22 °C) and light (1200 F/C). Sixteen replicates of each soil were employed; after each harvest one or two replicates of each soil type were used for soil analysis and for replenishment of the soil which remained in other pots in the replicates, to the original weight of 400 g per pot. The soil was air dried and then separated from the roots by straining through a sieve with 2-mm-diam. openings. In each pot, 75 mg N and 75 mg P_2O_5, in the form of NH_4NO_3 and $NH_4H_2PO_4$, respectively, were added to 400 g dry soil; each pot was sown with 100 seeds. No K was added during the entire growth period. The pots were watered daily to bring the soil moisture content to 'pot capacity'. Growth cycles were terminated with the appearance of marked potassium deficiency in some of the plants. After each of the six growth cycles (21 days), the yield (as dry matter) and percent K in the plant were determined. The equilibrium soil K parameters were determined.

Table 3. Crop rotation, yields and equilibrium parameters of soil potassium during ten years from the no-K fertilized treatment plots in a permanent plot experiment

Season		Crop	Average yield	Plant part measured	Response to K fertil.	Soil Potassium				
						K in $CaCl_2$ ppm	K exch. me/100 g	% K exch.	$-\Delta F$ cal/mol	C.R. $\times 10^{-3}$ mol/l$^{1/2}$
1960/61	Winter	Wheat	2310 kg/ha	grain yield	—					
1961	Summer	50 cm plowing								
1962	Winter	Chickpea	2020 kg/ha	grain yield	—					
1962/63	Winter	Sugar beet	89.6 t/ha	root yield	—	6.6	0.94	1.9	3610	2.4
1963	Summer	Pearl millet	2210 kg/ha	green yield	—					
1964	Summer	Cotton	4680 kg/ha	total row cotton yield	—	4.3	0.70	1.4	3890	1.5
1965	Summer	Sorghum	8040 kg/ha	grain yield	—	5.5	0.82	1.5	3750	1.83
1965/66	Winter	Wheat	1380 kg/ha	grain yield	—	5.6	0.84	1.5	—	—
1966	Summer	50 cm plowing								
1966/67	Winter	Chickpea	2330 kg/ha	grain yield	—	3.6	0.68	1.3	3650	2.24
1967/68	Winter	Sugar beet	71.1 t/ha	root yield	—				3800	1.75
1968	Summer	Corn	8.35 t/ha	dry green yield	—					
1969	Summer	Cotton	4530 kg/ha	total raw cotton yield	+	3.8	0.65	1.3	4020	1.21
1969/70	Winter	Wheat	3040 kg/ha	grain yield	—	6.0	0.80	1.5	3780	1.81

Similar techniques were used with corn cropping on Nir Dawid soil. Forty days of growth were allowed during four consecutive cycles.

The amount of K release from non-exchangeable sites for each growing cycle was calculated from the difference between the amount of K uptake by the plant minus the amount of exchangeable K. The average rate of K release from 1 g illite per day was calculated on the assumption that the K release from non-exchangeable sites is contributed only from illite and that it occurred during the last 16 days of the wheat experiment and the last 35 days of the corn experiment.

Results and Discussion

Field Experiments

The amount of illite in the sandy loam soil (table 1) of the citrus orchard is 3.6% of the soil weight.

No response to potassium fertilization was found in the citrus yield during ten years of cropping. The K concentration in the leaves of the citrus plant was only 0.6–0.9% (table 2) and the amount of K removed by citrus fruit is known to be only 2 kg K/ton (*Smith* [*20*]). In this experiment the total amount of K removed by the fruit in ten years was 545 kg K/ha. The total amount of K in the clay fraction of this soil in the root zone depth (80 cm) is 14,600 kg K/ha. The load imposed by the citrus crop amounts on the average to only 0.37%/year of the K in the clay fraction.

An almost constant level of exchangeable K, and very small fluctuations in the ΔF and in the concentration ratio (table 2) were found during ten years. This finding, coupled with the presence of 25% illite in the clay fraction and the relatively low demand for K by citrus, suggests that the rate of K release from non-exchangeable sites is enough to restore the equilibrium concentration of K in the soil solution.

The amount of illite in the clay soil of the permanent plot experiment for field crops is 5.1% (table 1). Ten years of continuous cropping without potassium addition, at a regular field crop rotation [*16*], resulted in fluctuations of 1.3–1.9% exchangeable potassium percentage (E.P.P.) in the soil (table 3). Of the 13 crops grown in this field, only cotton, as the twelfth crop in 1969, responded to an addition of K fertilizer (table 3). Continuous depletion of K by intensively grown field crops caused a temporary decrease in 1969. However, within one year the release from the illite fraction restored the potassium value to that found in 1965.

Growth Chamber Experiments

The detailed soil and plant data for wheat and corn in the growth chamber experiments are presented in tables 4 and 5. In all cases the plant yield decreased with the sequence of cropping. The equilibrium parameters that are commonly used to estimate potassium in the soil also decreased with cropping sequence. In this experiment a heavy load was imposed on the potassium-supplying power of the soil. The recharge rate of exchangeable K from inside lattice sources was not high enough to supply plant demand. This finding is in agreement with that of *Thomas* and *Hipp* [*22*], who stated that in soils containing mainly dioctahedral mica and montmorillonite, the rate of release is inadequate to maintain the level of exchangeable potassium under intensive cropping.

The soil properties, as presented in table 1, show that the dominant clay material is montmorillonite in all the soils studied except Ze'elim. The calculated average rate of release from non-exchangeable sites to wheat roots in growth chamber conditions ranges between 0.2 and 0.02 me/100 g/day of the illite fraction in all the soils studied (tables 4, 5). After the second or third cropping a constant rate is observed, in the range of 0.10–0.08 me/100 g/day. A similar constant rate of release from Fithian illite was found by *Quirk* and *Chute* [*18*] using 0.03 N NaCl at 20 °C.

From a practical point of view, the problem remains to predict for each crop on each soil the overall potassium rate of supply of the whole soil mass. The rate of consumption and, especially, the surface area of the root system, differs between crops and depends on the supply of other nutrients in the nutrient solution *(Bar-Yosef* [*12*]*)*. The concentration of roots found by *Barber* [2] at the end of corn growth in the field was 10–90 mg/100 g soil. In the growth chamber experiment (table 5), we found 120 mg/100 g after 40 days in the first crop. Dry matter production of corn in a growth chamber is 30 times more intensive (6 mg/g soil/5 weeks) than that in the field (0.2 mg/g soil/5 weeks) *(Kafkafi, Bar-Yosef* [*15*]*)*.

In order to support dry matter production of 6 mg/g soil/40 days with 6% K concentration, the soil must supply 0.01 mg K/g/day. When diffusion of potassium from inside crystal sites control the rate of release of potassium from Fithian illite *(Quirk* and *Chute*

Table 4. The effect of six consecutive growing cycles on soil potassium parameters, plant uptake and rate of release of non-exchangeable K

Data from wheat experiment (Growth Chamber)

Soil	Soil analysis				Plant analysis			Rate of K release from non-exchangeable site me K/100 g illite/day
	$-\Delta F$ cal/mol	K in $CaCl_2$ ppm	K exch. me/100 g	% K exch. from CEC	D.M. mg/100 g soil	% K in dry matter	K uptake me/100 g soil	
Ze'elim 1	2560	22.0	0.89	9.35	327	4.02	0.339	—
2	3350	4.8	0.30	3.16	247	3.17	0.201	0.22
3	3570	3.2	0.25	2.63	207	2.58	0.137	0.19
4	3670	2.4	0.22	2.32	132	2.12	0.072	0.10
5	3670	2.4	0.17	1.79	107	0.97	0.054	0.08
6	3850	2.4	0.17	1.79	82	1.47	0.031	0.04
after cropping	3790	2.8	0.17	1.79				
Zrifin 1	3270	24.2	0.84	6.20	322	2.85	0.235	—
2	3650	3.0	0.29	2.13	192	2.13	0.105	—
3	3700	2.0	0.15	1.17	180	1.68	0.077	0.10
4	3660	1.8	0.13	1.03	145	1.95	0.072	0.09
5	3710	2.0	0.11	0.86	132	1.31	0.044	0.08
6	3840	2.2	0.11	0.86	200	1.37	0.070	0.12
after cropping	3590	3.0	0.12	0.87				
Hazor 1	3500	7.6	1.00	2.38	395	5.19	0.524	0.14
2	3910	3.4	0.61	1.45	302	4.15	0.321	0.20
3	4200	2.0	0.48	1.14	235	3.47	0.208	0.15
4	4160	1.8	0.42	1.00	237	3.18	0.205	0.10
5	4310	2.0	0.31	0.74	207	2.73	0.174	0.12
6	4610	1.1	0.26	0.62	240	2.07	0.126	0.13
after cropping	4780	1.4	0.31	0.74				
Nir Dawid 1	2500	21.4	2.25	6.85	377	6.63	0.639	—
2	3080	12.8	1.57	4.77	355	5.88	0.534	—
3	3480	5.2	0.98	2.98	215	4.98	0.274	0.07
4	3790	4.0	0.82	2.47	217	4.54	0.258	0.06
5	3840	4.0	0.66	2.00	197	4.18	0.210	0.10
6	4180	2.4	0.61	1.85	207	3.55	0.189	0.54
after cropping	4110	2.4	0.51	1.55				

Table 5. Changes in equilibrium parameters of soil potassium, plant yield, potassium uptake and rate of release of K from non-exchangeable sites in four consecutive harvests of corn

Growth chamber experiment

Nir Dawid Soil	Soil analysis				Plant analysis				Uptake me/100 g soil		Rate of K release from non-exch. site me K/100 g illite/day
	$-\Delta F$ cal/mol	K in $CaCl_2$ ppm	K exch. me/100 g	% K exch. from CEC	D.M. mg 100 g soil		% K				
					plant	root	in plant	in root	plant	root	
1	2500	22.0	2.25	6.85	475	121	5.90	1.23	0.716	0.038	0.02
2	2920	12.0	1.63	4.95	450	62	4.50	0.58	0.517	0.009	0.03
3	3310	6.5	1.12	3.40	301	45	3.82	0.89	0.293	0.010	0.05
4	3670	5.0	0.99	3.01	337	57	3.93	1.24	0.339	0.018	0.07
after cropping	4100	4.0	0.88	2.67							

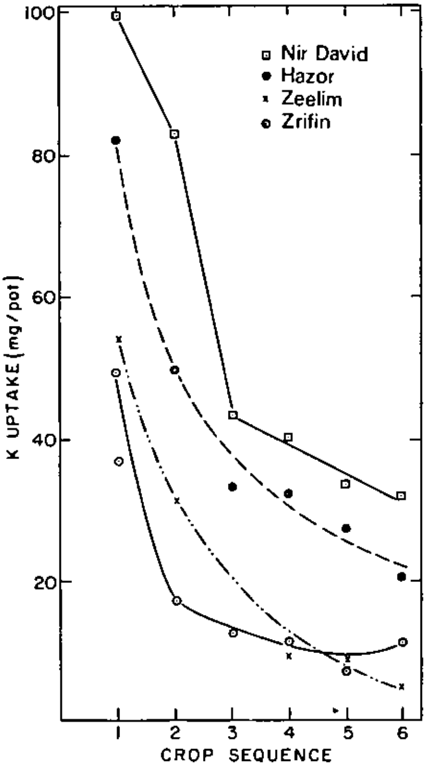

Figure 1. Yield of potassium in wheat as a function of crop sequence.

[*18*]), a rate of 0.055 mg K/g *clay*/day is obtained. That is, only soils which contain at least 20% illite of the total soil weight will be able to supply enough for very intensive cropping like in the growth chamber study [*5*]. Of the soils studied, none contained this amount of illite. The soil of Nir Dawid is the richest in illite and, as expected, released the highest amount of K to the wheat plant (figure 1), but even this soil was able to supply enough potassium only to the first and second crops in the sequence. The differences in intensity and in time scale between the field and growth chamber studies demonstrate the importance of rate consideration in determining the K-supplying power of a soil.

It can be concluded that for prediction of potassium supplying power of a soil, the methods that measure equilibrium condition can yield only first approximation results based on many field observations and correlation studies. An improvement in prediction can be expected if the illite content and rates of release measurements can be added. Even if a complete description of the soil as a source of K is achieved, the prediction of plant response to potassium will depend also on the characteristic of the sink for potassium, *i.e.*, the characteristics of the root distribution, root radius and total active surface area and rate of plant growth which determine the rate of potassium uptake.

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2nd Working Session: Some Remarks on the Discussion on Ion Exchange System of the Soil

Prof. Dr. U. SCHWERTMANN, Director of the Institute of Soil Science, Faculty of Agronomy, Freising–Weihenstephan/Federal Republic of Germany

Rather than discussing more details about how to describe the ion exchange system of the soil – and also in view of the fact that this symposium ought to have some results applicable to practical problems of K supply from soils, I would suggest to try the various possibilities for describing the soil K status offered in these papers for their usability for practical purposes: i.e. *prediction of K availability*. This follows the proposals made by Dr. *Walsh* and Prof. *Schuffelen*.

It is my feeling that we are now in a stage where *on one hand* we are supplied with numerous thorough treatments of the K-soil-systems and on the other hand in practice we are still using 'witch brew' *(Nye)* methods to characterize this system for predicting K need.

We would possibly all agree that the description of the K situation should consist of three elements *intensity, quantity* and *rate*.

As *intensity* the reduced K–Ca ratio in soil solution has been used with good success (e.g. by *Feigenbaum*), although it has strong opponents (e.g. *Mengel*). One question here is, should Al in acid soils be included?

The *quantity* taken from Q/I curves is certainly in many soils not high enough to include all K available under field conditions over a growing season. Its subdivision into 3 categories as done by *Schuffelen* may not be very helpful here and also not too realistic. Is an answer given by Dr. *Talibudeen* enough for characterizing a soil saying that below a certain f-value the soil releases K and vice versa which is a 'yes or no answer' rather than a quantity?

Dr. *van Bladel* used the thermodynamic treatment of *Gaines* and *Thomas* to describe the exchange system using the whole isotherm. Can this be used for practical purposes?

Dr. *Feigenbaum* offered the illite content as a suitable quantity which in some soils may be replaced by the total K in clay. The method proposed by Dr. *Németh* finally covers as he thinks a wide range of K sites of varying bonding strengths.

Furthermore, proposals for combining several parameter of the Q/I curve have also been made (e.g. *Zandstra* and *Mackenzie*).

The *rate* is probably the most difficult part of the story because it consists of several subprocesses difficult to measure. A proposal has been made by Dr. *Feigenbaum* who used in her paper the overall uptake rate by the plant. This appears to be questioned by Dr. *Talibudeen*. Does the method used by Dr. *Németh* also measure the rate?

A final remark may be permitted: It may be suggested that instead of keeping the method of investigating thousands of soils every year by simple routine methods it might be more useful to characterize single soils representative of a soil province by a larger number of pertinent data and thereby gaining informations applicable to a larger soil area *(Nieder-*

budde). This would mean high analytical efforts on a few soils instead of low efforts on many soils resulting in equal time requirements and also would make better use of what has been worked out by the local Soil Survey. Consideration of geological and soil formation circumstance has also been proposed by Dr. *Darab* at this symposium.

It may be useful then to discuss the validity of all these possibilities for overcoming our rather unsatisfactory ways of determining the K supplying status of a soil presently in use.

Report on the 2nd Working Session: Ion Exchange System of the Soil

Dr. T. Walsh, Director of the Agricultural Institute, Ireland; Member of the Scientific Board of the International Potash Institute

My difficulty in trying to appraise and summarise the main points of this Session is that this in fact can only be adequately done in the context of the other Sessions.

In attempting this summary, it must be asked to what extent the papers presented meet the objectives of this Colloquium. I see the latter in the first place as bringing to light new material relating to the factors which influence the availability of soil potassium to plants; secondly, seeing how the various pieces of new knowledge might be synthesised into systems of practical value, in other words, how these new facts complement, supplant or supplement one another; and thirdly, it might be expected that the results would point the way to new work to fill the lacunae which now exist in our knowledge of this subject.

Against the background of the above three criteria, this evaluation is approached.

The opening paper on the *Cation Exchange System* of the Soil by Prof. Dr. *A.C. Schuffelen* was basically a review of the development of information down the years. This is first class reference material listing as it does attempts to quantify cation exchange phenomena from *Way*'s original work to the present day. Professor *Schuffelen* especially made it clear that the ion exchange system is very complex, with many different soil components involved and that there are many interactions. The kernel of the problem rests in his statement that 'the not constant relationship between the composition of the soil solution (intensity factor) and the absorbed amount (capacity factor) makes it very difficult to assign an agricultural interpretation on these values'. This conclusion is of basic importance in considering the contribution of the other papers. In essence, from the practical aspect, it is suggested that under moist conditions with quick growing crops, the concentration of K in the soil solution should indicate the K status of the soil while under dry conditions, or in the case of slow growing crops, the amount of exchange in K should be a better indicator.

The paper of Dr. *van Bladel* on the *Thermodynamics of Cation Exchange in Soils* applies formal thermodynamic reasoning to cation exchange reactions in soils.

In the first part of this paper, dealing with K–Na exchange, the author points out that thermodynamic measurements depend completely on the (arbitary) choice of standard states of the reactants and also on the assumption that exchange is completely reversible. He chooses for his standard state an infinitely dilute solution of an ion in equilibrium with the exchanger. While this is sound thermodynamically, it eliminates the effect of K-release from the mineral lattice and thus measurements using this standard state would be remote from agricultural practice.

The second part of the paper dealing with K–Ca exchange is more interesting to plant uptake studies. The author attempts to predict the 'surface-activity' of an exchanger but leaves it up to the reader to decide what value such measurements have in soil research.

While this paper is essentially theoretical in nature, it does present an imaginative approach to a problem which up to now has been especially elusive.

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* Ref. Boyle Lecture. Royal Dublin Society, Vol. 2, Series B. No. 29.

In his paper on the *Exchange of Potassium in Soils in Relation to Other Cations,* Dr. *Talibudeen* essentially discusses the complex factors affecting the exchange of potassium in soil. Among these are (1) the ability of K ions to sit tightly on certain exchange sites; (2) the heterogencity of exchange sites; (3) the nature of the competing cations and (4) the nature of the soil, e.g., its mineralogical composition and percentage of clay sized fractions.

The use of thermodynamic functions to evaluate some of the above factors is discussed. Their usefulness is in many cases remote, as they tend to integrate a variable quantity over a range of K-saturations to give a kind of 'average' value which may be intellectually satisfying but not always useful.

The author finally discussed the use of natural and artificial cropping to determine the ability of soils to supply K to plants. He concludes that natural crops cannot safely be used, because during senescence some K is replaced and thus prevents further exchange. He rightly rules out artificial cropping methods, e.g. H-saturated resins which cause breakdown of the clay minerals and holds out most hope for gentle extracts such as .0033 *M* $CaCl_2$ or .25 *N* dodecylammonium chloride which extract K without harming the mineral lattice.

Essentially this is a penetrating review and assessment, the reasoning being philosophically sound in so far as it was one of the papers at the meeting which recognised soil as an entity, hetrogenous in nature, with each part interacting with the other, sometimes in a positive and often in a negative way.

The paper by Prof. Dr. *A. Cottenie* and Ir. *L. Kiekens* on the *Exchange of Zn, Mn, Cu and Fe in Relation to Saturation of the Soil Complex* is of special interest to those concerned with the interactions between major and trace elements. It is a highly important field of work as in intensive agriculture where high levels of nutrients must be used and may build up in soils the question arises as to how the availability of trace elements is affected. So far the knowledge of this subject has been very limited and in this context this contribution is of considerable value.

Essentially the paper reports on the adsorption, fixation and precipitation reactions between soil and the trace elements listed, over a range of pHs. The authors have been specially concerned with definitions and this is right – for instance, adsorption is taken as insoluble but exchangeable; fixation is insoluble and non exchangeable. I feel that some of the reactions described in the paper as adsorption or fixation are probably precipitation, a reaction which could take place in the absence of soil.

The principal results show that the trace elements are adsorbed or fixed at high pHs but remain soluble at low pHs. This is not especially new and I am particularly aware, for instance, that there is a considerable background of the chemistry of manganese already in the literature. A good deal of data refers to pHs below 4 where of course there can be considerable breakdown in the soil. I feel there would be considerable difficulty in transferring some of the results presented to actual field conditions; for instance, that concerning the reversibility of manganese adsorption. This depends on oxidation which varies very substantially from soil to soil.

Overall, it must be concluded that the objective of the authors is very important, and certainly the points in relation to energy and binding and the competition between elements for different sites on the soil fixing complex merit further attention.

The paper presented by Dr. *Niederbudde* on *Changes in K/Ca Exchange Properties of Clay in Loess-derived Soils in Soil Formation* is a distinct departure from the other papers discussed previously. It gets down to more practical, tangible factors.

In this paper the Q/I method of *Beckett* for determining K/Cs exchange properties was applied to soils from central and southern Germany and K/Ca exchange properties were related to the degree of weathering of the soil clays. This is a new and interesting application of the Q/I method which in effect appears to be a sensitive parameter for determining clay mineral changes.

It is of special interest that the values of the K/Ca exchange curves were the most important for the explanation of transformation of clay minerals in loess soils and that in fact X-ray analysis did not tell much more than could be learned from relatively conventional methods. It is of interest that the change from montmorillonite to mica type clay during the Halocene period in these soils is the reverse of the more common clay mineral weathering.

This paper certainly scores under the heading of identifying and synthesising information into a form where it can meet some practical requirements.

This is also the position with the paper by Drs. *Feigenbaum* and *Kafkafi* on *The Effect of Illite Content in Soils on the Potassium Supply to Plants.*

This paper is the result of a painstaking and thorough piece of experimental work linking in effect crop response to clay mineral characteristics.

The three experiments reported especially bring out the following conclusions:

1. *10 years work with citrus:* There was no response to K and no reduction in soil values of K over 10 years, with the conclusion that illite 3.6% by weight supplied enough. Perhaps it could be that this lack of response was due to failure of K to move to the roots from the clay surface.
2. *10 years rotation of field crops:* With a soil of 5.1% of illite only a 12th crop of cotton was shown to give a response coinciding with a drop of K value. The subsequent recovery of the crop due probably to release of K from illite is a general experience.
3. From *growth chamber experiments* under very intensive conditions there is a suggestion that K supply is related to the illite content.

Overall this paper is useful from a practical aspect under the experimental conditions concerned.

The main merit of this Session is that it highlighted the lack of really new advances in this whole field of activity. It was not clear from some of the papers whether the authors were dealing with binding or bonding and with which of these effects fixation was synonymous. One point was emphasised especially, i.e. the complexity of the interactions and the difficulty in drawing conclusions from artificial media or soil separates. Too little was heard of the mineral-organic matter complex and how it affected the result.

One important point which did not come up in the Session which has a direct relevance to the discussion was the information presented in a supplementary paper by *Kiely* and *Ryan* who showed that out of a variety of parameters tested, mica edge surface was the only mineralogical parameter which related to the ability of the soils studied to supply K to grass under continuous cropping.

On the basis of the material presented during this Session one might logically question the extent to which we have progressed. Some 30 years ago we knew from our work* that soils varied widely in capacity to supply potassium to plants and that plants on the other hand varied widely in capacity to utilise soil potassium in its different forms, i.e., sugar beet v. grasses. We knew that soils fix potassium and that indeed a fixation measurement was successfully used as an index of capacity to supply this nutrient. We knew too that there were different categories of potassium in the soil, such as readily available, exchangeable, difficultly available and unavailable – mineral bound. It was known, for instance, that soils released potassium on weathering and that availability was profoundly affected by such factors as moisture regime and calcium supply, particularly in relation to immobilisation of applied potassium. At that time too, we understood the difference between capacity and intensity. Indeed we had testing methods the interpretation of which reflected this. Shortly afterwards we distinctly associated K supply conditions with specific clay minerals.

Consequently, as a result of what we have heard in this Session, one must question the extent we have advanced in laying a better basis for practical use of K in fertiliser use recommendations. As a final comment, it might be advanced that perhaps at least some of the work now in progress becomes too theoretical and academic, being far removed from what actually happens to the soil as a specific entity in the field. Finally because these questions have been raised the Session can be regarded as clearly fulfilling its purposes.

3rd Working Session:

Ion Transport System in the Soil

Chairman of the Session:

Prof. Dr. A.C. SCHUFFELEN,
Director of the Institute for Soils and Fertilizers, State University, Wageningen/The Netherlands; Member of the Scientific Board of the International Potash Institute

Localised Movement of Potassium Ions in Soil

P.H. Nye, Soil Science Laboratory, Department of Agricultural Science, University of Oxford/United Kingdom

Summary

The mobility of the potassium ion in soil may be measured by its diffusion coefficient, which ranges from less than 10^{-20} cm^2/s for exchange with interlayer K in unexpanded illite to c. 10^{-8} cm^2/s for K in a dry soil and 10^{-6} cm^2/s in a moist one. Although exchangeable K in pure montmorillonite and kaolinite is fairly mobile, and there is considerably more K in the surface exchangeable than solution form in soils, it seems that in soil most of the diffusion occurs through the soil pore solution.

By combining knowledge of diffusion through the soil and K uptake rates derived from experiments in nutrient culture we may deduce that diffusion of K through soil to root surfaces is a rate limiting step when plants are suffering from K deficiency. Experiments with single roots, root planes and whole root systems all provide evidence that the concentration of K at the root surface is considerably below that of the bulk soil solution when this approaches 10^{-4} M.

The topic *'Transport of potassium in soil'* could embrace the whole range of studies from microscale movement of potassium within clay and mineral lattices to weathering of rocks and the balance of potassium in drainage basins; and include between these extremes such important matters as the movement of potassium in the rhizosphere around plant roots, its movement within the profile in response to drainage and evapotranspiration, and its cycling through crops and vegetation. These large scale aspects of potassium transport are still mainly descriptive, and I do not know that any new ideas about them have recently emerged. I think, however, that the explanation of them is likely to come from the understanding we are now gaining of small scale localised aspects, so that I propose to concentrate on these.

The mobility of potassium in soils

The mobility of potassium is exceedingly low as a mineral lattice ion, much greater as an exchangeable ion, and greatest as a free ion in the soil solution. If the mobility of an ion, u, is defined as the velocity attained under unit force, then this is related to the diffusion coefficient, D, by the *Nernst-Einstein equation*

$$D = ukT$$

where k is the *Boltzman constant,* and T is the thermodynamic temperature. We may therefore regard the diffusion coefficient of potassium in various states as a measure of its mobility. D has the dimensions of length²/time. Its values, in systems of interest, range from 2×10^{-5} cm²/s in aqueous solution to 10^{-23} cm²/s for potassium in an illitic clay. The physical significance of these values may be more readily appreciated if it is remembered than an ion will, on average, diffuse a distance $\sqrt{2Dt}$ in time, t. Thus the potassium ion will move 1 mm in 250 s in solution, but only 1 nm in 5×10^{8} s (16 years) in the illite.

The slow release of potassium from minerals

Some illustrative values for the apparent diffusion coefficient of potassium determined from its rate of release from various micaceous minerals into salt solutions are collected in table 1.

Table 1. Apparent diffusion coefficients for release of potassium from micaceous minerals

System	Apparent Diffusion Coefficient (cm²/s) at lab. temps.	Reference
Self-diffusion of K in illite	10^{-23}	de Haan, Bolt and Pieters (17)
Illite	c. 10^{-19}	Quirk and Chute (23)
Muscovite 50 μm in NaTPB	c. 5×10^{-14}	Smith et al. (26)
Biotite in 1N $SrCl_2$	c. 5×10^{-11}	Rausell-Colom et al. (24)
Vermiculite (interstratified 10–14 A°) in NaTPB	c. 7×10^{-9}	Smith et al. (26)

The very low self-diffusion coefficient, 10^{-23} cm²/s, measured for the exchange of potassium in an illite with the isotope K^{40} is a true diffusion measurement, and reflects the very slow movement possible when the lattice does not expand in the course of the weathering process.

Release at an appreciable rate involves expansion of the mineral lattice and hydration of interlayer ions. The exact nature of the rate controlling step in K release is not clear, but it seems very unlikely to be diffusion within the already hydrated interlayer positions lying between the site of release and the external solution, since this is a relatively rapid process. If a simple diffusion process were controlling the overall rate, the amount released would vary as $t^{.5}$; in fact, the amount released varies from $t^{.56}$ to $t^{.98}$ *(Wells* and *Norrish [30]).* The rate of release is very sensitive to the concentration of potassium in the solution. For example, in a solution of .01 *N*-$CaCl_2$ release from biotite ceased when the potassium concentration was .43 me/l, and from a phlogopite at .07 me/l. Release from trioctahedral micas is more rapid than from the dioctahedral forms. The reason may lie in the structure of the octahedral layer. In the trioctahedral forms the O-H bond near the centre of the hexagonal network of tetrahedrally co-ordinated silicon atoms is directed along the c-axis. In the dioctahedral forms the direction of the O-H group is altered; consequently a cation in the interlayer will be less shielded by the proton from the negative O atom, and will occupy a more stable position *(Rausell-Colom, et al. [24]).*

Surface diffusion of potassium in clay gels

Turning now to hydrated clay, the mobility of potassium in 'salt-free' montmorillonite gels was found by conductivity measurements to be 0.06 of the mobility in free aqueous solution. The corresponding figure for kaolinite gel was 0.08 *(Cremers [11])*. In another system diffusion measurements indicated the mobility of potassium ion in a montmorillonite gel to be 0.23 of the free solution value *(Gast [16])*. Potassium is rather less mobile than sodium and more mobile than rubidium and caesium in pure clay systems. When we recall that the amount of potassium on exchange surfaces is usually at least 10 times the amount in the soil pore solution it might be anticipated that surface diffusion would play a major part in the diffusion of potassium in soil.

Diffusion of potassium in soils

In the overall movement of potassium ions through soil the proportions and mobilities of potassium in both solid and liquid are involved. However, in so heterogeneous a medium it is impossible to develop a theoretical equation to express accurately the overall flux in terms of the mobilities and concentration gradients of the ions in the constituent parts *(Nye [20])*. Nevertheless, so long as we are concerned with diffusion in volumes large enough to take an average over the microscale variations, we may regard the soil as a quasi-homogeneous body for which we may define a diffusion coefficient D by *Fick's First Law:*

$$\text{Flux} = -D\,dC/dx \tag{1}$$

C is the concentration of diffusible ions in the system; i.e. all those ions which are in or pass through a mobile phase during a period of time which is short compared with the time over which the diffusion is measured. C will thus include the exchangeable potassium and the potassium in the soil solution.

To understand the measured values of the diffusion coefficient, and to predict its value, we may consider the total rate of transfer of ions through unit cross section of soil as being due to a flux through the pore solution alone together with an excess flux created by the mobility of the ions on the solid.

Hence $$\text{Flux} = -D_l v_l f_l dC_l/dx + F_E \tag{2}$$

where D_l is the diffusion coefficient of the ion in free solution;
v_l is the fraction of the soil volume occupied by solution, and gives the cross section for diffusion;
f_l is an impedance factor
C_l is the concentration of ion in the soil solution
F_E is the excess flux created by the exchangeable ions.

Combining equations (1) and (2) we obtain

$$D = D_l v_l f_l\, dC_l/dC + D_E \tag{3}$$

where D_E is an excess term which is zero when the ions on the solid have no surface mobility, but represents their extra contribution to the diffusion coefficient if they are mobile.

It will be noted that the diffusion coefficient depends on the slope of the sorption isotherm dC_l/dC. If this has the typical form shown in figure 1, dC_l/dC increases with C_l. This provides a means of assessing the importance of the excess term, D_E, at levels of

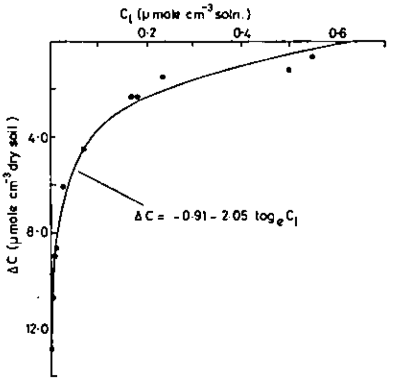

Figure 1. K desorption isotherm for Upper greensand sandy loam soil in 12.5 mMCa NO_3.
Ex K = 19 μe/g. C.E.C. = 140 μe/g.

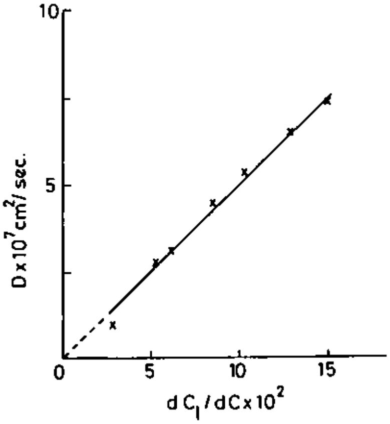

Figure 2. D for K in Coral Rag clay related to the slope of the K sorption isotherm.

potassium characteristic of soils. *Vaidyanathan et al.* [*29*] measured the diffusion coefficients of potassium in a soil prepared at different levels of potassium. The values of D are plotted against dC_l/dC in figure 2. It will be seen that the curve extrapolates to cut the y-axis near the origin, indicating that the value of D_E is small. Similar behaviour has been found for other cations using both transient and steady state methods of measuring the diffusion coefficient *(Tinker* [*28*]*)*. Thus, to our present knowledge, it seems likely that in soils the contribution of exchangeable potassium by surface diffusion may be neglected, though this conclusion needs to be tested over a wider range of soils. If confirmed, it is very convenient, because it means that the diffusion coefficient may be calculated from a knowledge of the isotherm, the moisture level, and the impedance factor. The relation between the impedance factor and moisture fraction is roughly linear between the wilting point where it is nearly zero, to saturation, where is about 0.5 *(Porter et al.* [*22*], *Rowell et al.* [*25*]*)*. For more accurate assessment it may be determined from the self-diffusion coefficient of a non-adsorbed ion such as chloride for which equation (3) reduces to $D_{self} = D_l f_l$.

The values of potassium diffusion coefficients range from c. 10^{-6} cm^2/s in a moist poorly buffered soil to c. 10^{-7} cm^2/s in a well buffered soil. In dry soils the corresponding values will be one or two orders of magnitude lower.

Movement of potassium near plant roots

With this knowledge of the diffusion of potassium it is possible to develop a theory for its movement to plant roots, and the associated concentration gradients in the surrounding soil.

If a soil behaved like a stirred nutrient solution the problem of predicting the uptake of potassium by a plant would lie entirely in the realm of plant physiology. The essence of the soil-plant root problem is that the concentration of potassium at the surface of the root differs from that in the bulk soil solution because of the need for diffusion through the soil. As *Tinker* [27] has written 'there is no question that transport processes must occur in soil – the critical problem is whether they are important in the nutrition of plants'. The root surface concentration ratio C_{l_r}/C_{l_i} (where r refers to the concentration at the root surface, and i to the initial concentration in the soil solution), will depend on the balance between the demand imposed by the root and the ease of movement through the soil.

These ideas may be expressed quantitatively by solving the conservation equation

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right) \tag{4}$$

In order to do this it is necessary to relate the flux across the root surface to the concentration at this surface. The equation:

$$\text{Uptake rate per unit root length} = 2\pi\alpha r C_{1_r}$$

expresses the fact that the rate of uptake is related to the concentration in solution at the root surface. α is not a constant though it may be nearly so at low concentrations.

Figure 3 shows the way the concentration at the surface of a single root in an infinite volume of soil should vary with time (*Carslaw* and *Jaeger* [10], *Bouldin* [6]). Each curve is for a different value of $\alpha r/D_l v_l f_l$, αr is a measure of the root demand; and $D_l v_l f_l$ is the measure of the ease of diffusion through the soil.

It will be noted that the concentration falls rapidly at first and then much more slowly. If $\alpha r/D_l v_l f_l$ exceeds ten, the root surface concentration ratio falls to a very low value. Clearly then, it is necessary to know the range of values of $\alpha r/D_l v_l f_l$ likely to be encountered in the potassium nutrition of plants.

The value of $D_l v_l f_l$ for K in a moist soil is about 10^{-6} cm²/s and in a dry soil is about 10^{-8} cm²/s. We can derive a knowledge of αr from experiments in solution culture in which the rate of K uptake by the whole root system of intact plants has been measured over periods of several days. The data in table 2 has been abstracted from a recent review by *Brewster* and *Tinker* [9] and the values of αr calculated from their figures. The inflow rate is the rate of uptake per unit length of root. In most instances the radius of the roots is estimated.

Thus work with stirred solution culture would lead to the conclusion that αr is likely to exceed 10^{-6} cm²/s when the solution concentration at the root surface is below 10^{-4} M.

Table 2. Values of the root demand coefficient for potassium determined from solution culture experiments

Ref.	Species	Age at start days	Uptake period days	Root radius cm	Inflow rate mols/cm s $\times 10^{-13}$	Soln. conc. mols/l $\times 10^{-4}$	Root demand coefficient αr cm²/s $\times 10^{-6}$
31	Barley	−42	35	.025		.026	70*
						.26	8*
						13	.2*
1	Vetch	10	31	.02	4	.25	2.5
1	Capeweed	10	31	.02	15	.95	2.5
2	Maize	20	.04	.03	15	2	1.2
18	Barley	7	7	.025	11	4	.43
18	Barley	7	14	.015	1.5	4	.06
7	Leek	14	53	.03	11	4	.43
19	Pea	0	42	.02	4.3	3	.23
19a	Maize	0	32	.02	11	30	.06

* Calculated by *Nye* and *Tinker* [21]

Thus in a moist soil $\alpha r/D_l v_l f_l$ will be greater than one, and hence the root surface concentration ratio will be less than 0.5. We should anticipate that diffusion will severely limit the rate of uptake of K by plants when the bulk soil solution is less than 10^{-4} M. *Beckett* [5], in a review, concludes that the activity ratio $K/\sqrt{Ca + Mg} = .001$ (mol/1)½ is the level below which crops may respond to potassium fertilizers. Since the concentration of Ca + Mg in the soil solution is of the order 10^{-2} M, the critical concentration of potassium appears to be about 10^{-4} M. Thus it is possible from these theoretical considerations to answer the question posed by the quotation from Tinker, and conclude that if a crop is responding to potassium fertilizers then its rate of potassium uptake is severely limited by diffusion through the soil.

Experimental evidence that diffusion of potassium is a rate limiting process

When plants are grown in soil the concentration in the soil solution at the root surface has to be derived indirectly. *Drew et al. 12*] measured the uptake of potassium through a one cm length of the root of an intact onion seedling from soils on which they also measured independently the K concentration of the bulk soil solution and the diffusion characteristics of the soil. Since the inflow rate depends on αr and C_{lr} (eqn. [5]), and C_{lr} is related to αr and the diffusion characteristics of the soil (figure 3), then it is possible to derive the root surface concentration ratio from the measurements made. It is now well established that an element of root surface continues to absorb actively for many days, and in these experiments there was little decline in the uptake rate over 16 days. Using the same technique over a very wide range of soil types *Bagshaw et al.* [*3*] obtained the results shown in figures 4, 5 and 6. The uptake v. bulk soil solution concentration is shown in figure 4. The root surface concentration ratio v. concentration in the bulk solution is shown in figure 5. The potassium flux is plotted against the solution concentration at the root surface in figure 6. It may be calculated from figure 6 that the value of αr when the concentration at the root surface is that required for half the maximum uptake rate (about 10^{-4} M) is 3.5×10^{-6} cm²/s. Diffusion is clearly a limiting process at initial solution concentrations below about 5×10^{-4} M (figure 5). The apparently negative values calculated for the root surface concentration ratio at very low solution concentrations imply a greater uptake rate than the exchangeable potassium could supply by diffusion, and are probably caused by release from non-exchangeable potassium – an effect which must be taken into account in further work along these lines. Since the one cm layer was the only source of K in these experiments the root demand coefficient may be expected to be somewhat high.

These indirect determinations of the root surface concentration clearly need to be supported by more direct measurements. The root plane technique developed by *Farr et al* [*14*] enables this to be done. Briefly, the single roots of intact seedlings are aligned and placed alongside each other to form a plane, and blocks of soil are pressed against this plane on either side. After several days of nutrient uptake the blocks are removed, rapidly frozen, and sectioned parallel to the plane. ***Dunham*** [*13*] has used this technique to study the effect of moisture level on the uptake of potassium by onion seedlings, and on the concentration gradients of K developing near their root surfaces.

Figure 7 shows the concentration gradients at two moisture levels after 4½ days uptake. The figures show how the zones of depletion spread further at the high moisture level.

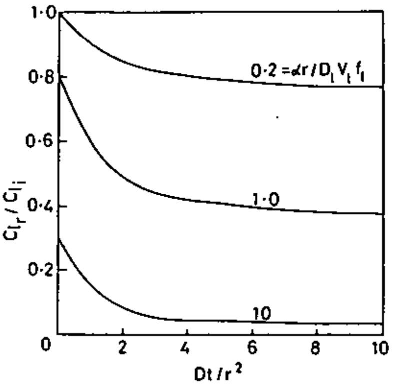

Figure 3. Relative concentration at the root surface v. time.

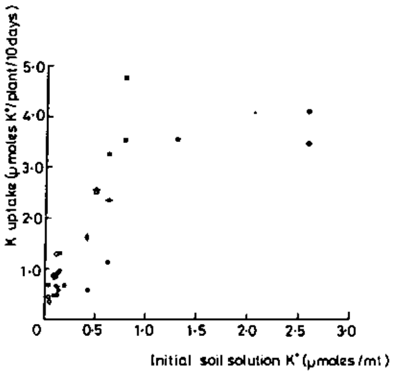

Figure 4. K uptake v. initial concentration of K in soil solution.

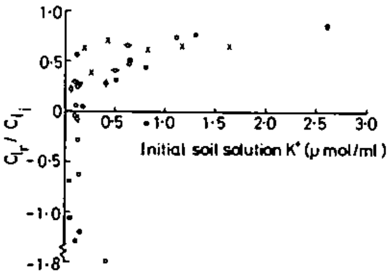

Figure 5. Root surface concentration ratio v. initial concentration in soil solution.

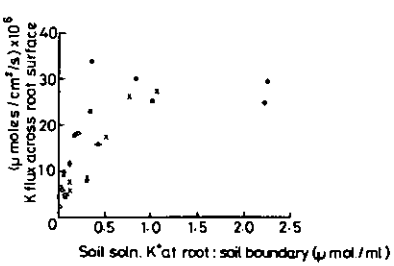

Figure 6. K flux across the root surface v. concentration of K at the root surface.

From the potassium desorption isotherm shown in figure 1 it may be deduced that the K concentration in the soil solution at the root surface has been reduced to $1-3 \times 10^{-5}$ M. The value of αr that may be derived is $.3-1.5 \times 10^{-6}$ cm²/s.

The depletion zones that were predicted from independent measurements of the soil diffusion characteristics are shown. The reasonable agreement between the form of the curves predicted and those measured gives confidence that the model I have outlined is not seriously inaccurate, though the experimental technique is at present too difficult to permit closer agreement.

Potassium uptake by a complete root system

The next step is to integrate the movement of potassium around individual roots over the whole root system. This has been taken by *Brewster* and *Tinker* [*8*]. They determined the course of uptake of potassium by leek plants with an unrestricted root system over a period up to 85 days from sowing. During this time they also measured the length and

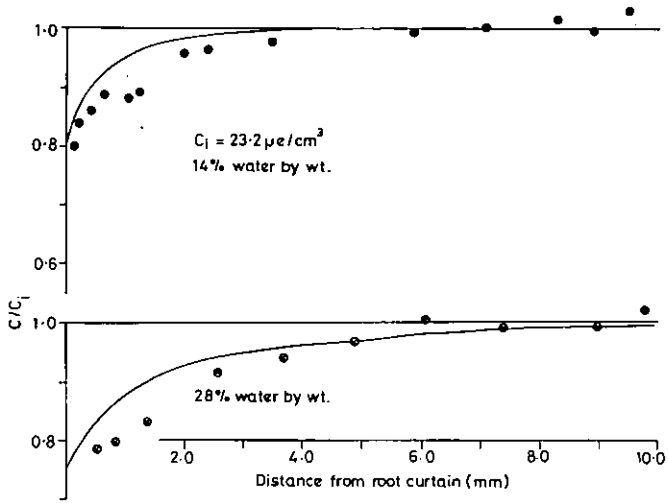

Figure 7. K depletion zones near a plane of onion roots after 4½ days in a moist and dry soil.

distribution of the roots and the transpiration. The calculated average values of αr, and of the root surface concentration ratio are shown in table 3.

The bulk soil solution concentration remained unexpectedly steady over the experimental period at 4.3×10^{-4} M. The values of αr are consistent with those determined from solution culture experiments at this concentration given in table 1.

Table 3. Potassium inflow, water inflow, fraction of uptake supplied by apparent mass flow, root demand coefficient, and root surface concentration ratio for leek plants.

Days from sowing	Water inflow cm^3/cm s $\times 10^{-6}$	Potassium inflow mol/cm s $\times 10^{-13}$	Apparent *Mass Flow* ÷ Inflow	αr cm^2/s $\times 10^{-4}$	C_{lr}/C_{li}
49–62	0.24	14.8	0.07	3.9	0.14
62–70	0.23	11.8	0.08	1.3	0.33
70–85	0.24	10.0	0.10	0.9	0.40

Movement of Potassium by mass flow

In addition to transport by diffusion some potassium may be convected to the root surface by water movement. By comparing average soil solution concentrations with plant uptake of potassium and water, *Barber et al.* [*4*] showed that this process would not in general satisfy a plant's potassium requirements.

It will be noted in Table 3 that in *Brewster* and *Tinker's* experiment with leeks the contribution to the total inflow from apparent mass flow did not exceed 10 percent. The word 'apparent' is used because diffusion and mass flow interact, and it is not strictly correct to treat the total inflow as the sum of the two processes acting independently.

Thus we see that in carefully controlled experiments with homogeneous soil, we are approaching the stage of being able to predict the uptake of potassium from a soil if we know the geometry of a plant's root system and its root demand coefficient and the soil's diffusion characteristics.

It is necessary to emphasize that in the work with soil I have described, the concentration of anions in the soil solution has been fairly constant; and in determining the relation between C_1 and C, the sorption isotherm has been determined with the appropriate anion concentration. Since the concentration of K in the soil solution depends not only on the composition of the exchange complex, but also on the anion concentration, the prediction of uptake by plants in the field is usually more complicated. Slow release of non-exchangeable potassium has already been mentioned, and we badly need a clearer idea of the kinetics of this process under field conditions. Leaching of potassium during the growing period, and mutual competition between the roots present further complications. Methods are being developed of examining and modelling these processes in detail, e.g. *Frissel et al.* [*15*], *Baldwin et al.* [*1a*], and there seems reasonable hope of a clearer understanding within the next few years, with the ultimate prospect of our being able to predict the uptake of potassium by crops in the field.

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Model Calculations on the Vertical Transport of Potassium Ions in Soil

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Summary

The formulation of involved mathematical models requiring numerical methods for their solution is largely facilitated by the use of computer simulation languages. These languages are rather easy to handle and permit the scientist, while programming himself, to focus his attention to the main problem which is the development of a suitable model.
A model has been worked out to describe vertical transport of potassium in a soil. It includes submodels for a four cation exchange mechanism and for the fixation and release of Potassium. The technical possibilities of such a model are demonstrated at the hand of two examples. Experimental data are not included.

1 *Introduction*

1.1 *Conservation equation*

A general theory for the description of the vertical transport of ions in a soil may be formulated by the conservation equation:

$$\frac{\partial Q_i}{\partial t} = -\operatorname{div} J_i + \mathrm{Prod}_i$$

in which ∂Q_i is the variation of the quantity of species i at a point P during the time interval ∂t.

The term div J_i is the divergence of the flux J of species i; so it is the flow rate of species i towards point P minus the flow rate of species i from point P. The production term Prod_i stands for processes such as dissolution, fixation, release and so on.

Analytical solutions of this equation are only possible when making simplifying assumptions. Solutions of the general equation require numerical methods. Systems in which an instantaneous equilibrium between adsorbed and dissolved ions have been assumed are described systematically by *Reiniger* [*1*]. He explains that, unless a simple situation is selected, an analytical solution is not possible. Systems in which the reaction rates (e.g. adsorption and desorption rates) have been explicitely taken into consideration are described by *Reiniger* [*1*], by *Hiester* and *Vermeulen* [*8*] and by *Vermeulen* and *Hiester* [*9*]. The latter authors arrive at special functions to describe these processes.

It is therefore not surprising that general theories which take into account both reaction rates and instantaneous equilibriums have not been presented.

In this contribution a numerical method for the simultaneous description of two of such processes is given.

1.2 *Numerical methods*

Due to the recent development of the computer software the use of numerical methods has evoluated rapidly. For biological systems in which equations like the conservation equation play an important role it is mainly the development of computer simulation languages which contributed to this evolution. Without the use of simulation languages a numerical solution requires, besides mathematical skill, more time than the average biologist has available.

Simulation languages are set up so that the complete numerical solution is carried out automatically. In the most advanced languages it is even possible to make a choice out of 8 integration methods, e.g. trapezodial, Simpson, Runge-Kutta, etc.

If the conservation equation is taken as a start, it is, in principle, only necessary to replace this equation by suitable difference equations, and to define the boundary conditions. In addition, it is of course necessary to define the time period over which the integration has to be carried out.

A disadvantage is the necessity to have a large computer at ones disposal; with the most sophisticated languages one is even rather limited in choice. For example, the language used in this study, CSMP/360 (Continuous System Modelling Program), can only be used on computers of the type *IBM System/360 model 40 G* and larger.

1.3 *Models*

A complicated problem requires many more parameters to describe its situation than a simple problem. Sometimes this is a disadvantage, it requires such a refined model, that it cannot be applied to other situations.

Model builders try to meet this difficulty by building up their main model out of smaller sub-models, each sub-model describing a particular situation. If now a modification is required, it is only necessary to replace the sub-model which describes the particular situation to be modified.

The underlying study must be seen as a demonstration of the possibilities of model calculations on potassium transport in a soil. Experimental data are not considered. Papers in which the author presents both results of model calculations and of experiments are published elswhere [*1, 2, 3*].

2 *Model for the vertical transport of ions in a soil*

2.1 *Overview of the structure of the model*

To set up the model the soil is divided into a variable number of layers, usually 20. The aim is to calculate the ion fluxes between those layers – including the ion flux towards the top layer – and the integration of those fluxes, to obtain the distribution of the various species over the profile.

Figure 1 presents a diagram of the processes which are considered. Four cations are taken into account, namely K, Na, Ca and Mg-ions. In the model the transport itself is only caused by the flow of the soil solution in which the ions are dissolved. Both diffusion and dispersion are accounted by choosing an appropriate layer thickness. The ions of the soil

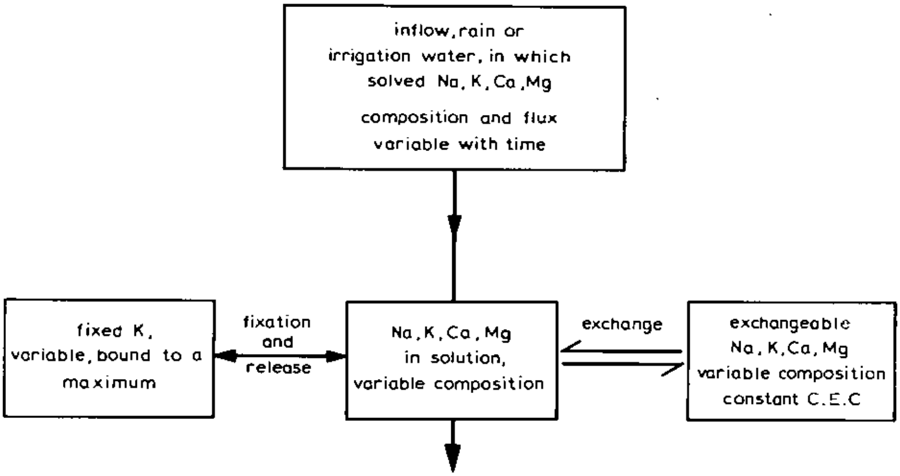

Figure 1. Diagram of processes which are considered for the vertical transport of ions in soil.

solution react in two ways with the solid phase. On the right hand side an instantaneous exchange with 'easily exchangeable' cations of the soil complex is shown. The composition of this soil complex is variable; its total capacity, the C.E.C. is constant.
The left hand side shows the so-called fixation. Fixation is considered by me as a rather slow exchange reaction with ions bound on special sites of the soil mineral. The main characteristic is that it specially applies to K-ions. Further the fixation rate is much higher than the release rate.

2.2 *Detailed description, Assumptions*

Figure 2 shows the scheme which is used for the calculations. The processes are the same as in Figure 1, but they are arranged as four separate sub-models:

- Calculation of the supply of the upper layer.
- Calculation of the fluxes between the layers.
- Calculation of the fixation and release rates.
- Calculation of the distribution of the available ions over the liquid and solid phase.

Each of the sub-models can be modified independently or replaced by another sub-model. The scheme also shows how the result of the sub-models are combined to calculate eventually the variation of the total amount of ions per layer and the amount of potassium fixed per layer.

2.3 *Supply to upper layer*

I have assumed that the supply of ions to the upper layer takes place via the liquid phase. Both the quantity and composition of the solution can be varied at will as a function of

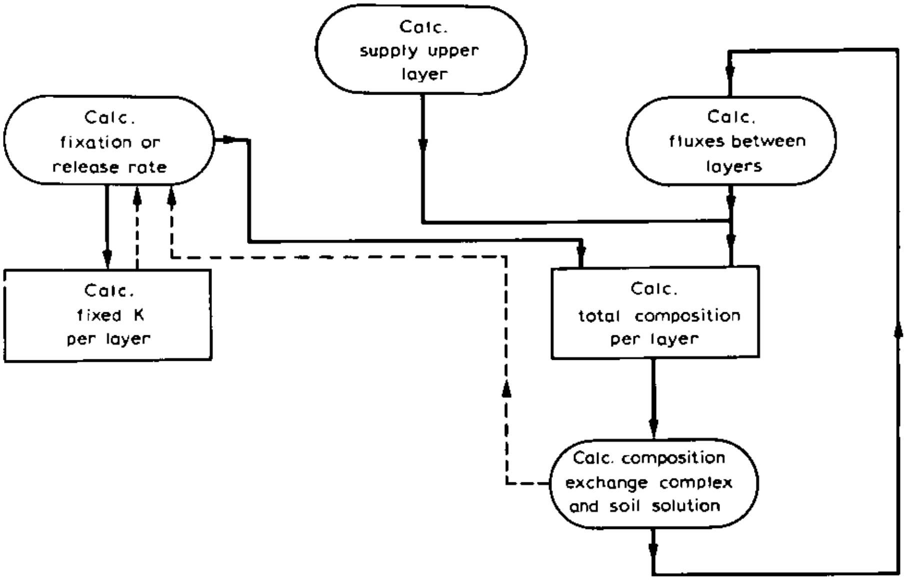

Figure 2. Calculation scheme for the vertical transport, exchange and fixation. It shows the arrangement of the 4 submodels (elipsoides) and the variables which are eventually calculated (rectangles).

time (flux in ml cm^{-2} day^{-1}, K, Na, Ca and Mg in me ml^{-1}). So each assumption concerning the solution rate of a fertilizer can be used.

Introduction to the computer program takes place with tables. As an example the instruction

FUNCTION FLOWT =(0., 0.) ,(2., 1.) ,(3., 2.) ,(6., 0.) ,(7., 0.) states that at time=0 the flux equals 0, at time=2 the flux equals 1, at time=3 the flux increases to 2, at time=6 the flux goes down to 0 and remains 0 till the 7th day. The flux for intermediate times is found by interpolation (linear, quadratic or other order).

2.4 *Calculation of composition of the exchange complex and the soil solution*

The subroutine *CATEX* [*6*] was used in the program for the description of the exchange equilibrium of the four cations. To describe the relations between four cations three exchange equations are needed. The two equations which describe the homovalent exchange are:

$$\frac{K_{sol}}{Na_{sol}} = X_{Na,\,K} \cdot \frac{K_{ads}}{Na_{ads}} \text{ and} \tag{2}$$

$$\frac{Mg_{sol}}{Ca_{sol}} = X_{Ca,\,Mg} \cdot \frac{Mg_{ads}}{Ca_{ads}} \tag{3}$$

in which the subscripts *sol* and *ads* refer to the dissolved and adsorbed ions respectively. (All concentrations in me cm^{-3} bulk soil). $X_{Na,\,K}$ and $X_{Ca,\,Mg}$ are the exchange constants. For the heterogeneous exchange the equation which first was used by *Vanselow* was choosen, except that all concentrations are again expressed in me cm^{-3} bulk soil:

$$\frac{Ca_{sol}}{(Na_{sol})^2} = X_{Na,Ca} \cdot \frac{Ca_{ads}}{(Na_{ads})^2}$$

in which $X_{Na,Ca}$ is the exchange constant.
Besides this relation there exist of course also the relation:

$$Na_{ads} + K_{ads} + Ca_{ads} + Mg_{ads} = CEC. \qquad (5)$$

As said before the CEC is a variable which only depends on the depth. If K_{tot}, Na_{tot}, Ca_{tot} and Mg_{tot} are used for the total amounts (solid + liquid phase) and the ratio between Na_{sol} and Na_{ads} is defined by $X_1 = Na_{sol}/Na_{ads}$ the equations (2), (3) and (4) can, after rearrangement, be substituted in equation (5).
All but the ratio for sodium X_1 can then be eliminated leading to:

$$CEC = \frac{Na_{tot}}{1+X_1} + \frac{K_{tot}}{X_{Na,K}(1+X_1)} + \frac{Ca_{tot}}{X_{Na,Ca}(1+X_1^2)} + \frac{Mg_{tot}}{X_{Na,Ca} \cdot X_{Ca,Mg}(1+X_1^2)} \qquad (6)$$

X_1 is found from equation (6) by the *Newton-Raphson iteration* using the IBM-SSP subroutine RTNI, modified to facilitate the choice of a correct initial value for the iterative procedure.
Substitution of the value of X_1 in the preceding equations gives the values for Na_{sol}, K_{sol}, Ca_{sol}, Mg_{sol}, Na_{ads}, K_{ads}, Ca_{ads} and Mg_{ads}.

2.5 *Validity of the submodel CATEX*

The validity of this submodel (called CATEX, derived from CATion EXchange) depends on the validity of the assumptions. e.g. it has been assumed that the exchange occurs immediately, and with high flow rates this will lead to errors.
Bolt [*4*] explains in his review on 'Cation exchange equations used in soil science', that all equations have their limitations. Usually this limitation will manifest itself in changes of the exchange constant with total concentration and with the composition of the exchange complex.
Furthermore it was assumed that the value of the exchange constant valid for a mixture of 2 species can also be used for more than two species. This is not verified by thermodynamical considerations and has only occasionally been proved in practice. It must be noted however, that as soon as the dependence of the exchange constants $X_{Na,K}$, $X_{Ca,Mg}$ and $X_{Na,Ca}$ on the composition of the soil complex is determined, it should be possible to modify the iteration procedure and to include this dependence in the model.
Some readers may wonder why the equation of *Gapon-Erikson* has not been used to describe the heterogeneous exchange. The validity of this equation is very good, because up to situations with 40 percent monovalent cations, the exchange constant appears to be a constant indeed.
The main difficulty is found in the iterative procedure. As soon as due to extrapolation a situation emerges in which about 50 percent of the cations are present as monovalent cations, the iteration derails and thus prevents a successful calculation.

2.6 *Calculation of the fixation and release rate*

For K-fixation various mechanisms are proposed. I have rather arbitrarily assumed that the fixation can be described by the following statements and equations:
K-fixation is regarded as an exchange with cations present on a particular part of the soil complex. This part of the soil complex is not considered as part of the CEC, so a fixation of K-ions does not decrease the CEC. The ions which are replaced have the same mutual composition as the ions of the immediately exchangeable part of the soil complex. The amount which can be fixed is limited in two ways:

- In the first place only a certain fraction, F_{fr}, of all K-ions present per layer can be fixed.
- In the second place the amount is limited by an absolute maximum, K_{max} (me cm^{-3} bulk soil).

The amount giving the lowest fixation is taken into consideration.
The specific fixation rate $'F_{rate}$ and specific release rate $'R_{rate}$ are independent variables. Usually the specific release rate will be chosen much slower than the specific fixation rate. Both the actual fixation rate, F_{rate}, and actual release rate, R_{rate}, are proportional to the difference between the actual K-fixation and the equilibrium situation. So both rates are highest far from equilibrium.
In equations: If $'K_{tot}$ is the total amount of K in a layer, the amount which will be fixed in the equilibrium situation, K_{eq}, is found from:

$$K_{eq} = F_{fr} \cdot {}'K_{tot} = F_{fr} \cdot (K_{fixed} + K_{ads} + K_{sol})$$

in which K_{fixed} is the actual amount which is fixed (me cm^{-3} bulk soil) and F_{fr} is the fraction of K-ions per layer which can be fixed.
If, however, $K_{eq} > K_{max}$ then K_{eq} is set to K_{max}.
If $K_{eq} > K_{fixed}$, the fixation rate is found from:

$$F_{rate} = {}'F_{rate}(K_{eq} - K_{fixed})$$

If $K_{eq} < K_{fixed}$, the release rate is found from:

$$R_{rate} = {}'R_{rate}(K_{fixed} - K_{eq})$$

If $K_{eq} = K_{fixed}$, neither release, nor fixation takes place. As both F_{rate} and R_{rate} are expressed as me cm^{-3} d^{-1}, the dimension of $'F_{rate}$ and $'R_{rate}$ is: d^{-1}.

2.7 *Validity of the fixation model*

As said before the validity of a model depends on the validity of the assumptions. Both the release and fixation are considered to be first order reactions. This is of course only an approximation.
Furthermore it has been assumed that the composition of the exchangeable ions for all exchange sites is identical. This cannot be true, the sites on which K-ions are fixed show a preference for ions of a particular size. Unfortunately, the composition of the ions which are replaced by K-ions is unknown. An alternative possibility should be to consider all ions replaced by the K-ions as Ca-ions.
If the K-fixation is seen as an adsorption on 'normal' exchange sites followed by a collaps of the clay mineral lattice it is better to modify the program such that the fixation causes a decrease of the CEC.

2.8 *Calculation of the fluxes between the lavers*

Transport of ions between layers results from mass flow, ionic diffusion and hydrodynamic dispersion. The combined effect of the latter two is often described by the apparent diffusion coefficient, D_A. The relation is:

$$D_A = \Theta \gamma D + \mathrm{DISP.FLOW} \tag{7}$$

in which Θ is the moisture content, γ the tortuosity, D the ionic diffusion coefficient in water, DISP the hydrodynamic dispersion coefficient in cm and FLOW the vertical velocity of the liquid phase in cm sec^{-1}, if both D_A and D are expressed in $cm^2\ sec^{-1}$. The equations for mass flow and diffusion are of course well known.
Another indirect way to calculate the effects of diffusion and dispersion is the introduction of the mixing stage, as is done in chromatography plate theories, see e.g. *Glueckauf* [*5*]. The latter method is used here, its mathematics is simpler, but it has no flexibility.
The diffusion effects which are obtained equal the effects resulting from a hydrodynamic dispersion coefficient of 0.25 cm for flow velocities of 0.2 cm d^{-1} to 2.5 cm for flows of 10 cm d^{-1} and higher. For velocities lower than 0.2 cm d^{-1} the diffusion is underestimated ($\Theta\gamma D$ is estimated at $0.2 \times 10^{-5}\ cm^2\ sec^{-1} \simeq 0.17\ cm^2\ d^{-1}$).
Because in this paper diffusion is not of primary concern a more sophisticated method is not introduced. Models which describe the diffusion and dispersion in more detail and which can be introduced in this calculation because they are set up in the same fashion are published by *Frissel et al*[*2*], *Reiniger et al* [*6*] and by *de Wit* and *van Keulen*[*7*].

2.8 *Integration*

If all the transport rates, release rates and fixation rates are known, integration can be performed giving respectively the amounts of fixed K, total Na, total K (fixed K excluded), total Ca and total Mg per layer.

In the next section some details of the calculation are explained. For more details the readers are referred to the computer program which is available on request. Within the program the explanation of the symbols and equations is given by comments. Those readers who are conversant with FORTRAN and/or CSMP/360 will find the program more precise than the text.
To perform the integration, first the net rates have to be calculated. The net rate for Na-ions of the top layer ($R\ Na_1$) will be written out, the subscript 1 will be omitted.

$$R\ Na = Na' - Na'' + Na\ F \tag{8}$$

Na' = in flow of Na
Na'' = out flow of Na
Na F = change in Na conc. due to fixation

$$Na' = FL_t \cdot Na\ IN_t \tag{9}$$

FL_t = in flow rate solution supplied to top layer at time t, derived from tables by interpolation.
$Na\ IN_t$ = Na conc. in solution supplied to top layer at time t, derived from tables by interpolation.

$$Na'' = FL_t \cdot Na\ SOL \tag{10}$$

Na SOL = Na conc. in soil solution in top layer, calculated by sub-routine CATEX.

$$Na\ F = FRATE \cdot Na\ ADS/CEC \tag{11}$$

FRATE = fixation rate (if negative: release rate) of K-ions, calculated with sub-model FIXATION.
Na ADS = Na adsorbed in top layer.

If Na_0 is the initial amount of Na in the top layer and R Na is the net rate which cause the changes in the amount of Na in this layer, the integration equation is:

$$Na_t = Na_0 + \int_0^t RNa\,dt \tag{12}$$

The simulation language, used in this calculation, enables to carry out such integration by the statement

$$\text{NA T} = \text{INTGRL (NAO, R NA, 20)} \tag{13}$$

The symbols have the same meaning as in equation (12).
The integer 20 takes care that the integration will be carried out for all the 20 layers. Comparable statements have to be written for K, Mg, Ca and fixed K.

3 *Result of simulations*

The results of 2 simulated situations are presented below. Case 1 shows the transport of a K-Ca-fertilizer through the profile under moderate leaching circumstances. K is dissolved in 12 days, Ca in 20 days. The soil fixes K-ions, but the upper layers of the soil are at the beginning almost saturated with K-ions so that transport to deeper layers occurs. For case 2 a much higher flow velocity is used. During the first 10 days a 0.03 N K solution is supplied to the soil, there after the K is leached out by a 0.02 N Ca solution. As said already in the introduction, the results are not verified by any experiment, they must be seen as a demonstration of the technical possibilities of describing a rather complicated vertical chromatographic transport.

Input data case 1.
(A star denotes an initial condition)

* *Exchangeable cations:* Na, 0.06 me at the soil surface, gradually increasing to 0.10 me at a depth of 50 cm, K 0.05 me, Ca 0.25 me, Mg 0.06 me, all per cm^3 bulk soil.

* *Fixed K:* 0.15 me in the upper 2.5 cm, thereafter gradually decreasing to 0.05 meq at a depth of 50 cm, all per cm^3 bulk soil.
Fraction of K to be fixed: $F_{fr} = 0.95$, *absolute maximum to be fixed* (saturation) 0.15 me cm^{-3} bulk soil.
Exchange constants: $X_{Na,K} = 0.2$, $X_{Ca,Mg} = 0.4$, $X_{Na,Ca} = 0.25$
Specific fixation rate: $0.2\,d^{-1}$, *specific relase rate:* $0.04\,d^{-1}$.

* *Conc. soil solution:* Na 0.001 *N*, K 0.001 *N*, Ca 0.007 *N*, Mg 0.001 *N*.
Conc. of fertilizer in rain water: K 0.015 *N* at the beginning, decreasing to 0.005 after 3 days, decreasing to 0.001 *N* after 6 days and going to zero after 12 days.
Ca 0.010 *N* at the beginning, going down to 0.005 after 6 days, going to zero after 20 days, no Na and Mg supply.
Moisture content: 0.3 $cm^3\,cm^{-3}$.
Rain: 0–3 days 1 cm d^{-1}, decreasing to 0.5 after 5 days, going up to 2 cm after 6 days, going down to 0.1 cm at the 12th day, rain stops after 15 days, starts again at day 20 going up to 0.2 cm at day 30 and to 0.3 cm d^{-1} after 100 days.

Figure 3 shows the composition of the soil solution in the upper layer as a function of the time.

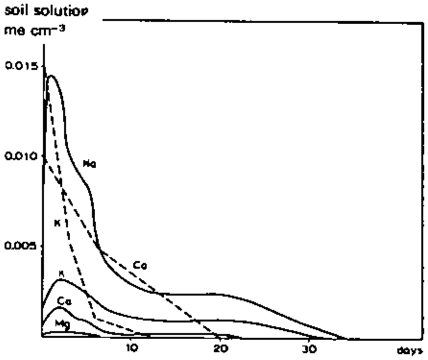

Figure 3. Case 1. ______ : Concentration of cations in the soil solution of the upper layer.._______ Concentration of cations in the solution supplied to the soil.

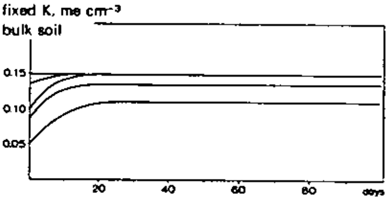

Figure 4. Case 1. Fixation of Potassium. From top to bottom: Layers 1, 4, 10, 13 and 20.

Although only Ca and K ions are supplied to the soil, as a result of exchange all four ions are present in the soil solution, Na being the major component. After 35 days all soluble salts are leached from the upper layer. (This is of course not realistic, but it was assumed for this case that the rain from the 20th day on contained not any ion; this can be changed by changing the input conditions).

Figure 4 shows the amount of fixed K in the layers 1, 4, 10, 13 and 20. Layer 1 has already reached its saturation value (0.15 me K cm^{-3} bulk soil) at the beginning, layer 4 and 10 reach it in about 15 days. The supply of K is not high enough to saturate the layers 13 and 20.

Figures 5a, 5b and 5c show the total amounts of the various ions as a function of the depth, respectively after 0, 10 and 100 days. It appears clearly that Na is leached from the upper layers. The K fixation has reached its saturation value in the beginning only in the upper layer. At the end the upper 10 layers have been saturated. This has considerable influence on the amount of non-fixed K; in the lower 10 layers, where fixation is still possible, there is almost no non-fixed K; in the upper 10 layers there is sufficient non-fixed K.

Input data case 2.

The conditions are identical with case 1 except:

* *Exchangeable cations:* Na 0.08 me cm^{-3} bulk soil.

* *Fixed K:* No fixed K.
Specific fixation and release rate: Both 0.2 d^{-1}.
Leaching solution: Na 0–100 d 0.001 *N*
: K 0–10 d 0.03 *N*, 10–100 d # no potassum
: Ca 0–10 d 0.001 *N*, 10–100 d # 0.02 *N*
: Mg 0–100 d 0.002 *N*
Leaching intensity: 2 cm d^{-1}.

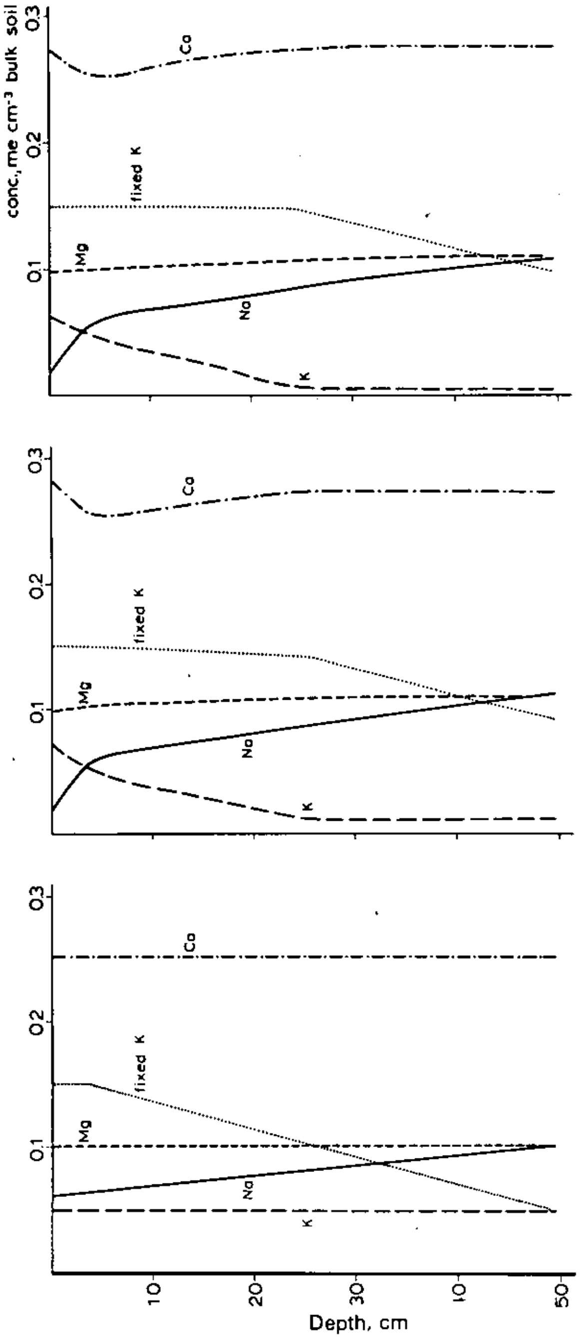

Figure 5. Case 1. Cation distribution over het soil profile. From left to right after 0 days, 10 days and 100 days.

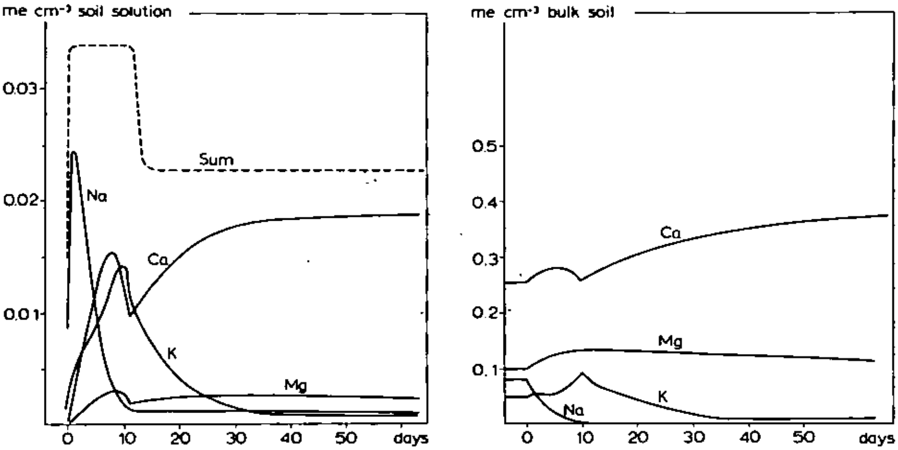

Figure 6. Case 2. On the left the composition of the soil solution, on the right the composition of the exchange complex.

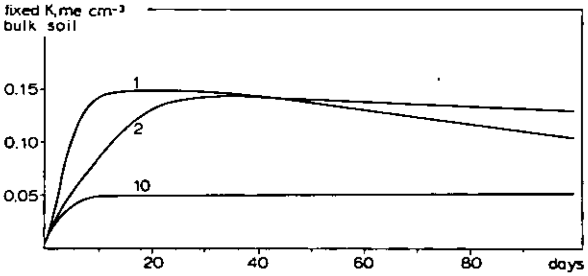

Figure 7. Case 2. Fixation of Potassium. From top to bottom in the layers 1, 2 and 10.

Figure 6a shows again the composition of the soil solution in the upper layers. First the Na ions of the complex are replaced by the K ions; they are followed by the Ca and Mg ions. The increase in the K-ion concentration is rather slow because the fixation process removes many K ions from the solution. After 10 days Ca ions are supplied. This does not lead to an increase of the Na ions in solution, they are already leached out, the Mg ion concentration increases indeed a little. Figure 6b shows the amount of exchangeable ions in the upper layer, the processes are somewhat less pronounced.

Figure 7 shows the fixation respectively in the layers 1, 2 and 10. The fixation reaches saturation for the first layer in 15 days; leaching starts after 30 days. The second layer does not become saturated, maximum fixation is reached after 35 days; it appears that there exist both a delay in fixation and in release. Most fixation occurs in the upper layers, the tenth layer reaches only 30 percent of its saturation value.

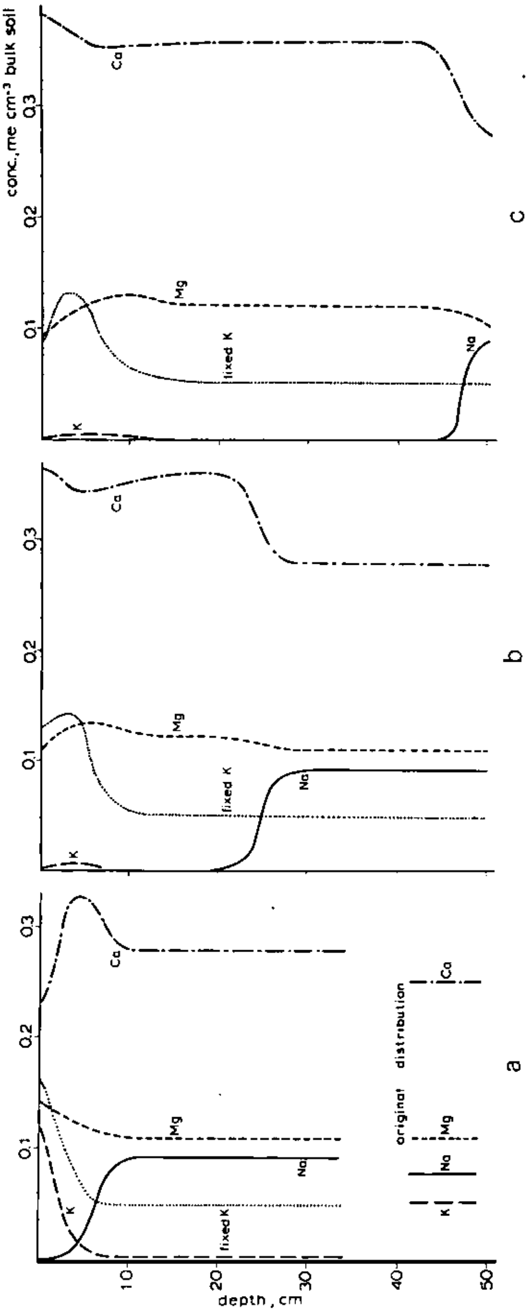

Figure 8. Case 2. Cation distribution over the soil profile, from left to right after resp. 10 days, 50 days and 100 days. The original distribution, which was uniform, is denoted at the bottom of the left figure. The original profile contained no fixed K.

The figures 8a, 8b, 8c and 8d show the ionic composition as a function of the depth after 0, 10, 50 and 100 days. The almost complete removal of Na is the most remarkable facet. At the end of the calculation practically all K is fixed; compared to Na the leaching rate is extremely slow. The Mg distribution is hardly influenced, neither by the supply of K, nor by the supply of Ca.

4 *Conclusion*

It appears that calculations with simulation models enable one to obtain a good quantitative insight in the dynamics of the processes which result from the assumptions used for the model. This is exactly what is expected from mathematical methods; the advantage of the use of simulation languages is however that it is possible for the average soil scientist to do the programming himself with a minimum effort and so spend his main attention on the real problem: the development of a suitable model. The model developed in the present paper treated simultaneously rate dependent reactions (K-fixation) and instantaneous reactions (ion exchange) in the vertical transport of K-ions through soils.

Acknowledgement

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The Determination of Desorption and Solubility Rates of Nutrients in the Soil by Means of Electroultrafiltration (EUF)

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Summary

The availability of nutrients depends on the rate of their desorption and solubility in the soil. This rate is determined by various soil properties. Statements on desorption and solubility rates of soil nutrients can only be made when these soil properties are well known.

The essential advantage of the EUF method is that it enables direct measurement of desorption and solubility rates. It is thus possible to obtain, in a single extraction run, various nutrient fractions which are of vital importance for plant nutrition and to assess also further essential soil properties.

Introduction

Plants grown under natural conditions take up the nutrients from the soil solution. The higher the nutrient concentration in this solution, the more ions can reach the plant roots by diffusion *(Vaidyanathan et al. [15])* and mass flow *(Barber [1]; Barber et al. [2]; Oliver* and *Barber [8])* within a given time and the greater is the amount of nutrients that can be taken up by the plant *(Grimme et al. [3])*.

For adequate plant nutrition it is essential to know whether the nutrient concentration in the soil solution decreases rapidly during the growing period or not. This depends on the rate of supply from the stock of nutrients present in the soil.

The concentration of nutrient ions in the soil solution and the rate of supply from the stock of nutrients, i.e. the desorption rate of cations and the solubility rate of phosphates, carbonates etc., can be determined by EUF *(Németh [6])*.

Methods

Figure 1 shows the EUF equipment. 5 g soil and distilled water are filled into the centre chamber. The soil suspension is kept apart from the electrodes by a semipermeable membrane. In the electric field the cations (Na^+, K^+, NH_4^+, Ca^{++}, Mg^{++}, iron, aluminium etc.) are attracted by the cathode and the anions (phosphate, sulphate, nitrate, negatively charged clay etc.) by the anode. Thus the soluble and sorbed ions cannot come to equilibrium so that sorbed ions will be released continuously into the solution. The desorption rate of cations and the solubility rate of phosphates, carbonates etc. is directly proportional to the voltage applied and inversely proportional to the binding power of the ions. Through adequate choice of desorption and solubility times and voltage it is possible

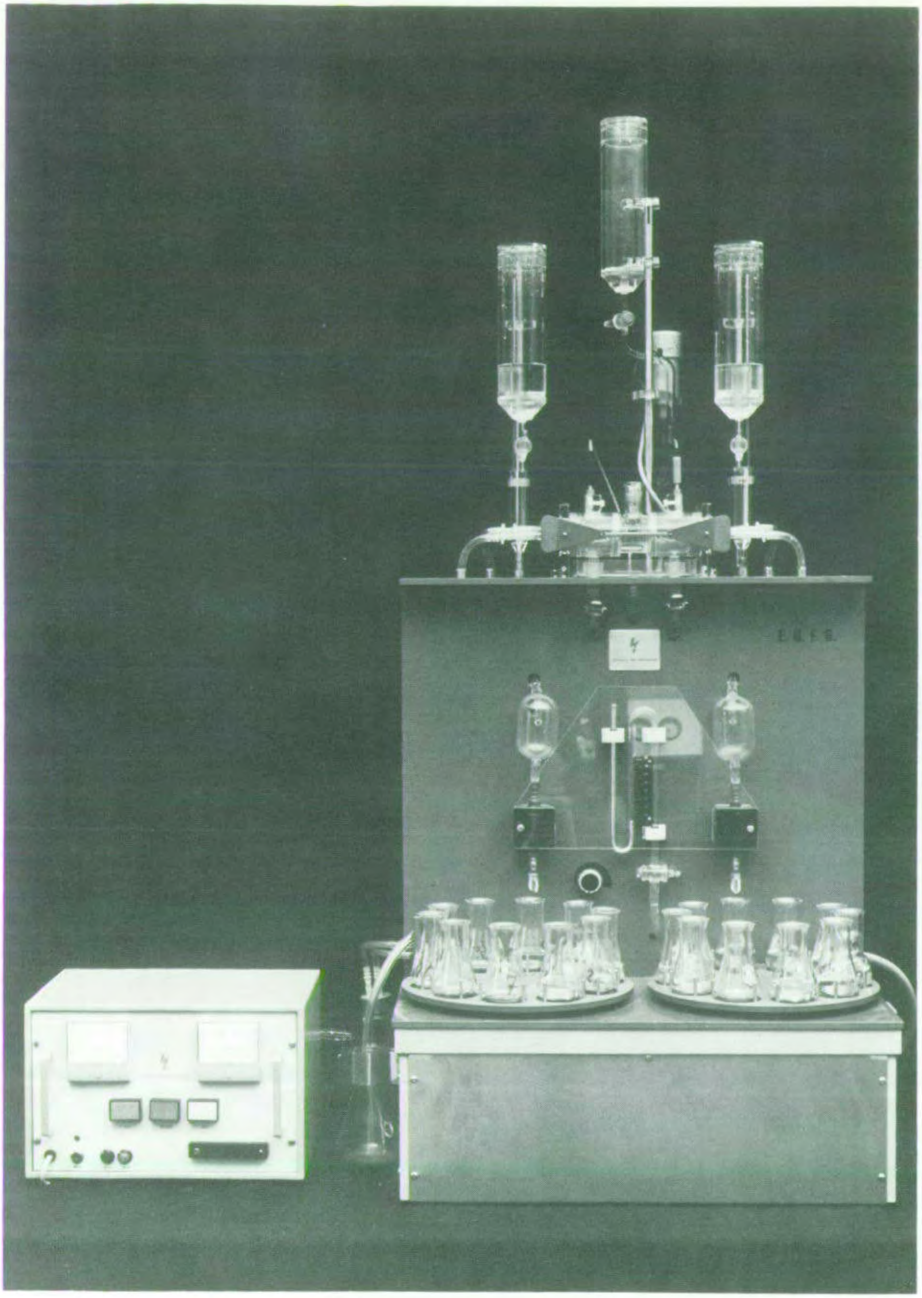


Figure 1. Electro-ultrafiltration (EUF) apparatus.

to separate several fractions of different binding power in a single run. From the shape of the respective curves also information on the desorption and solubility kinetics can be obtained.

Results

1. *Na desorption curves of various clay minerals with different Na saturation*

Figure 2 shows the desorption curves of Na-saturated standard clay minerals. The amounts of Na (in meq./100 g soil) desorbed by EUF are plotted on the y-axis whilst the x-axis shows the desorption time and the voltage applied. As can be seen in figure 2, desorption of sodium from the three clay minerals (montmorillonite, illite and kaolinite) was terminated after 25 minutes. Most of the sodium is already set free after 10 minutes (see the distinct peak after 10 minutes).

Figure 2 furthermore shows that Na desorption from clay minerals saturated both in Na and Ca is also terminated after 25 minutes. The major fraction of sodium from montmorillonite and kaolinite, however, is already desorbed after 5 minutes. In contrast to this, Na desorption from illite proceeds somewhat slower. The greater part is desorbed after 10 minutes only. It can therefore be concluded that the Na ion is more intensively bound by illite than by montmorillonite and kaolinite.

1.1 Evaluation of Na desorption curves in soil testing practice

The evaluation of the Na desorption curves in the daily practice of soil testing is rather simple. The content of exchangeable Na is equivalent to the amount of Na desorbed after 25 minutes. There is a statistically significant correlation between the exchangeable Na and the Na concentration of the soil solution and that independent of the clay content and its mineral composition *(Mengel* und *Németh* [*4*]; *Schuffelen* [*13*]*)*.

2. *Ca desorption curves of various clay minerals and soils*

The desorption of exchangeable Ca from clay minerals free from organic matter is terminated after 25–30 minutes (figure 3). In contrast to Na, however, most of the Ca is not yet desorbed after 10 minutes but after 15–20 minutes only. This clearly reveals the greater binding power of divalent Ca in clay minerals, as compared with monovalent Na, because of the difference in valence and hence attraction by the sorption sites (or charged clay surfaces). The Ca desorption from clay rich in organic matter proceeds even slower because the Ca ion is more selectively bound by organic matter than by clay minerals *(Schachtschabel* [*11*]*)*.

Figure 4 shows the desorption curves of different soils. The soil of the pot experiment contains a large amount of soluble Ca in the form of $CaCl_2$ since the anions in pot experiments are not subject to leaching. The Ca curve shows a peak after 10 minutes. The higher this peak, the greater the amount of Ca in the soil solution. $CaCO_3$, on the other hand, goes more readily into solution at 400 v. This applies especially to the C_v-horizon in which the Ca curve reaches a peak at 400 v.

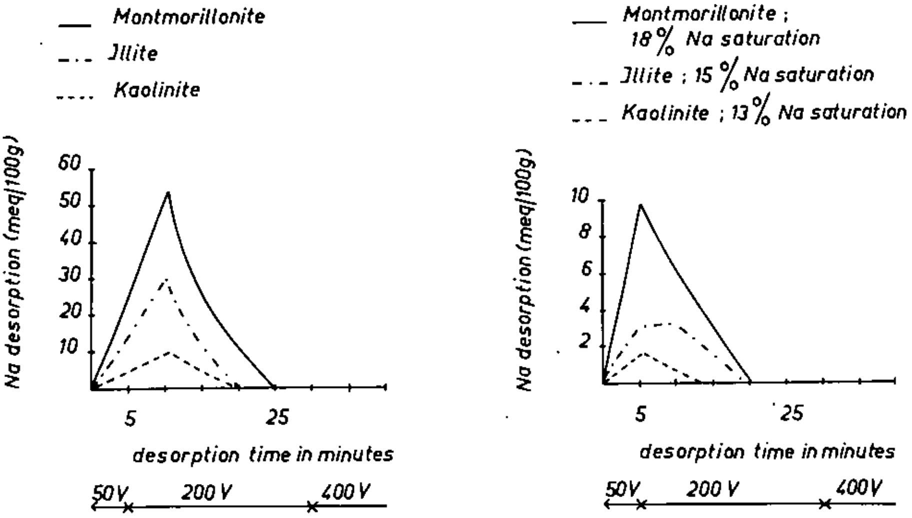
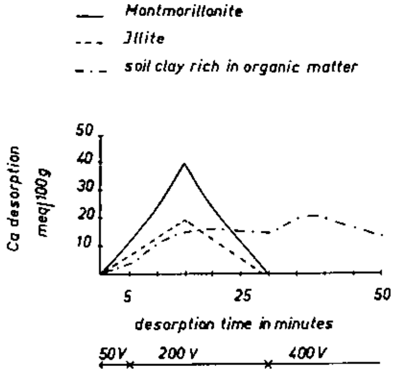


Figure 2. Desorption of Na from Na-saturated and from Ca- and Na-saturated standard clay minerals (at left Na-saturated and at right Ca- and Na-saturated standard clay minerals).



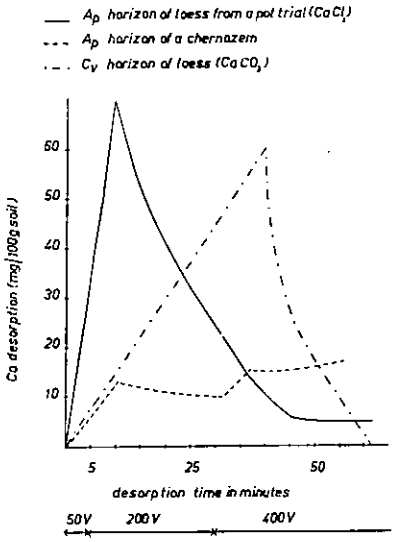


Figure 3. Desorption of Ca from Ca-saturated standard clay minerals and from soil clay rich in organic matter.

Figure 4. Ca desorption curves of different soils.

The release of exchangeable Ca ions is slowest in the chernozem soil although this soil contained the highest amount of exchangeable Ca. This demonstrates that the binding power of Ca in the soil can easily be assessed by EUF. It is also obvious that the content of exchangeable Ca does not furnish reliable information on the Ca concentration of the soil solution.

3. *Determination of Mg availability by EUF*

Similar to Ca, also the binding power of Mg in the soil can be determined by EUF. The more Mg is released by EUF at 200 v, the higher is the Mg concentration in the soil solution. There is a good correlation between the amounts of Mg released by EUF after 40 minutes and the amounts of Mg extracted in 0.025 n $CaCl_2$, unless the anion concentration of the soil differs widely. Great differences in the anion concentration of the soil solution can, for instance, be observed when soils from pot experiments are being compared with soils from field experiments. In pot experiments the anion concentration in the soil solution is much higher (5–60 meq./l) than under conditions prevailing in the open field (3–25 meq./l) where the anions are subject to leaching *(Mengel* und *Aksoy [5]; Németh et al. [7])*. In pot experiments the anions remain in the soil solution so that also the cation content of this solution will be higher. With equal content of exchangeable Mg, the Mg concentration in the soil solution is therefore the higher, the more anions are present in the soil solution. As a consequence, the exchangeable Mg cannot in all cases serve as an indicator for the Mg concentration of the soil solution whereas EUF gives reliable results in this respect.

4. *The form of K desorption curves as dependent on soil properties*

The K ion is selectively bound by some clay minerals *(Schwertmann [14])*. At a given K status, the K desorption curves are therefore affected primarily by the type and amount of clay minerals present in the soil. Figure 5 shows the desorption curves of K-saturated standard clay minerals and also the desorption curves of standard clay minerals saturated both with Ca and K which have no sites for the selective binding of K. The desorption of K from these clay minerals is terminated after 25 minutes at 200 v. At lower K saturation, K desorption takes a similar course.

In contrast to this, a lasting supply of K, after an increase in voltage to 400 v, can be observed in K-saturated illites in which K is sorbed not only at planar sites but is also present in the interlayers (figure 6). *(Schouwenburg* and *Schuffelen [12])*. In this case, the K ions released do not originate from planar sites but from interlattice sites since the non-selectively bound K ions have already been desorbed after 25 minutes (see Figure 5).

The rate of K desorption from clay minerals with sites for selective sorption of K depends essentially on the degree of K saturation. Whether the K ions will be present at planar sites or in the interlattice is determined by the level of K saturation. This is clearly demonstrated by figure 7. It shows K desorption curves of a chernozem with different K saturation of the inorganic CEC. The accompanying x-ray diagrams inform on the mineral composition of the clay fraction. With predominance of expanded illites, the K curve shows that in all fractions comparatively small amounts of K are released, because the desorption rate is low. The curve shows two peaks (similar to the x-ray diagram), one

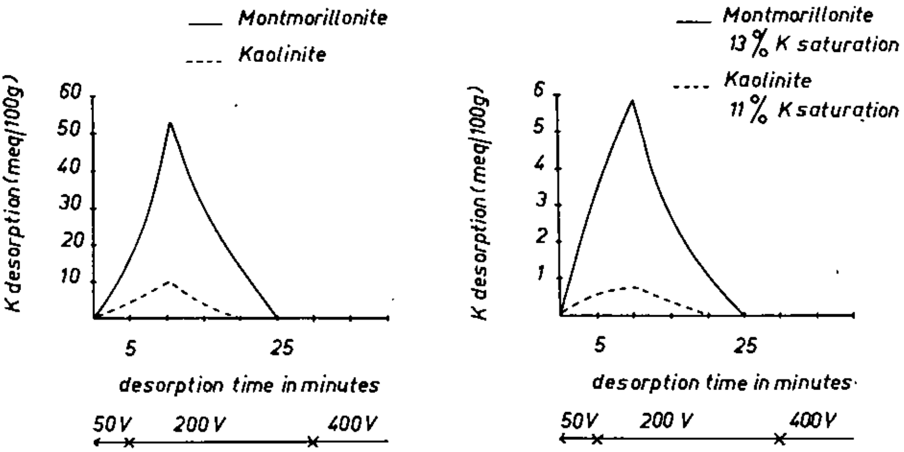


Figure 5. Desorption of K from K-saturated and from Ca- and K-saturated standard clay minerals (at left K-saturated and at right Ca- and K-saturated standard clay minerals).

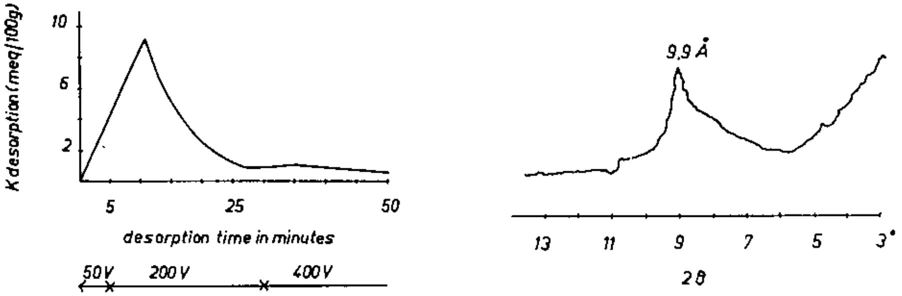


Figure 6. Desorption of K from K-saturated illite and the corresponding x-ray diagram.

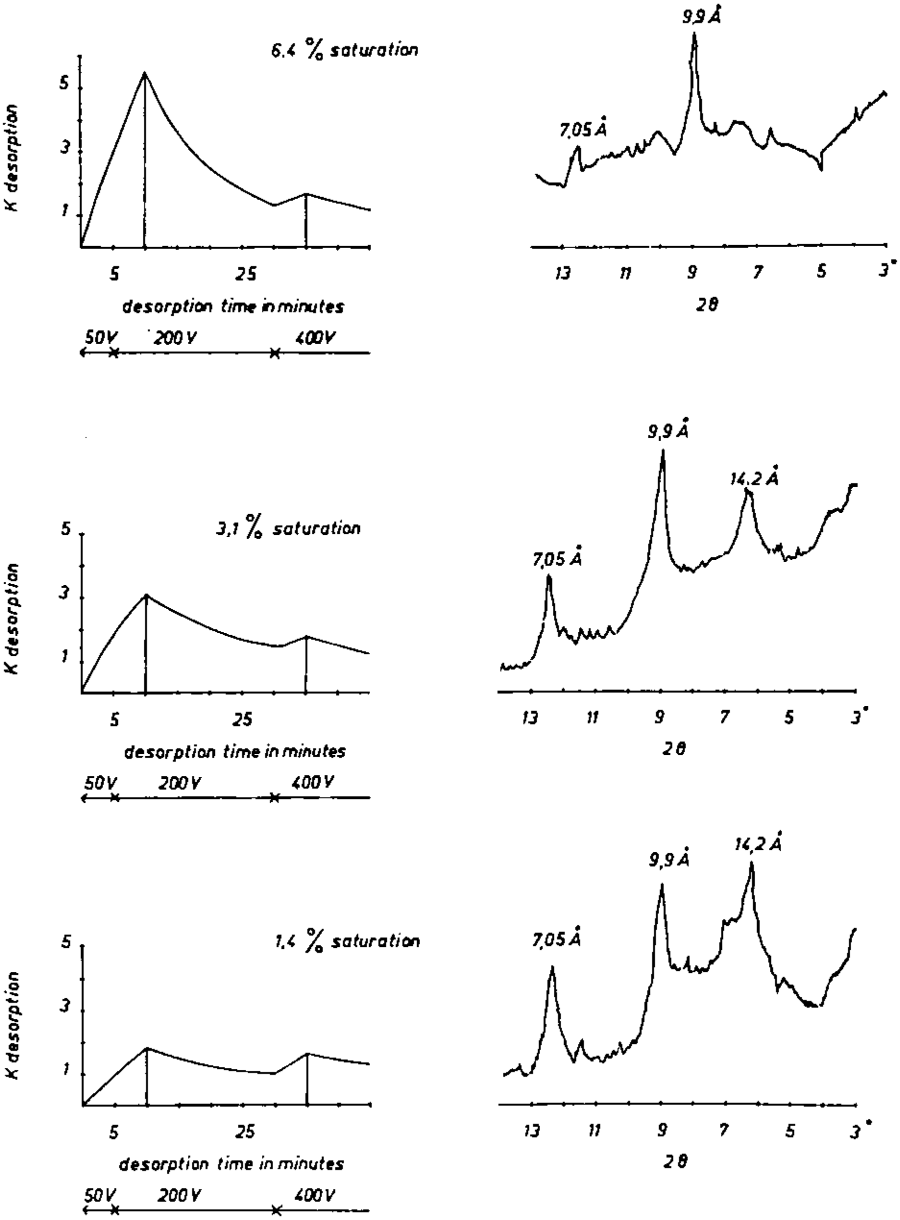


Figure 7. K desorption curves of a chernozem with different K saturation of the inorganic CEC and the corresponding x-ray diagram.

after 10 minutes and another after 35 minutes at 400 v. The second peak, after 35 minutes, is nearly as high as the first one.

With increasing K saturation (diminution of K-fixing clay minerals), the first peak increases relative to the second one. There is consequently a relation between the shape of the K desorption curves and the degree of K fixation. The higher the first peak in comparison with the second one, the higher is the K saturation and the less K will be fixed. Only the presence of a second peak indicates whether there are sites for selective K sorption or not. If the K ions are mainly bound at such sites, the first peak, in comparison with the second one, is relatively low (ratio 1:1). Besides, the absolute amount of potassium desorbed after 10 minutes is below 3 mg/100 g soil. In such soils the fertilizer K is subject to fixation. Only in case that the K-selective sites are much more occupied by K ions, the first peak, i.e. the K concentration of the soil solution, will show a marked rise after K fertilization. This is the case when the first peak is three times as high as the second one.

At a given content of exchangeable K, the percentage K saturation is the lower, the higher the clay content of the soil is. A relation between the clay content of the soil and the shape of the K desorption curves can therefore also be stated.

Apart from the type of clay and the percentage K saturation, the course of the K desorption curves also depends on the content of exchangeable aluminium. For a given K status, K desorption is the faster, the higher the content of exchangeable Al (figure 8). With increasing Al content there is apparently a competition for the sites which selectively bind K *(Rich* and *Black* [*9*]; *Rich* [*10*]*)*. Such soils do not manifest any K fixation, even when low in K. It must, however, be admitted that fertilizer potassium is being leached more readily. Liming, on the other hand, gives rise to K fixation.

The rate of K desorption also depends on the anion concentration of the soil solution. At a given K saturation, K desorption is faster, the higher the anion concentration in the soil solution (figure 9). (The rate of Ca and Mg desorption likewise depends on the anion concentration of the soil solution). In the assessment of nutrient availability the different binding power of K, Mg, Ca etc. in dependence on the anion concentration has to be taken into account.

4.1 Evaluation of K desorption curves in soil testing practice

The course of the K desorption curves depends on the type and the amount of clay minerals as well as on their saturation and also on the content of exchangeable Al and the anion concentration of the soil solution. Since K desorption can be measured directly by means of EUF, the course of the K curves allows to draw conclusions as to these soil properties. Furthermore, the following relations could be found between the individual EUF fractions and the different K fractions determined according to conventional methods:

a) The amounts of K desorbed after 10 minutes by means of EUF inform on the K concentration of the soil solution (intensity factor).

b) The sum of the amounts of K released during 35 minutes indicates the content of exchangeable K (quantity factor).

c) The amount of K desorbed between 30 and 35 minutes at 400 v (CD) allows to make statements on the possible decrease of potassium concentration in the soil solution during the growing season. The greater the length of this part of the desorption curve,

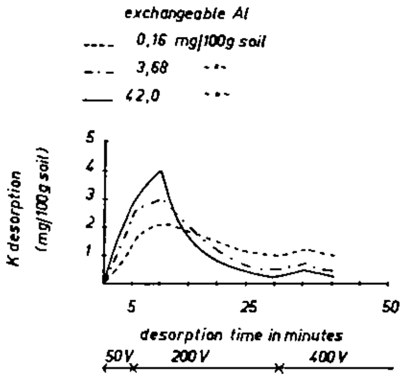


Figure 8. K desorption curves of textural B horizons derived from loess with equal contents of exchangeable K and clay but different contents of exchangeable Al.

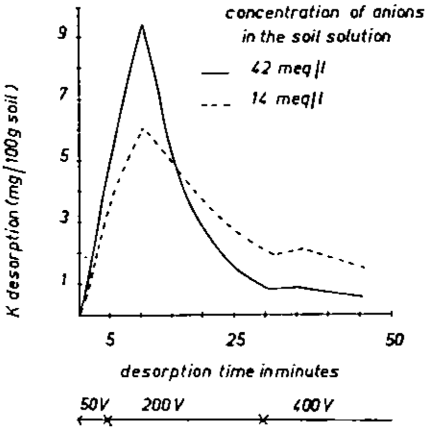


Figure 9. K desorption curves of A horizons derived from loess with equal K saturation but different concentration of anions in the soil solution.

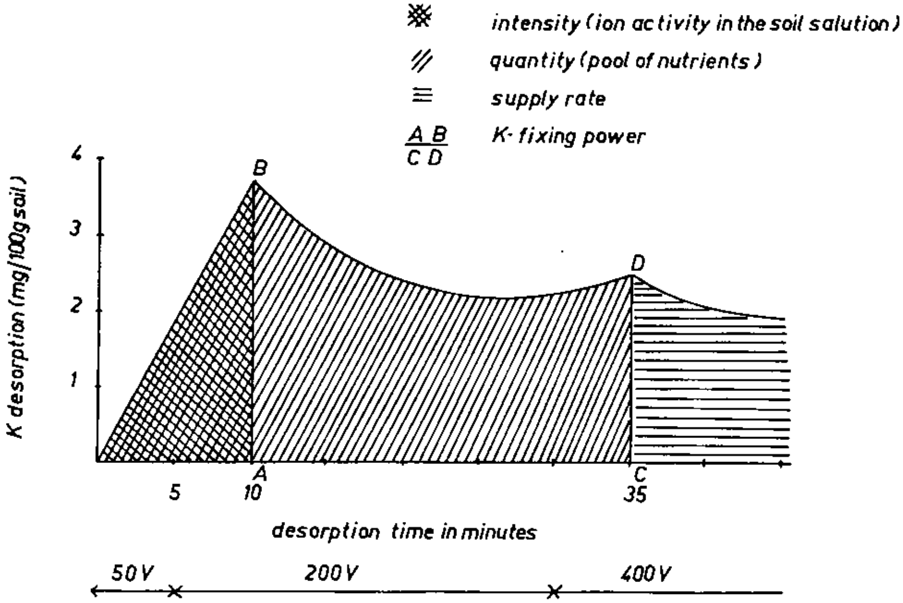


Figure 10. Various K fractions of a soil, essential for plant nutrition, determined by EUF.

the higher is the concentration over the whole growing season. If this section is lacking, then the soil cannot buffer the decrease in concentration.

d) The ratio of the K amounts released between 5 and 10 minutes and those desorbed after 30—35 minutes indicates the K fixing power of a soil. The wider the ratio of the sections AB and CD, the weaker is the K fixing power. If the section AB is three times as long as the section CD, no more K will be fixed by the soil. Apart from the above mentioned ratio the total amount of K obtained after 10 minutes by EUF extraction is important in assessing the K fixation capacity.

5. *P solubility curves*

The solubility rates of phosphates, carbonates, sulphates etc. can also be determined by EUF. According to the time and voltage applied, different P fractions are rendered soluble so that P availability can easily be assessed in this way.

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Root System, Transpiration and Ion Movement in the Soil

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Summary

An experiment conducted under conditions close to those described by *Stanford* and *de Ment* [7] on soils conditioned in different ways in respect of their compaction, humidity and chemical enrichment, illustrates the interactions operating between root system development and the movements of water and ions in the soil, and also their repercussions on the nutrition of the plant. The amounts of elements absorbed by the plant depend at least as much on the physical conditions of the medium as on the size of the nutrient reserves in the soil, whose availability is subject to the extent of exploration by the roots, and to ion movements, particularly through the intermediation of the liquid phase.

A highly favourable physical medium does not necessitate the provision of very high reserves, and inversely, enrichment of the soil can mitigate by its nutritional effect the consequences of the soil's physical defects.

The inorganic nutrition of plants growing in soil depends both upon the exploration of the medium by the roots, and on the movements of ions towards these roots. The main factors determining such movements are the constitution of the soil, its richness in nutrients, its moisture content, and the flow of liquid phase occurring within the soil in consequence of transpiration by the plants. Although the study of each of these various aspects individually is being pursued actively by numbers of research workers, the interactions that occur between the one and the other, and the overall consequences for the nutrition of the plant, are much less well known. What we wish to present here, therefore, are some results of experiments in which different degrees of root development were induced, and the movements of water and of ions were also caused to vary.

Experimental Techniques

These experiments were done by the technique of *Stanford* and *de Ment* [7] that is to say by placing young barley plants previously under-nourished N, P and K on columns of soil 25 cm high, each representing either a homogeneous medium, or a micro-profile of soil. The treatments carried out were as follows.

1. *Homogeneous media.*

The soil used was a sandy silt containing 6.4% of clay, 2.2% of organic matter, 0.14 parts per 1000 of available P_2O_5, 0.11 part per 1000 of exchangeable K_2O; pH = 6.7, CEC (cation exchange capacity) = 61 meq/kg.

To induce development of roots in greater or lesser abundance *(Maertens [3])* the soil was compacted to different degrees (total pore space of 45% or 38%), and moistened to different degrees (field capacity, or pF 3.7, maintained right through the period of culture). Additionally, it was either kept poor in nutrient elements, only 40 mg of N per 4 kg column of soil being supplied, or else markedly enriched, with 300 mg N, 300 mg P and 500 mg K intimately mixed into similar columns. S, Ca, Mg and trace elements were present in quantities more than adequate for the needs of the plants, which remained in culture for 16 days after transplanting. The combinations used, with three replicates for each, were the following.

No. 1 Soil moist (field capacity), not compacted (pore space 45%), enriched with N, P and K (300 mg nitrate-N, 300 mg P, 500 mg K, as $Ca(NO_3)_2$, KH_2PO_4, and KNO_3).
No. 2 Moist, not compacted, not enriched (40 mg N only).
No. 3 Soil dry (pF 3.7), not compacted, enriched with N, P and K.
No. 4 Dry, not compared, not enriched.
No. 5 Moist, compacted (pore space 38%), enriched with N, P and K.
No. 6 Moist, compacted, not enriched.
No. 7 Dry, compacted, enriched with N, P and K.
No. 8 Dry, compacted not enriched.

The amounts of water consumed were recorded through the course of the growing period. The plants in the drier media having a tendency to wilt, we supplied them with water via the 'pre-culture' compartment containing sand, whilst avoiding any drainage into the soil itself. When the plants were harvested the root profiles were determined by cutting the columns into slices 5 cm thick and extracting the roots from each slice. Amounts of elements absorbed were determined by difference, that is to say by comparison with control groups that were harvested at the time of transplanting.

2. *Superimposed media*

These experimental dispositions (figure 1) in which root penetration was prevented by a compaction and smoothing of the soil surface, were set up with the intention of inducing moisture flows of varying intensity towards the root mat, transporting correspondingly variable amounts of fertilizing elements. The treatments set up in this way are shown schematically in figure 2. Each comprised three replicates, and they were maintained under conditions strictly similar to those with homogeneous media, so that results might be compared.

In the superimposition 'relatively dry sandy silt/moist sandy silt' (nos. 13 and 14) the flow of moisture towards the roots could operate quite easily, taking up mineral elements in its course. With 'dry subsoils' (nos. 15 and 16) such a flow could not take place and the plants were supplied with water by moistening the sand in which the seedlings were started. Movement of ions then took place only by diffusion from the column of soil towards the root mat.

In the next series, in which the lower component was of a clayey texture (37.3% clay, CEC = 206 meq/kg, 0.085 parts per 1000 of available P_2O_5, 0.065 parts per 1000 of available exchangeable K_2O), the flow of the liquid phase was quite small on account of the low demand for water originating in the sandy loam compartment (in accordance within the mechanisms shown to operate, notably by *Puech [5])*. Water supply for nos. 19 and 20 was through the 'pre-culture' sand only, and in this series we have, therefore,

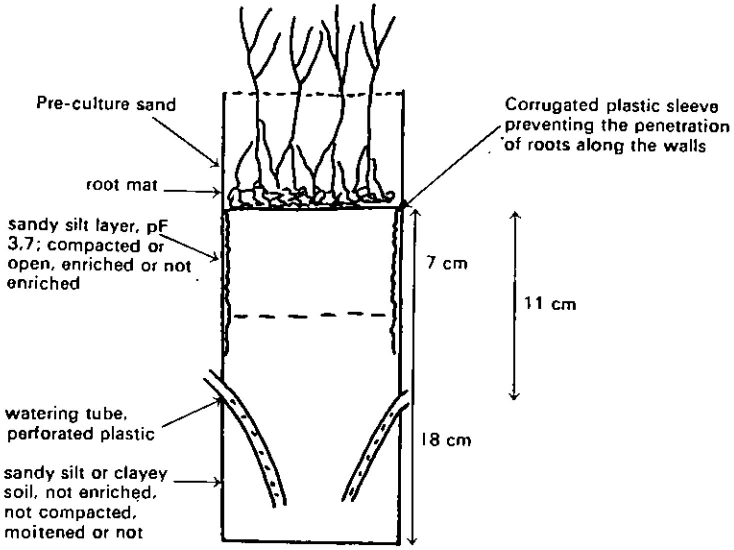

Figure 1. Diagram of the experimental set-up for study of plant growth in superimposed media.

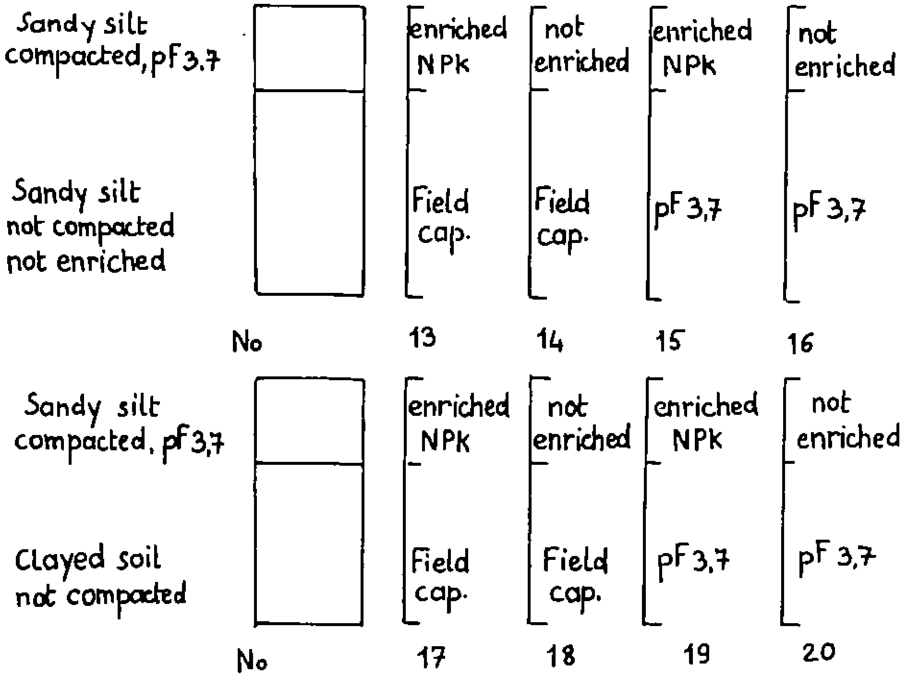

Figure 2. Scheme of the treatments carried out with superimposed media.

conditions of diffusion identical to those of the preceding case but with a lesser mass flow of liquid.

Lastly, we may say that as we expected, the roots made practically no penetration into the upper component, dry and smoothed off, and the differences of moisture content between the superimposed compartments, as adjusted at the beginning, were effectively maintained until harvest of the plants even in nos. 13 and 14 for which the moisture content was not homogeneous *(Puech [6])*. The comparisons intended were therefore valid.

Results

A. The repercussions of the different constraints on nutrition, in homogeneous media

Table I, in which the results are presented in decreasing order of quantities of elements absorbed in the homogeneous media, shows the considerable range of the observed differences, even between soils having the same stock of nutrients elements. Thus the uptake of potassium, from an enriched medium, varied between 117 mg and 39 mg, and from a non-enriched medium it varied between 80 mg and 9 mg. The behaviour of the three elements N, P and K was quite similar in this respect and this allows of an overall study being made in the first instance.

This shows up first of all the importance of the exploration of the soil by the roots, even for the uptake of highly mobile ions such as nitrate (the only form in which nitrogen was introduced into these media). Compaction, and low moisture content, greatly reduced the development of the roots *(Maertens [3]* and in consequence, the nutrient uptake. One notes also that this was greatly affected by dryness of the soil, particularly for phosphorus. The variations in the quantity of water taken up, and of P taken up, were closely linked. This effect is due, no doubt, both to the extent of occupation of the soil by roots and to an action of moisture itself in allowing movement of PO_4 ions.

Figure 3 is an attempt at a graphical summary of the effects of the constraints introduced. Amounts of potassium and nitrogen taken up under the different treatments are plotted as ordinates and abscissae respectively, and lines parallel to the axes are drawn in as far as

Table I. Results obtained in homogeneous media, ranked in decreasing order of nutrient uptake

		Moist soils	Moist soils	Moist soils	Dry soils	Dry soils	Moist soils	Dry soils	Dry soils
		Not compacted	Not compacted	compacted	Not compacted	compacted	compacted	Not compacted	compacted
		enriched	poor	enriched	enriched	enriched	poor	poor	poor
No.		1	2	5	3	7	6	4	8
Depth reached by roots	cm	25	25	10	12	8	8	12	8
Dry weight of roots	g	0.36	0.39	0.41	0.27	0.26	0.23	0.26	0.38
Dry matter of aerial parts	g	3.14	2.16	2.13	1.47	1.45	1.56	1.33	1.17
Water absorbed from soil	g	625	493	593	# 0	# 0	395	# 0	# 0
N absorbed	mg	121	66	49	41	25	20	18	7
P absorbed	mg	9.2	5.2	6	1.7	0.5	1	# 0	# 0
K absorbed	mg	117	80	69	53	39	33	22	9

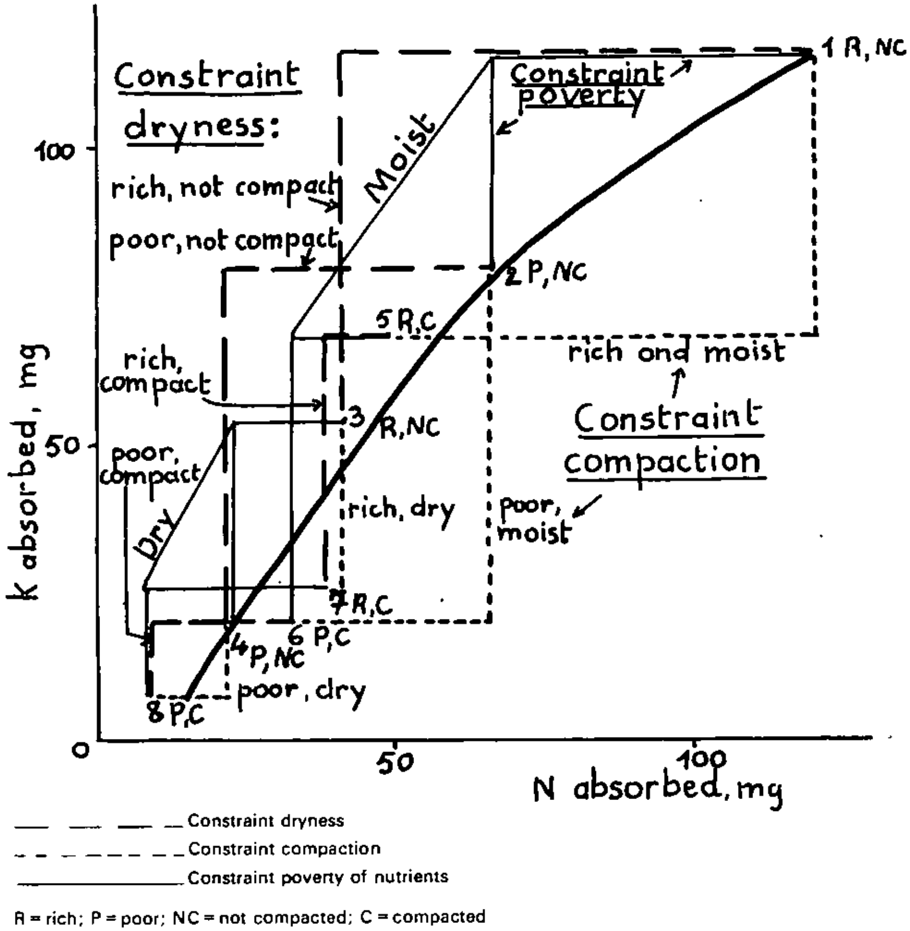

Figure 3. Graphical representation of the influence on plant nutrition of the various constraints introduced experimentally.

their points of intersection, starting from the points representing treatments that are capable of being compared. The lengths of these straight lines are thus an indication of the restriction on absorption caused by a constraint, that is to say absorption of N (horizontal lines) or of K (vertical lines) by comparison with a medium not subject to that same constraint. For example, comparison between no. 1 (moist) and no. 3 (dry) shows that uptake of N, and also of K, was reduced by about half on account of dryness. Similarly, comparing 1 (not compacted) with 5 (compacted) one finds that the compaction brought a reduction of the order of 40% for K and 50% for N. The same modes of comparison apply to the effect of richness of the medium: 1 enriched and 2 poor, 5 and 6, 3 and 4, 7 and 8. Overall, the effect of the richness of the soil showed itself in every case, and all the more so where the state of the medium was unfavourable (dry or compacted). It was in the best physical conditions, as represented by nos. 1 and 2 with the soil moist and open, that the differential action of nutrient enrichment was least perceptible, very probably on account of excellent exploration by the roots. This being much reduced by compaction, it was likely result that compaction should have its greatest repercussions on plant nutrition in a nutrient-poor medium (nos. 2 and 6, 4 and 8), although nutrient uptake was markedly restricted by it even in a moist and rich soil (1 and 5).

Finally, soil dryness in every case brought about a very strong reduction in absorption by restricting the development of roots and at the same time the movement of ions towards the rhizosphere. The effect was, furthermore, a little marked in a poor medium than in a rich one. The second part of this experiment, on the water flow and ion flow occurring in superimposed layers, helps us to be more precise about these findings.

B. Influence of water movement on plant nutrition, in superimposed media

Table 2, in which the principal results are brought together, indicates at once the considerable differences in nutritional status that were obtained, and also shows that all these values were below those recorded in the homogeneous media well colonised by the roots (table 1). And so we find once again the importance of the exploration by the roots, particularly evident in the case of phosphorus for which the quantities absorbed were here very small, or even zero. The current of liquid phase traversing the upper enriched compartments did nevertheless exert a marked effect, particularly for potassium and nitrogen. For the latter element, uptake depend directly on the richness of the media and the flow-movements of the liquid phase, which were the lesser in the presence of inorganic enrichment, in spite of a slightly higher production of dry matter; in this instance it was probably a question of reduction in transpiration due to better inorganic nutrition *(Blanchet et al.* [2]*)*. The values were further reduced again, as expected, in the clay soil *(Puech* [6]*)*.

The case of potassium is a little more complex, and table 3 allows precise statements to be made about the movements of K^+ ions involved. We note first that absorption by diffusion, without movement of water, was closely comparable in nos. 15 and 19 (enriched) on the one hand, and in nos. 16 and 20 (not enriched) on the other hand. These treatments, then, can serve as controls respecting the ones which were sites of a mass-flow of liquid, in

Table 2. Amounts of elements taken up from superimposed media

No.	Moisture lower compartment *	Nutrient enrichment upper compartment *	Yield dry matter g	Water absorbed from the soil g	Elements absorbed, mg			Mechanisms involved
					N	P	K	
13	+	+	2.02	171	58	2.4	83	Diff. + M.F.
14	+	—	1.76	283	45	0.6	59	Diff. + M.F.
15	—	+	1.45	# 0	25	0.2	31	Diff.
16	—	—	1.27	# 0	8	# 0	13	Diff.
17	+	+	1.39	59	29	0.3	37	Diff. + M.F.
18	+	—	1.29	159	16	# 0	19	Diff. + M.F.
19	—	+	1.28	# 0	20	# 0	27	Diff.
20	—	—	1.16	# 0	6	# 0	9	Diff.

* + : high; —: low Diff.: diffusion; M.F.: Mass-flow

assessing the nutritional effectiveness of the latter, by means of the comparisons indicated in table 3. In this way it is at once established that the mass-flow had indeed been very efficacious, and had been responsible for the greater part of the potassium uptake, in nos. 13 and 14 of sandy-silt texture and small cation exchange capacity. By contrast, its effect was less in combination with the clayey texture (and higher CEC) of nos. 17 and 18, confirming in this way the results that we have obtained before *(Blanchet* and *Bosc [1])*.

Discussion and Conclusions

This set of results cannot of course be extrapolated directly to field conditions, but as they were obtained under conditions in which all lots of plants were identical at the beginning of the experiment, with root system already partly developed, these results would seem to offer quite a faithful representation of processes capable of operating in the course of crop growth. On this understanding we think the main indications that emerge are as follows: —

The alimentation of plants is the resultant of numerous factors, the main ones being the exploratory function of the roots, moisture transfer, the inorganic reserves in the soils, and the possibilities of mobilisation of the latter through ion movements. According to the degree of openness of the soil and of colonisation by roots, the humidity of the different horizons and the possibilities of transference of moisture, the same mineral reserves will satisfy the requirements of the plants to very diverse extents and it seems to us illusory to confer upon these nutrient-reserve levels anything more than an indicative value, which is relative to the pedoclimatic conditions that the plant will meet with. It is reasonable therefore to fix attention much more on the overall nutritional context, than on the determination of precise figures supposedly predictive of reaction or non-reaction to fertilizer dressings.

As we have emphasised already *(Blanchet et al. [2])* a favourable moisture regime, and irrigation in particular, greatly assists inorganic nutrient uptake, through mechanisms that vary with the different ionic species concerned. The higher yields permitted by an adequate rainfall or by irrigation do not, then, necessarily imply an urgent demand for higher nutrient reserves in the soils, provided of course that the needs of the plants are well covered (of nitrogen in particular, of potassium for crops that call for it, and so on).

In situations far from favourable to root development, especially with soils having poor physical properties and in comparatively dry pedoclimates, adequate fertilization can give a better assurance that the needs of the crops will be met, and avoid incidents of malnutrition due for example to temporary flooding, inadequate soil preparation and so on. A variety of observations in the field offers good confirmation of these views.

Lastly, the nature and the physico-chemical properties of soils exert a very marked

Table 3. Effect of mass-flow on the uptake of potassium

Textures	Upper compartment	Comparison made	Difference in uptake (M.F.-diffusion)	Water absorbed g	mg K transported per g of water
Sandy Silt a Sandy Silt	enriched	No. 13–15	83–31 = 52	171	0.30
	poor	No. 14–16	59–13 = 46	283	0.16
Sandy Silt a clay	enriched	No. 17–19	37–27 = 10	59	0.17
	poor	No. 18–20	19– 9 = 10	159	0.06

influence on the movements of ions and of water, especially of potassium for which a lower CEC allows greater mobility. As low CEC figures generally go with the light textures that facilitate water movements, it follows that potassium uptake is much easier in soils of this character.

In the general situation, the root systems, the flow of the liquid phase induced by transpiration, and the movements of ions are intimately linked together to assure the feeding of the plant, and this can be done by a small amount of roots if the rhizosphere is sufficiently stocked with nutrients *(Maertens* [*4*]*)*, or on the contrary by a whole mat of roots, which will not need such a rich medium.

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The Distribution of Mobile and Potential Potassium Reserves in Soil

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Summary

1. The strength of chemical bonds within the minerals and compounds determines the aviability of nutrients, the reserves of nutrients, the degree and velocity of release of elements from their natural sources in soils.
2. According to the classification proposed by Gorbunov the soils potassium compounds in soil may distribute as follow:
a. The reserves of immediate supply: the water soluble potassium compounds and the exchangeable potassium.
b. The short-term reserves of 'mobile' potassium: which includes the potassium containing minerals in the clay fraction.
c. The potencial reserves of 'mobile' potassium: which includes the potassium containing minerals in the coarser fractions of soils.
3. Taking into account the classification of potassium compounds, mentioned above, the typical soils of the Hungarian Lowland where investigated for the different form of potassium and for their mineralogical and micromineralogical composition.
On the basis of the data of macro and micromineralogical and chemical determinations the balances of potassium have been established in the investigated soils.
4. The typical minerals of the clay fractions in the investigated soils are the hydromicas, the typical minerals of soils formed on young alluvial deposits.
The total amounts of potassium containing minerals in the soils and in the clay fraction were estimated taking into account the total K_2O contents in soils and in the clay fractions.
5. The quantities of short-term potassium reserves were in close correlations with the particle-size distribution in each investigated soil.
6. The distribution of potassium reserves is following not only the change in the particle size distribution, but they are influenced by the geological and soil forming factors, too. It means, that the distribution of potassium compounds and different fraction of potassium reserves depends on the mineralogical composition of the clay fraction and on the degree of weathering and hydratation of the potassium containing minerals.

It is well known that the mineralogical and micro-mineralogical composition influences the physical, chemical, and physico-chemical properties of soils. The mineralogical association of parent material and soil, and the degree of the physical and chemical weathering have an effect on the particle-size distribution as well as on the movement and balance of chemical elements in soils.

The strength of the chemical bonds within minerals determines the availability and reserves of nutrients, the degree and velocity of the release of elements from their natural sources in soils.

Likewise the amount and kind of clay minerals may influence the degree and form of the adsorption of nutrients given in fertilizers into the soils.

In a former period of the development of soil science when the doses of applied mineral fertilizers were low, diluted acid solutions were applied for the determination of the 'mobile' nutrient in soils. These solvents may extract not only the water-soluble compounds and exchangeable ions, but they do extract a certain amount of elements from the minerals in the clay fraction as well.

In certain countries, among them in Hungary, the 'soluble part' of nutrients as well as their total amount were determined. The total amounts were evaluated as the reserves or the 'capital' of them. The necessity for the determination of the immediate nutrient supply increased with the increase in the production of mineral fertilizers, and methods were developed with the application of neutral and slightly acidic, buffered solutions.

In the present period, when the applied doses are high and important part of the nutrients given in fertilizers remains in the soils for the enrichment of nutrient reserves, the importance of the study of natural nutrient reserves and the necessity of the investigation of the nutrient movement comes forward. The data related to the mineralogical composition of clay fractions and the results connected with the conditions of secondary mineral formation have given valuable informations for the investigation of nutrient movement and balance. We have to mention here the investigations of *Barshad* [*1*] *Brown* [*3*], *Jackson* [*6*] *Gorbunov* [*4*], *Gradusov* [*5*].

The data for the mineralogical composition of the coarser fractions, published in the papers of *Marshall* [*8*]. *Rode* and *Mjagkova* [*16*], *Parfjonova* [*12*], *Labenec* [*7*] and *Popov* [*13*] make possible to complete the evaluation of the data connected with the natural reserves of nutrient compounds.

Several investigations have been done in relation to the mineralogy and micro-mineralogy of potassium sources in soils. The modern conception of the potassium mineralogy was established by *Bray* and *Turk* [*2*] in 1939, with the conclusion that the secondary minerals of the clay fraction serve as a special type of buffer system in the potassium release and adsorption processes.

In this recent publications *Mortland* [*10*] discusses the dynamic character of the potassium movement in a similar way.

Several methods have been published for the determination of the non-exchangeable potassium reserves. We have to mention here the publications of *Reitemeier* et al. [*15*], *Matson* [*9*], *Németh* [*11*], *Gorbunov* [*4*]. Gorbunov in his latest publications proposes the following classification of potassium compounds:

The reserves of immedaite supply: water-soluble compounds and the exchangeable part of potassium containing minerals.

The short-term reserves of 'mobile' potassium which include the minerals containing potassium in the clay fraction.

The potential reserves of 'mobile' potassium: minerals containing potassium in the coarser fractions.

Taking into account the distribution of potassium compounds, mentioned above, we investigated the different potassium fractions in the typical soils of the Hungarian Lowland. On the basis of the data of macro- and micromineralogical and chemical determinations we tried to establish the balance of potassium in the investigated soils.

The investigated soils are representing the following types:

- Profile No. 504: Meadow chernozem with a sandy loam mechanical composition
- Profile No. 4: Meadow chernozem with a silty-clay mechanical composition
- Profile No. 6: Alluvial meadow soils with a sandy-loam mechanical composition
- Profile No. 1: Meadow solonetz with a silty-clay mechanical composition
- Profile No. 22: Meadow soil with a silty-clay mechanical composition

Table 1. The amounts of water soluble, exchangeable and NH_4 lactate soluble potassium in the typical soils of Hungarian Lowland

Type of soil	Depth of samples	Water soluble	Exchangeable	NH_4-lactate soluble	Immediate supply	CEC
	cm	K_2O mg/100 g				meq l/100 g
Meadow chernozem	0–10	1.9	18.4	14.0	20.3	17.6
	15–25	6.1	25.0	20.0	31.1	18.0
	27–32	6.1	22.6	13.0	28.7	18.7
Meadow soil	7–17	2.0	38.1	43.6	40.1	
	35–45	1.2	40.0	34.5	41.2	
Solonetzic meadow soil	5–17	2.8	47.3	50.6	50.1	20.4
	30–42	2.8	38.1	38.4	40.9	30.0
Deep meadow solonetz	8–16	5.7	33.0	36.6	38.7	36.8
	26–37	5.7	37.2	32.6	42.9	63.0
Meadow solonetz	1– 5	0.9	19.3	16.0	20.2	14.3
	5– 9	1.9	19.3	20.0	21.2	11.9
	15–23	2.3	31.6	27.0	33.9	22.8
	40–50	1.9	36.8	27.0	38.7	17.4
Meadow solonetz	1– 5	2.8	73.0	36.0	75.8	16.3
	9–15	2.4	36.0	23.0	38.4	15.9
	26–32	0.9	36.0	22.0	36.4	21.1
	38–45	0.9	20.2	15.0	21.1	17.4

The total K_2O content in the soil and in the clay fraction was determined. We determined the mineralogical composition of clay fractions by X-ray and thermal-analytical methods. In case of meadow soil, seven fractions with different particle-size were separated from the samples taken from the 'A', 'B' and 'C' horizons and their mineralogical composition was determined by microscopical, X-ray and thermal-gravimetric methods. We determined from the above mentioned and other soils (table 1) the following potassium compounds:

— water-soluble potassium content from saturation extracts
— exchangeable potassium content by ammonium acetate method
— 'soluble' potassium content by ammonium lactate method

The amount of water-soluble potassium compounds was 1—5 mg K_2O/100 g soil. In the samples of some salt affected soils somewhat higher amounts were measured. The amount of the exchangeable potassium was 10—73 mg K_2O/100 g soil. The amounts of the exchangeable potassium have not given any close correlation with the mechanical composition and with the CEC values, but they seemed to be influenced by the mineralogical composition of the clay fraction. The quantities of the NH_4-lactate soluble potassium were close to the values of the exchangeable potassium content and correlated with the values of the immediate supplies.

According to the mineralogical investigations, the typical minerals of the clay fractions are the hydromicas as the typical minerals of soils formed on young-alluvial deposits (tables 2, 3 and 4). Chlorite, feldspars, montmorillonite and the inter-stratified forms of illite-chlorite and illite-montmorillonite were present in smaller amounts.

The total amounts of potassium containing minerals in the soil and in the clay fraction were estimated, taking into account the total K_2O content in the soils and in the clay fractions.

The quantities of short-term potassium reserves were in close correlations with the particle-size distribution in each investigated soil type. Dependance of the short-term

Table 2. The amounts of potassium containing minerals and compounds

Soil type and No	Depth of sampling	Particles <1 u %	The mineralogical composition of the clay fraction	Total amount of K-containing minerals		Total K_2O		
				in soil	in clay fraction	in soil	in clay fraction	
				g/100 g soil		g/100 g soil	g/100 g clay	g/100 g soil
Meadow chernozem No.504	0–10	3.3	I>Cl=Q=Mo>Fsp	26.9	1.29	3.32	4.59	0.124
	15–25	4.5	I>Cl=Q=Mo>Fsp	28.2	1.40	3.89	5.31	1.143
	27–32	3.9	I>Cl=Q=Mo>Fsp	26.9	1.30	4.06	5.01	0.165
Meadow chernozem No.4	5–15	28.2	I>I–Cl=Cl=Q=Fsp	13.1	4.5	2.00	1.00	0.282
	27–33	27.9	I>I–Cl>Cl=Q=Fsp	15.4	5.0	2.10	1.00	0.279
	44–55	23.4	I>I–Cl>Cl=Mo=Q=Fsp	11.1	4.7	1.70	1.10	0.258
	72–79	22.8	I>I–Cl=Fsp>Cl=Mo=Q	10.9	4.5	1.70	1.10	0.240
	90–100	21.7	I>I–Cl=Fsp>Cl=Mo=Q	10.4	5.0	1.80	1.20	0.260
Alluvial Meadow soil No.6	5–15	17.2	Q>I>Cl=Fsp	13.1	5.7	1.20	2.30	0.396
	20–28	16.1	Q=I>Cl=Fsp	12.3	3.8	1.20	2.20	0.255
	34–45	5.4	Q=I>Cl=Fsp	14.4	2.1	1.45	2.30	0.119
	60-68	2.7	Q>I>Cl=I–Cl Fsp	15.0	0.98	1.30	2.40	0.089
	90-100	3.8	Q>I>Cl=I–Cl Fsp	14.3	1.26	1.25	2.25	0.085
Meadow soil No.22	7–17	51.03	I>Q>Cl=Fsp>Mo	25.9	9.1	2.20	1.40	0.720
	35–45	49.90	I>Q>Cl=Fsp>Mo	26.2	18.1	2.00	1.27	0.630
	92–108	41.94	I>Q>Fsp>Cl=Mo	16.2	4.9	1.40	1.00	0.419
Maedow Solonetz No. 1	0–9	8.4	I=Q>Cl=Fsp=I–Cl	21.8	1.24	2.25	0.95	0.080
	15–20	29.1	I>Q>Cl=Fsp=Mo=I–Cl=I–Mo	26.2	5.6	2.25	1.00	0.290
	26–32	32.7	I>Mo>Q>Cl=Fsp=I–Cl=I–Mo	26.1	6.3	2.45	1.01	0.330
	44–55	37.4	I>Mo>Q>Cl=Fsp=I–Cl=I–Mo	24.8	6.2	2.30	1.05	0.394
	60–68	5.7	I>Mo=Q>Cl=Fsp=I–Cl=I–Mo	22.3	1.4	2.35	1.20	0.069

Table 3. Mineralogical composition of the clay fraction in the investigated soils

Soil type and No.	Depth of sampling	Micas and hydromicas	Chlorite	Interstratified hydromicas chlorite	Montmorillonite	Feldspars	Quartz
Meadow chernozem No.504	0–10	++++	++	–	–+	+	++
	15–25	+++	++	–	+	+	++
	27–32	+++	+	–	++	+	++
Meadow chernozem No.4	5–15	+++	+	+	–	+	++
	27–33	+++	+	++	–	+	++
	44–55	+++	+	++	+	+	++
	72–79	+++	+	++	+	++	++
	90–100	+++	+	++	+	++	++

+++++ = >60%, ++++ = 40–60%, +++ = 20–40%, ++ = 10–20%, + = 5–10%.

Table 4. Mineralogical composition of the clay fraction in the investigated soils

Soil type and No.	Depth of sampling	Micas and hydromicas	Chlorite	Interstratified hydromicas chlorite	Montmorillonite	Feldspars	Quartz
Alluvial meadow soil No.6	5–15	+ + +	+	–	–	+	+ + + +
	20–28	+ + +	+	–	–	+	+ + +
	34–45	+ + +	+	–	–	+	+ + +
	60–68	+ + +	+	–	–	+	+ + + +
	90–100	+ + +	+	–	–	+	+ + + +
Meadow soil No.22	7–17	+ + + +	+	–	+ + +	+	+ +
	35–45	+ + +	+	–	+ + +	+	+ +
	58–72	+ + +	+ +	–	+ + +	+	+ +
	92–108	+ + +	+ +	–	+ + +	+	+ +
Meadow solonetz	0–9	+ +	+	+	–	+	+ +
	15–20	+ + +	+	+	+	+	+ +
	26–32	+ + +	+	+	+ +	+	+ +
	44–55	+ + +	+	+	+ +	+	+ +
	60–68	+ + +	+	+	+ +	+	+ +

+ + + + + = >60%, + + + + = 40–60%, + + + = 20–40%, + + = 10–20%, + = 5–10%.

potassium reserves on the mechanical composition is highly observable in the alluvial meadow soil. The total amount of potassium in this soil and in the clay fraction did not change in the whole profile. The amount of clay fraction decreased from the top to the 'C' horizon of the soil, from 17.2% to 3%, and the short-term potassium reserves were reduced parallel with the decrease in the amount of clay particles. Comparing the short-term potassium reserves in different soils it can be stated that the correlation with the amount of clay particles is not so close and it can be influenced by the mineralogical and micro-mineralogical composition of the samples. The total amount of the K containing minerals in the alluvial meadow soil was 12—13%, and their part in the clay fraction changed with the change in the amount of clay fractions.

In the meadow chernozem soil having a coarse texture the total potassium quantities in the soil and in the clay fraction were twice as large as in the alluvial meadow soil and the total amount of potassium containing minerals was 27—28% in the soil. The amount of potassium containing minerals in the clay fraction was small as well as that of the short-term potassium reserve, in accordance with the coarse texture.

Comparing the values of the short-term potassium reserves in the alluvial meadow soil and meadow chernozem soil it can be stated that the amounts of short-term potassium reserves are higher in the meadow chernozem soil. They reflect the different mineralogical composition of the two soils.

The other investigated meadow chernozem soil has a heavier texture and the amount of clay fraction varies between 20% and 28%, showing a slow decrease downward in the soil profile. The dominant clay minerals were the hydromicas. Besides these, the clay fraction contained montmorillonite, the inter-stratified form of illite-chlorite and illite-montmorillonite as well as chlorite and feldspars. The amount of minerals containing potassium in the different soil horizons was between 10% and 16%, and 30—40% of their total amount was in the clay fraction. Their amount and distribution were the same as those in the upper layer of the alluvial meadow soil. The total K_2O content of the soil samples was 1.7—2.1%, and that of the colloid fraction was 1.0—1.2%. The low potassium content of the clay fraction can be due to the intensive hydration of the hydromicas. The degree of hydration has to be higher in the meadow chernozem than in the alluvial meadow soil. In spite of its heavier texture the short-term potassium reserves were present in smaller amounts in the meadow chernozem soil than in the alluvial meadow soil.

Among the investigated soils the meadow soil has the heavier texture. The amount of clay fraction is as high as 40—50%. The amount of the total potassium containing minerals is 25—26%. 35—70% of their total amount is in the clay fraction. The total K_2O content of the soil samples is 2.2—1.5%, that of the clay fraction is 1.4—1.0%.

Seven fractions were separated from these samples, according to their particle-size distribution, and their total potassium content and mineralogical composition were determined. In case of the coarser fraction the analyses were done by microscopical method (table 5). In case of the clay fraction and coarse fractions the analyses were done by X-ray and thermo-gravimetric methods (tables 6 and 7). According to the data of the mineralogical investigations it can be stated that the feldspars were distributed uniformly in the fractions with different particle-size. The quantities of micas and hydromicas decreased with the increase in the particle-size. The clay fraction contained montmorillonite in each soil horizon.

We did not determine separately the amounts of micas and hydromicas during the X-ray analyses. The data of chemical analyses indicate the degree of hydration and weathering of potassium containing minerals. The low potassium content of the clay fraction indicates that, similarly to the profile No. 4, the degree of hydration of micas is high. We can compare the amount of micas and hydromicas in the clay fractions and in the fraction with 1—5 μ diameter to the total potassium content of the particles having the same ranges of sizes. The analytical data show that the highest potassium content was measured in the particles within the size of 1—5 μ and the highest amount of micas and hydromicas was determined in the clay fraction. It means that the degree of hydration of micas was high in the clay particles and low in the particles within 1—5 μ.

The amount of short-therm potassium reserves in this soil was not large in comparison with its heavy mechanical composition. The supply of short-therm potassium reserves from the potential ones was slow.

In the solonetz soil the amount of potassium containing minerals was 22—26%. The total

Table 5. Microscopic examination of the coarser fractions in the meadow soil

The genetic horizon of soil and particle siz [mm]		Quartz	Feldspars	Muscovite	Pyroxene + amphibole	Other minerals*
A	0.1 <	+ + + + +	+	+ +	+	+
	0.1 -0.05	+ + + + +	+	+ +	+	+
	0.05-0.02	+ + + + +	+	+	+	+
B	0.1 <	+ + + + +	+	+ +	+	+
	0.1 -0.05	+ + + + +	+	+ +	+	+
	0.05-0.02	+ + + + +	+	+	+	+
C	0.1 <	+ + + + +	+ +	+ +	+	+
	0.1 -0.05	+ + + + +	+ +	+ +	+	+
	0.05-0.02	+ + + + +	+ +	+ +	+	+

* Mostly garnets and opaque minerals.

+ + + + + = > 60%, + + + + = 40-60%, + + + = 20-40%, + + = 10-20%, + = 5-10%.

Table 6. Mineralogical composition of the different particle size fractions in the meadow soil

Genetic horizon and particle size [mm]	Chlorite	Micas + hydromicas	Quartz	Feldspars	Montmorillonite	Carbonates
A >0.001	+ +	+ + + +	+ + +	+ +	+	−
0.001–0.005	+	+ +	+ + + + +	+ +	−	−
0.005–0.01	+	+ +	+ + + + +	+ +	−	+
0.01 –0.05	+	+	+ + + + +	+ +	−	+
0.05 –0.1	+	+	+ + + + +	+ +	−	+
0.10 –0.2	+	+	+ + + + +	+ +	−	+
0.2	+	+	+ + + + +	+ +	−	+
B >0.001	+ +	+ + + +	+ + +	+ +	+	−
0.001–0.005	+	+ +	+ + + + +	+ +	+	−
0.005–0.01	+	+	+ + + + +	+ +	−	−
0.01 –0.05	+	+	+ + + + +	+ +	−	+
0.05 –0.1	+	+	+ + + + +	+ +	−	+
0.10 –0.2	+	+	+ + + + +	+ +	−	+
0.2	+	+	+ + + + +	+ +	−	+
C >0.001	+	+ + + +	+ + +	+ +	+	−
0.001–0.005	+	+ + +	+ + + +	+ +	−	−
0.005–0.01	+	+ +	+ + + + +	+ +	−	−
0.01 –0.05	+	+	+ + + + +	+ +	−	+
0.05 –0.1	+	+	+ + + + +	+ +	−	+
0.10 –0.2	+	+	+ + + + +	+ +	−	+
0.2	+	+	+ + + + +	+ +	−	+

+ + + + + = >60%, + + + + = 40–60%, + + + = 20–40%, + + = 10–20%, + = 5–10%.

Table 7. Ignition losses in the different particle size fractions of meadow soil

Genetic horizon particle sizes [mm]	Weight loss %			
	20–300 °C	300–700 °C	700–1000 °C	Total
A >0.001	7.00	5.75	0.50	12.25
0.001–0.005	6.50	4.25	0.75	11.50
0.005–0.01	3.50	1.50	0.75	5.75
0.01 –0.05	1.50	1.50	0.75	3.75
0.05 –0.1	1.00	1.00	0.75	2.75
0.1 –0.2	0.70	1.00	0.50	2.20
0.2 –2.0	0.50	1.00	0.50	2.00
B >0.001	8.00	6.00	0.80	14.80
0.001–0.005	6.00	5.50	1.00	12.50
0.005–0.01	2.50	3.00	1.00	6.50
0.01 –0.05	1.25	1.50	0.75	3.50
0.05 –0.1	0.75	1.25	0.50	2.50
0.1 –0.2	0.50	1.50	0.50	2.50
0.2 –2.0	0.50	1.30	0.50	2.30
C >0.001	8.00	5.80	0.50	14.30
0.001–0.005	4.75	5.75	0.75	11.25
0.005–0.01	2.25	4.00	0.75	7.00
0.01 –0.05	1.00	2.75	1.00	4.75
0.05 –0.1	0.50	2.50	0.75	3.75
0.1 –0.2	0.50	2.00	0.5	3.00
0.2 –2.0	1.00	1.50	0.50	3.00

K_2O content was 2.25–2.45% in the soil and 0.95–1.20% in the clay fraction. The amount of the potassium containing minerals and the total amount of K_2O gave maximum values in the 'B' horizon of the soil. The amount of potassium in the clay fraction increased from the top to the 'C' horizon. The 'A' horizon of the solonetz soil is always strongly weathered and leached, which reflects in the small quantity of clay particles as well as in the potassium content of the clay fraction. In the 'B' horizon the mica minerals have been strongly hydrated as a result of the slow water movement (table 8).

Table 8. Data of the total elemental analysis of the different particle size fractions in the "B" horizon of meadow soil

Particle sizes	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O
mm	%						
>0.001	53.99	9.89	14.71	2.45	2.39	1.27	1.17
0.001–0.005	68.05	8.95	10.86	3.89	1.23	2.48	2.60
0.005–0.01	80.01	4.33	6.63	4.26	0.64	1.21	3.10
0.01 –0.05	81.60	4.81	5.60	2.74	0.78	0.95	1.82
0.05 –0.1	79.08	5.00	6.51	6.03	0.69	0.77	1.84
0.1 –0.2	85.22	4.73	6.62	2.44	0.73	0.44	1.90

The data indicate that the distribution of potassium reserves are following not only the change in the particle-size distribution even in soils with a domination of hydromicas in the clay fraction, but they are influenced by the geological and soil forming factors, too. It means that the distribution of potassium compounds and different fractions of potassium reserves depends on the mineralogical composition of the clay fraction and on the degree of weathering and hydration of the potassium containing minerals.

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3rd Working Session:
Some Remarks on the Discussion on Ion Transport System in the Soil

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It was evident from Dr. *Nye*'s paper (presented by Dr. *Tinker*) that diffusion has an essential influence on the transport of nutrients in the soil and diffusion is influenced by a number of factors. Under field conditions, moisture is one such important factor, as M. *Blanchet* showed.

Using the split root technique plants were grown with one part of the root system in nutrient solution lacking K^+ and the other in soil, so that K^+ had to be taken up from the soil. The water tension in the soil was controlled and maintained at four levels (pF 1.6, 2.0, 2.4 and 2.7).

Independent of the K supply of the soils, K uptake was best at optimal soil moisture of about pF 2.0, or field capacity. When pF was increased to 2.4 or 2.7 (which is in accordance with the decrease in water content) K uptake or K availability decreased by about 50%. However, with improved K supply K uptake rose, and even at pF 2.7 it increased significantly when exchangeable K content was increased from 31 to 46 mg/100 g soil. This clearly shows that poorer diffusion conditions prevailing at high water tension can be partially balanced by higher exchangeable K or, more precisely, higher K concentration in the soil solution. It should be stressed that a water tension of pF 2.7 is often found in the field without leading to water deficiency of the plant although nutrient availability is appreciably affected.

Report on the 3rd Working Session: Ion Transport System in the Soil

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In the last session dealing with *Ion Transport Systems in the Soil*, 5 papers were presented which together covered the whole problem.

Professor *Tinker*, who kindly and capably took the place of Dr. *Nye*, who was unable to come due to illness, discussed the transport of ions in the immediate vicinity of the root. For potassium, this transport is mainly a diffusion process in the liquid phase. It appears that the contribution of the double layer is of little or no importance. For this reason, a more or less simple model of the movement of ions to plant roots could be constructed and laid down in a formula. This model made it possible to account satisfactorily for the experimental results obtained. The fact that the ionic concentration in the root periphery can now be estimated, opens the way to further research. It will be possible to obtain a more reliable idea about the meaning of the ionic concentration in the soil solution. Furthermore, the model will be useful for an evaluation of hypotheses on the ion uptake which up till now were always based on the concentration of ion in the solution.

In the paper presented by Dr. *Frissel*, a computer model for the vertical transport in soil was introduced. In this transport, mass flow plays a much more important role than diffusion. For practical purposes it is important to construct a main model from a number of submodels (flux transport, exchange equilibria, release, fixation, etc.) which can be manipulated separately or jointly in the main model. In the paper, emphasis was laid on the lack of equilibrium – and rate constants for situations as prevailing in soils (low salt concentrations). This lack hampers to elaborate of simulation models. The results of simulations of two theoretical cases were presented as examples.

Both presentations started with a theoretical approach to the problem which subsequently was tested experimentally as much as possible. The latter three papers started with a presentation of experimental data, for which subsequently an explanation was given.

Dr. *Németh* dealt with electro ultra filtration as an analytical tool for studying the strength of binding of the K-ion to minerals and soils. The technique appears to supply much scientific information. A number of binding types – especially those pertaining to the K-ion – are in agreement with expectations. The binding of K to illite and the influence of the Al-ion were discussed in more detail. The results obtained form a valuable contribution to our knowledge on rate processes, both concerning the supply to the solution and the desorption of the K-ion. The information available is not yet sufficient to evaluate the possibilities of the method as a routine method for soil testing.

In his paper, Dr. *Blanchet* stressed the importance of moisture content, compaction and root development for ion uptake. The results of a pot experiment clearly showed the influence of these factors. For the uptake of NO_3 the water flux, and for the uptake of K both flux and diffusion could be identified as factors of importance. This presentation showed very clearly that single values are never sufficient to describe soil fertility with respect to a certain ion. Especially the physical condition of a soil influences the availability of nutritive ions. In the future, simulation models as discussed by Dr. *Frissel*, might supply useful information on this matter.

In the final presentation, Mrs. Dr. *Darab* showed once more how a proper combination of classical methods may characterize a soil. Various extraction methods, in combinations with X-ray analysis applied to minerals of various particle sizes, and to different soil types, appeared to supply useful informations on various aspects of soil fertility. Special attention was paid to the short-time reserve and the potential reserve, or, in other words, to the rate of release of the potassium ion.

This last presentation formed another variation to the main theme which was introduced in the first session and could be heard again at several other occasions. This main theme, namely the release of potassium from soil reserves, was well known qualitatively. The quantitative aspects have been studied before, but are not yet completely understood. It is therefore understandable that in this colloquium this release is sometimes looked upon as an undesirable complication, and at other occasions is introduced as possible object of study.

This release of potassium deserves our full attention in the light of the fact that our knowledge on the behaviour of minerally fixed potassium is incomplete in comparison with our knowledge on other forms of potassium occurring in soils.

Excursions during the Landshut Colloquium

One of the main reasons for the choice of Landshut as the Colloquium place for "Potassium in Soil" was – under scientific considerations – the widespread existence of K-fixing soils in this area. By field and pot experiments related problems were studied since a number of years esp. by the University of Munich nearby, and therefore theoretical and practical data were available for display and discussion during the excursions organized during the Colloquium.

Although these data are not reproduced in this volume, they have been made available to the participants of the Colloquium and may be obtained from International Potash Institute, P.O. Box, CH-3000 Berne 14/Switzerland.

Concluding Report:
Implications and Conclusions of Recent Findings on the K Nutrition of Plants

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Plants were supplied for millions of years by soil K released by weathering from various soil minerals. But in those early times there was no major removal of K from the soil, as the K of the plants was largely recycled. Even in early agriculture there was little nutrient withdrawal from the field. The situation changes when moving from extensive to intensive agriculture, in which, depending on the crop, large amounts of K can be exported from the soil. Therefore, under modern conditions the question arises whether, the soil K sources will flow forever or whether the K supply from the K-bearing minerals will some day be exhausted. The important K-bearing minerals are feldspars, micas and mica-derived clay minerals. As has become evident from various papers presented at this colloquium these K sources, are in principle not inexhaustible, although due to the quantity of K-bearing minerals and their degree of weathering in a given soil, the K release may last for rather a long time (years, decades), thus supplying K rates high enough to prevent K deficiency symptoms of the plants.

The weathering process of feldspars differs from that of micas. In feldspar particles especially the peripheral zones are depleted of K and with advanced weathering a kind of a Si—Al-oxide coating around the feldspar particle is formed, restraining the further weathering of the particle and leading to a decrease in the release rates of K. The coating itself has to some extent K-selective properties which affect the equilibrium conditions between the adsorbed K and the free K of the soil solution. Weathering of micas involves a release of interlayer K, resulting in expansion of the interlayers and leading to the formation of secondary clay minerals of the illite and vermiculite-smectite types. The more the interlayers of these expanded minerals are depleted of K, the more selective binding sites are created which affect the level of equilibrium between adsorbed K and free K. Furthermore, with continuous depletion of K more and more sites for K fixation will be produced so that the K fixation capacity increases. In this way, the K supply to the plants is not sufficient, and in extreme cases drastic yield depressions may occur as was demonstrated by field experiments seen during this colloquium. For this reason K applications, even on soils containing K-bearing minerals, should be sufficiently high for preventing major K depletion of the minerals resulting in K fixation.

With respect to crop performance, the K status of a soil cannot be expressed in terms of the total amount of K that can be released by a soil but rather by the rate of release and the level of K concentration maintained in the soil solution. Both K release rate and K concentration of the soil solution must be high enough to support good plant growth.

Under modern intensive cropping systems high yields per unit area are required as this is a prerequisite for reasonable profits. High yields demand high nutrient intensities in the soil. The term 'nutrient intensity' is defined as the amount of nutrients being transported towards the plant roots per unit time per unit of plant root material, a definition which differs from the general definition of 'nutrient intensity'. As outlined by various lecturers, this K intensity depends largely on the K concentration of the soil solution which is affected by various factors. It is governed mainly by the kind of clay minerals present in the soil and by the K saturation of the clay minerals. The more K selective binding sites are covered by K, the higher is the equilibrium concentration of K in the soil solution.

Provided that the transport of K from the various soil regions to the plant root be the main process of supplying the plant with K, the K concentration of the soil solution represents the most important parameter of K availability, as this transport takes place in the aqueous phase of the soil and its rate depends on the K concentration of the solution. There is no doubt that the K concentrations measured in practice are average values from which the actual concentrations at different locations in the soil may deviate appreciably, due to plant uptake and heterogeneous distribution of clay particles. For practical purposes the equilibrium K concentration in a water saturated soil is measured which gives a first information about the K intensity of the soil.

The question as to what is to be considered as optimum K intensity or, more precisely, as optimum K concentration in the soil solution, is difficult to answer. But the higher the potential growth rate of a crop, the more K per unit time and area is needed. Hence, plants well supplied with other nutrients and growing under favorable climatic conditions need higher K intensities than plants with poor growth rates. This relationship is demonstrated in Figure 1. Plants with a low yield potential reach their maximum growth rate at a lower K intensity than plants with a higher yield potential. Under extensive cropping conditions where other factors, such as insufficient water or N supply, limit the growth rate, rather low K intensities – as maintained by the release of K from soil minerals – may be sufficient. These conditions change as soon as the agricultural system shifts to more intensive cropping.

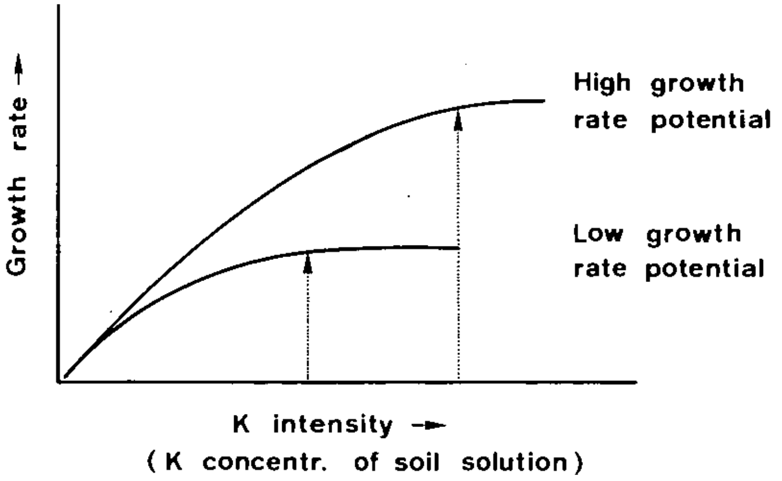

Figure 1. Growth rate vs. K intensity at a high and at a low growth rate potential.

The various efforts to define the K status in terms of thermodynamics, a problem discussed during this colloquium, may lead to the conception that the plant roots have to expend energy in order to withdraw these strongly adsorbed cations from the clay minerals, and also the idea that cations may hop from mineral binding sites to binding sites of the plant root (contact exchange) was mentioned. In my opinion this view is erroneous. The cell wall, even of a root hair, is a layer about 5000 A thick which separates the K adsorbed to clay minerals from the plasmamembrane (plasmalemma), where the active ion uptake occurs. The cation exchange capacity of the root cell wall material – expressed on a fresh weight basis – is rather low and in most cases largely saturated by Ca^{++}. A migration of K through the cell wall by hopping from one binding site to another is therefore most unlikely. It rather seems reasonable to assume that each ion has to pass the solution phase before it is actively taken up by the cells of the plant root.

As a consequence, the well-known fact that plants can use K of the 'non-exchangeable K fraction' cannot be explained by some mysterious force of the plant roots. As was outlined by one of the lecturers and in the discussion, there is, however, evidence that near the root surface rather low K concentrations may occur due to high K uptake rates of the plant roots. If this 'zero concentration' is close to K being selectively adsorbed to clay minerals, it must affect in some way the release or the exchange of the selectively bound K. It is assumed that by this process K of the so called 'non-exchangeable fraction' of the soil can also be exploited. The exploitation is the higher, the wider the extension of the root system. For this reason particularly grassland, possessing a dense and permanent root system, is highly efficient in utilizing the 'non-exchangeable K' of a soil.

Conclusive Remarks

Prof. Dr. D. SCHROEDER, Chairman of the Colloquium

Ladies and Gentlemen!

At the end of this fourth working session I should like to make some concluding observations. In my opinion, the main aim of our colloquium, as outlined in the introductory addresses has been achieved. We have received much information on the present state of knowledge concerning fundamental problems of potassium in soil and, I think, new lines for future research were suggested.

The chairmen of the three working sessions have summarized the results of their individual sessions and Prof. *Mengel* has given a résumé of recent findings with regard to the potassium nutrition of plants. This was complemented by our general discussion. I do not think it necessary to repeat these results by giving a summary of the summaries, but I would like to stress three points concerning the topics of the three sessions:

1. Progress in the field of *Potassium in Soil Minerals* is primarily due to improvements in technical facilities. We can now use the great possibilities of the scanning electron microscope, of the microprobe and of the infrared spectrometer to obtain deeper insight into the morphology and structure of the potassium containing minerals.
2. In the field of *Potassium in the Exchange System* it is my opinion that the thermodynamic approach has helped to overcome the stagnation of the past two decades.
3. In the field of *Potassium in the Transport System* the simulation of transport processes by models and their numerical treatment by computer opens up new possibilities.

Progress in basic knowledge is a prerequisite for determining the implications and consequences of fundamental research for applied purposes and for solving practical problems. This aspect will be covered at the next main Congress in Budapest in 1974.

Another purpose – not only of this Colloquium, but also of all the other activities of IPI – is to organize meetings of scientists from different countries, working with various methods in special fields, and with different aims, but all concerned in some way with potassium.

I think, this target was reached too. We have heard contributions to our general theme from quite different points of view: namely mineralogical, chemical, physicochemical, plant-physiological, pedological and also agricultural. In my opinion, this Colloquium – and the last in Sweden also – represents a very good example for international and interdisciplinary cooperation in scientific research, demonstrated with potassium as example.

In closing, I should like to express my greatest gratitude to IPI and all its members for organizing this Colloquium, especially the two directors, Mr. *Künzli* and Dr. *von Peter;* further I should like to express my thanks to our colleagues in Landshut-Schönbrunn and in Weihenstephan, who helped us in such an excellent manner, and finally my thanks to the chairmen of the three sessions for their coordination and cooperation, to the main speakers for their outstanding lectures, to the colleagues, who presented their interesting papers and to all who contributed to the discussions.

Discours de clôture

P. CHAUDET, Ancien Président de la Confédération helvétique, Président de l'Institut International de la Potasse

Les circonstances m'obligent à prendre maintenant congé de vous. Vous me permettrez de consacrer mon bref propos au terme de ce colloque,
– à des remerciements;
– à des remarques de la Direction technique de l'Institut sur vos travaux;
– à des réflexions personnelles sur le sens et la portée de la mission qui nous est dévolue.

Des remerciements, je les dois tout particulièrement à M. le *Doyen* de la Faculté agronomique de l'Université de Munich et à M. le Prof. *Schröder*, pour la préparation et la présidence du Colloque. Nous avons bénéficié de la compétence et de l'expérience de M. *Schröder* dans les conditions où il était le mieux placé pour conduire les débats et en dégager les enseignements nécessaires.

Merci également à MM. les Professeurs *Bach* et *Schuffelen*, qui ont préparé avec le concours de MM. *Mengel* et *de Tarragon* un programme dont vous avez pu apprécier la qualité dans l'opportunité.

Merci encore à MM. les Présidents des séances, M. le Prof. *Bach*, M. le Directeur *Walsh*, M. le Prof. *Schuffelen*. Je ne veux pas citer ici nommément MM. les *auteurs* des rapports et des communications qui ont introduit les discussions. Nous sommes reconnaissants à chacun de la part qu'il a prise à la réussite du Colloque.

Je n'aurais garde d'oublier dans ce message de gratitude nos Directeurs, MM. *Künzli* et *von Peter*, qui sont à la fois des organisateurs parfaits et des hommes bien conscients des problèmes auxquels l'Institut doit faire face. MM. *von Peter* et *Künzli* accomplissent au surplus leur travail avec une amabilité que vient parfaire l'excellente collaboration du personnel de l'Institut et la grâce souriante des secrétaires Mmes *Rohrbach* et *Mohn*.

Enfin, je renouvelle à M. le *Ministre de l'Agriculture* de Bavière, à M. l'*Oberbürgermeister* de Landshut, à M. le *Conseiller ministériel*, à MM. les *Directeurs* des Etablissements qui nous ont accordé leur hospitalité, à MM. les Professeurs *Rumpler*, *Schmidt*, *Amberger* et *Schwertmann*, à toutes les personnalités à qui nous devons une contribution d'accueil, de travail ou de présence, l'assurance d'un souvenir qui sera pour chacun d'eux l'expression la meilleure de nos sentiments de reconnaissance.

Le Directeur technique de l'Institut m'a remis à votre intention les deux remarques suivantes:

1. Seit dem letzten bodenkundlichen Kolloquium von 1954 in Zürich sind wesentliche neue Aspekte in der Pflanzenernährung gewonnen worden. Sie erlauben es heute der Landwirtschaft, die Nährstoffversorgung der Pflanzen viel gezielter vorzunehmen, als dies früher der Fall war.
2. Besonders auffallend war bei diesem Kolloquium, dass die Wissenschaft heute über ausserordentlich vergrösserte technische Möglichkeiten verfügt und viele der vorgetragenen Ergebnisse erst ermöglichten, wie Elektronenmikroskopie und Photographie, Elektronenrechner und mathematische Modelle usw.

Les travaux du Colloque ont donc démontré que vastes et inépuisables sont encore les champs de la recherche où doivent porter nos investigations.

Dans un certain nombre de pays, une tendance se manifeste au resserrement des crédits accordés aux universités ou aux instituts spécialisés en matière de science agronomique. Ces restrictions interviennent au moment où les responsables des hautes écoles éprouvent le besoin d'étendre le cercle de leurs activités. Ils y sont entraînés par l'interdépendance des facteurs qui jouent leur rôle dans les secteurs d'études. En effet, le simple constat d'un phénomène donné ouvre des perspectives sur des aspects nouveaux confirmés par des travaux effectués en d'autres cas, alors que certains résultats pouvaient paraître définitivement acquis. Si les possibilités budgétaires ne permettent pas de s'engager sur des chemins insuffisamment explorés jusqu'ici, à d'autant plus forte raison les échanges d'un colloque sont-ils nécessaires pour assurer la coordination des efforts et leur complémentarité sur des objets où des apports réciproques conduisent au but que chacun des interlocuteurs ressent la nécessité d'atteindre.

Une deuxième raison vient justifier le développement des travaux de l'Institut. C'est l'obligation de reprendre périodiquement l'étude de thèmes qui ont figuré déjà à des programmes de colloques ou de congrès précédents. Le temps qui passe impose impérieusement une remise en question sans cesse répétée de conclusions tirées à un degré de la connaissance et de l'expérience qui s'avère rapidement insuffisant. Le retour sur des disciplines abordées déjà en une première étape administre la preuve qu'en aucun domaine de la recherche on ne doit admettre que le dossier pourrait être un jour fermé. «Toujours en mouvement dans la continuité, toujours avancer» fut la consigne d'un homme d'Etat de mon pays qui contribua fortement au siècle dernier à forger les institutions grâce auxquelles nous avons connu la stabilité d'une vie politique, économique et sociale propice à l'expansion. On peut rapporter cette consigne aux hommes de science qui savent à quel point l'avancement de la recherche les place devant des espaces inexplorés, où ce qu'on sait permet d'entrevoir l'étendue de ce qu'on ignore.

Une troisième raison d'agir dans le domaine agronomique est celle de la situation dans laquelle nous serons placés dès lors que nous pousserons sur place l'étude des problèmes qui se posent aux pays tropicaux. Un colloque tel que celui d'Abidjan soulèvera sans nul doute des difficultés d'organisation, compte tenu du contexte dans lequel nous serons placés, mais ces difficultés résideront aussi dans la manière de reprendre les problèmes en concentrant l'effort sur les points essentiels découlant des exigences mêmes des productions à promouvoir en première urgence. C'est dans une optique quelque peu différente de celle de l'Europe qu'il conviendra d'envisager les travaux et d'opérer — si vous me permettez cette expression — une sorte de raccordement entre le niveau de nos habitudes et celui d'un milieu où le potentiel humain à disposition est insuffisant — en nombre tout au moins — pour tirer le parti voulu des résultats de nos études.

En me plaçant dans la perspective de cette étape déjà proche, je me réjouis de penser que le chemin que nous parcourons nous appelle à de nouveaux engagements. L'intérêt que vous portez à votre tâche est moins stimulé par ce que vous avez réalisé jusqu'ici que par ce qui vous attend dans une carrière dont le sens profond est de servir une cause qui est celle du dépassement de soi-même.

Je vous souhaite un bon retour dans vos pays respectifs et la satisfaction de retrouver vos activités avec un sentiment accru des nécessités auxquelles elles répondent dans une ambition et une volonté de progrès.

Le Colloque de Landshut est terminé. Mesdames et Messieurs, je vous remercie.

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Potassium and the Quality of Agricultural Products

Contents

Potassium and the quality of sugar beet

M. Simon, N. Roussel, R. Van Stallen	Le potassium dans la fumure de la betterave à sucre
C. Winner	Düngung, Überdüngung und Qualität der Zuckerrübe
P.M. McDonnell, P.A. Gallagher, P. Kearney, P. Carroll	Fertilizer use and sugar beet quality in Ireland
S. Trocmé, G. Barbier	Influence du «vieux» et du «jeune» potassium sur la teneur en sucre des betteraves
A.P. Draycott, G.W. Cooke	The effects of potassium fertilizers on quality of sugar beet

Potassium and the quality of ornamentals

F. Penningsfeld	Mineralische Ernährung und Qualität der Zierpflanzen unter besonderer Berücksichtigung des Kaliums
C. Van Assche	Influence du sol et de ses éléments nutritifs sur la résistance et la sensibilité des plantes aux maladies
J.C.R. Seager	The influence of potassium on quality and production of carnations
Denise Blanc	Influence du potassium sur la qualité de l'œillet «Sim»
G. Puccini	La fumure dans les cultures de fleurs en Italie
R. Arnold Bik	A. Influence of substrate and nitrogen on quality of azaleas B. Quality of potted chrysanthemums in relation to their nitrogen and phosphorus contents when fertilized with certain slow release fertilizers

Potassium and the quality of vegetables

J.P.N.L. Roorda van Eysinga	Mineral fertilization, yield and quality of vegetables
M. Lavalleye, H.M. Steppe	Effects of potash on pea growth and quality
W. Plumier	La chicorée de Bruxelles – Incidence de la fumure minérale sur la qualité du légume
P.A. Gallagher	The effect of potassium on yield and quality of carrots
A. Malquori	La fumure minérale des artichauts en Italie

K. Ehrendorfer	Die Abhängigkeit des Gesamtoxalsäuregehaltes von den Gehalten der Mineralstoffe N, P, K, Na, Ca und Mg in Spinatblättern (*Spinacea oleracea* L.)
J. Cornejo Aizperrutia	La producción de cebolla y el abonado de este cultivo en España
E. Bottini	La fumure minérale du poivron
G. W. Winsor	Potassium and the quality of glasshouse crops
M. Woods	The effects of some nutritional factors on fruit quality in tomatoes
C. Y. Chow	Studies of potassium effect on the quality of fruit crops in Taiwan

Survey of the quality problems in relation with potassium

I. Arnon	Quality criteria of agricultural produce and the influence of mineral fertilizers on quality
A. Kursanov, E. Vyskrebentzeva	Le rôle du potassium dans le métabolisme du végétal et la biosynthèse des composés déterminant la qualité des produits agricoles
A. Vessereau	Méthodologie des tests de qualité
A. Amberger	Mineraldüngung als Instrument zur Erzeugung qualitativ hochwertiger pflanzlicher Produkte
D. Lachover, I. Arnon	Observations sur la liaison entre la carence aiguë en potassium et la qualité inférieure de certains produits agricoles de grande culture
M. R. Teel	Nitrogen-potassium relationships and their influence on some biochemical intermediates and quality of crude protein in forages

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A. Reinberg	Potassium et santé humaine
J. W. Couston	Importance of mineral fertilizer for food and human health in developing countries
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Forest Fertilization

Contents

General subjects

N.A. Osara	Trends in wood production and consumption, and the role of forest fertilization
P. Riihinen	The importance of the forest and wood for the Finnish economy
W. Wittich	Überblick über Grundlagen und Aussichten der forstlichen Düngung

K. Salonen	Evolution of forest fertilization in Finland
S. Hagner	The evolution of forest fertilization in Sweden
O. Jerven	A brief summary on the evolution of forest fertilization in Norway

Growth factors and assessment of fertilizer needs of forest trees

C.P. van Goor	Kriterien zur Feststellung des Düngungsbedürfnisses in der Forstwirtschaft
Th. Keller	The influence of fertilization on gaseous exchange of forest tree species
R. Themlitz	Aussagewert von Boden- und Nadelanalysen
F. Franz	Düngungsversuche und ihre ertragskundliche Interpretation
P.J. O'Hare	A. Leader growth and foliar composition in Sitka spruce (*Picea sitchensis* Carr.) in relation to fertilizer application on blanket peat
P.J. O'Hare	B. The leaching of nutrients by rain-water from forest trees—a preliminary study

Fertilizing young trees and methods of applying fertilizers

T. Ingestad	Nutrient needs of seedlings and young trees
Miss *B. Benzian*	Manuring young conifers: Experiments in some English nurseries
Miss *B. Benzian*	Test on three nitrogen fertilizers—'Nitrochalk', formalized casein and isobutylidene diurea—applied to Sitka spruce (*Picea sitchensis*) seedlings in two English nurseries
V. Puustjärvi	Peat as a medium in the raising of forest tree seedlings

The results of fertilizer use

M. Bonneau	Die Auswirkungen der Düngung in verschiedenen Standorttypen auf Mineralböden
L. Heikurainen	The effects of manuring on organic soils
H.H. Krauss	Kaliernährung und Wachstum von Kieferkulturen und -beständen auf den verbreitetsten Standorten im nordostdeutschen Tiefland
E.L. Stone and *A.L. Leaf*	Potassium deficiency and response in young conifer forests in Eastern North America
J. Materna	Einfluss der Blattdüngung von Fichtenpflanzen mit verschiedenen Nährelementen auf einige Inhaltsstoffe in den Nadeln
R. Kreisl	Stand und Aussichten der Forstdüngung in Österreich
D. Brüning, H.-D. Trillmich, und *E. Uebel*	35 Jahre KMg-Kieferndüngungsversuche Templin
W. Zech	Über die Wirkung einer Kalium- und Stickstoffdüngung auf Wachstum und Ernährungszustand gelbspitziger Kiefernkulturen in Süddeutschland
N. O'Carroll	Forest fertilization in the Republic of Ireland
H. Holstener-Jorgensen	Experiences obtained from fertilization of Norway spruce in Denmark
B. Meshechok	Etwas über Startdüngung für die Aufforstung von Mooren in Norwegen

H. Holmen	Forest fertilization in Sweden
A. Ando	Forest fertilization trials on Japanese conifers in Yamanashi Prefecture
K. Paarlahti	Forest fertilization experiments in Finland

Quality and economical aspects of fertilizer use

U. Schindler	Einfluss der Düngung auf Forstinsekten
E. Björkman	Manuring and resistance to diseases
W. Jensen, O. Huikari and *I. Palenius*	Influence of fertilization of Finnish softwood grown on swamp on yield and quality of pulp
J.P. Maugé	Economic results of forest fertilization in the area of Landes de Gascogne
A. Reinikainen	The appearance of nutrient deficiency in plants growing in the experimental area for forest fertilization at Kivisuo
D. Brüning und *E. Uebel*	Düngung und Populationsdichte von Napfschildläusen
H.-D. Trillmich	Vorzeitiger Kurztriebabwurf zehnjähriger Weymouthskiefern als Folge von Kalimangel

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Proceedings of the 6th Colloquium of the International Potash Institute: Florence/Italy 1968

Fertilization of Protected Crops

Contents

Importance and development of protected crops; Economical aspects of fertilization of protected crops

A. Lecrenier	L'importance et le développement des cultures protégées
R. Favilli	Aspects principaux des cultures protégées, leur importance et perspectives de développement en Italie
R. Brun	Aspects économiques de la fertilisation des cultures protégées comparés aux cultures maraîchères et florales de plein champ
V. Patuelli	Aspects économiques de la fertilisation des cultures protégées
Y. Hori	Fertilization for Crop Cultivation Under Controlled Environment
F. Massantini	Rapport entre les caractéristiques des moyens de protection et les aspects biologiques et nutritionnels des plantes

Vegetable and flower crops in the open air and with forcing techniques; plastic mulching

I. Arnon	Introduction to Session No. 2: Characteristic Aspects of Fertiliser Application to Protected Crops
R. Barbieri	La fertilisation intensive des cultures maraîchères de plein champ
P.D. Fritz und *F. Venter*	Düngung von Gemüse im Freien bei intensivem Anbau für den Frischmarkt «unter nördlichen Bedingungen»
R. Landi	La fertilisation des plantes potagères de plein champ et les rapports d'interaction entre les éléments
J. Cardus	Sur la fertilisation de l'œillet en plein air dans la zone de «El Maresme»

F. Mucci	La culture du melon *(Cucumis melo L.)* en plein champ et sous protection .
G.P. Ballatore	Fertilisation intensive de la tomate forcée sous plastique
M. Guariento	Fertilisation de la fraise en cultures protégées
K. Van Nerum, A. Palasthy et *D. Lamberts*	Etude de l'aptitude des sols pour asperges
E. Špaldon et *J. Ivanič*	Influence des doses croissantes d'NPK sur le rendement et la qualité du piment condimentaire

Crops in greenhouses

A. Anstett	Principes généraux de la fertilisation des cultures maraîchères sous serres
J.-R. Ansiaux	Alimentation minérale et lumière
J. van den Ende	Analysis of greenhouse soils by means of aqueous extracts
H. Moulinier	Relation entre la salinité réelle du sol et la croissance des racines
F. Klinger	Bericht über die gärtnerischen Erden im Bereich von Wien
Mme *D. Blanc*	L'irrigation fertilisante en culture florale sous serre
G.W. Winsor	A long-term factorial study of the nutrition of greenhouse tomatoes
G.W. Winsor	Nutritional trials in greenhouse beds and borders

The fertilization of plants grown on artificial media

Y. Coïc	De l'agriculture à la culture sur substrat inerte: principes de nutrition minérale et application de ces principes à la fertilisation des cultures sous abris
A. Jungk	Influence of Nitrogen and Potassium Concentration of Nutrient Solutions on Yield
O. Steineck	Importance du potassium pour la synthése des composés organiques de la plante
A.A. Steiner	Soilless Culture
M.J. Woods and *T. Kenny*	Nutritional and Cultural Aspects of Peat as a Growing Medium for Tomatoes
T. Kavanagh and *T.J. Higgins*	Disease Aspects of Peat as a Growing Medium
J. Miranda de Onis	Production de tomate en cultures hydroponiques
F. Penningsfeld and *L. Forchthammer*	Essais pour la détermination de l'approvisionnement optimal en oligoéléments des fleurs à couper

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Proceedings of the 7th Colloquium of the International Potash Institute: Israel 1969

Transition from Extensive to Intensive Agriculture with Fertilizers

Contents

General Subject:

I. Arnon	Transition from Extensive to Intensive Agriculture in Israel with Fertilizers

Attaining maximum yield

K. Mengel	Factors Limiting Maximum Yield
J. Warren Wilson	Maximum Yield Potential
M. Thielebein, W.M. Tahit	Plant Breeding for Increased Efficiency in Fertilizer Use

Irrigation and nutrient uptake

G. W. Cooke	Plant Nutrient Cycles
G. Drouineau	Influence of Irrigation on the Distribution of Fertilizer Elements in the Soil Profile

Interaction between nutrition and other factors of plant growth

D. Shimshi	Interaction between Irrigation and Plant Nutrition
R. Blanchet, M. Bosc, C. Maertens	Some Interactions of Cation Nutrition and the Water Supply of Plants
Eloy Mateo-Sagasta Azpeitia	The Interaction between Irrigation and Plant Diseases
D. Lachover, Adelina Ebercon	Iron Deficiency Problems in Peanuts under Irrigation
G.C. Chisci	Interaction between Irrigation and Fertilization in Mediterranean Grassland
A. Bar Akiva	Methods of Diagnosing Nutrient Deficiencies in Citrus

Economics and planning of fertilizer use

H. Ruthenberg	The Economics of Introducing Fertilizer
J. Hagin	Problems of Fertilizer Requirement Prediction in Intensive Agriculture
L. Audidier	New Trends in the Use of Fertilizers, New Products and New Techniques of Application
M. Hasegawa	Changes in Agriculture and Fertilizer Use in Japan
E. Yalan	The Place of the Second Generation in Rural Space

Educating the farmer for the transition from extensive to intensive agriculture

G. Fradkin	Training of Agricultural Extension Officers
T. Gans	The Impact of Courses for Fertilizer Technicians
J. Noy	Irrigation and Fertilizer Extension

Agricultural research and fertilizer use in Israel

M. Giskin, A. Majdan	Problems of Plant Nutrition and Fertilizer Use on Huleh Muck Soils
Z. Karchi	Nitrogen Fertilization of Wheat in Israel
Sh. H. Dajani	Short Outline on Agriculture in the West Bank
D. Shimshi	Irrigation of Wheat in the Northern Negev
Sh. Feldman	Transition from Extensive to Intensive Agriculture with Fertilizers in the B'sor Area Israel
D. Sadan, D. Machol, U. Kafkafi	Soil Tests for Fertilizer Recommendations under Extensive Conditions

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Proceedings of the 9th Congress of the International Potash Institute: Antibes/France 1970

Role of Fertilization in the Intensification of Agricultural Production

Contents

General subjects

Role of fertilization in the intensification of agricultural production: Temperate zone

Role of fertilization in the intensification of agricultural production: Arid and semi-arid zone

D. Davidescu et *V. Davidescu*	La fertilisation et l'accroissement de la production du maïs en Roumanie
I. Szabolcs	Nutrient uptake by plants in saline and alkali soils

Role of fertilization in the intensification of agricultural production: Tropical and sub-tropical zone

R. Chaminade	Nutrition des plantes en relation avec le sol (zone tropicale et subtropicale)
P. Martin-Prével	Aspects dynamiques des éléments minéraux dans la production végétale: travaux sur bananier
J.D. Ferwerda	Soil fertility in the tropics as affected by land use
E. Malavolta	Intensive fertilization of coffee in Brazil
E. Bellis	Intensification of plantation rubber production by *Hevea brasiliensis* through manuring
Ng Siew Kee	Greater productivity of the oil palm (*Elaeis guineensis* Jacq.) with efficient fertilizer practices
M. Ollagnier et *P. Gillier*	Contraintes techniques et socio-économiques dans l'utilisation des engrais minéraux au Sénégal
H.R. von Uexküll	Role of fertilizer in the intensification of rice cultivation
J.G.P. Dirven	Yield increase of tropical grassland by fertilization
M.P. Compagnon	Interaction fumure-stimulation sur hévéa
H.R. von Uexküll	Some notes on the timing of potash fertilization of rice (nitrogen-potash-balance in rice nutrition)

Some factors limiting yield

R.F. Chandler, Jr.	Overcoming physiological barriers to higher yields through plant breeding
R. Pflüger	Der biochemische Weg zu höheren Erträgen unter Berücksichtigung der Auswirkungen auf die Düngungsmethoden
J.A. Meyer	Soil-borne diseases and fertilizer responses
D.A. Boyd	Some recent ideas on fertilizer response curves

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Skokloster-Uppsala/Sweden 1971

Potassium in Biochemistry and Physiology

Contents

Potassium in biochemistry and physiology of plants

H.J. Evans	Potassium and its role in enzyme activation
Ch. Hecht-Buchholz	The effect of potassium deficiency on fine structure of proplastids
T.Z. Nowakowski	Effects of potassium and sodium on the contents of soluble carbohydrates and nitrogenous compounds in grass
H. Marschner	Why can sodium replace potassium in plants?

R. Scott Russel, D.T. Clarkson	The uptake and distribution of potassium in corp plants
Y. Coic, C. Lesaint	The equilibrium between potassium and the other cations in the organs of higher plants
F. Van Egmond	Inorganic cations and carboxylates in young sugar beet plants
M. Viro, H.E. Haeder	The effect of the potassium status of tomato plants on the transport of organic compounds to the fruits
A. Kylin, G. Hansson	Transport of sodium and potassium, and properties of (Sodium + Potassium)-activated adenosine triphosphatases; possible connection with salt tolerance in plants
W. Höfner	Influence of potassium on water economy

Potassium in biochemistry and physiology

V. Koefoed-Johnsen, H.H. Ussing	Ion transport through biological membranes
A. Reinberg	Biological rhythms in potassium metabolism
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M. Apfelbaum	The role of potassium in nitrogen balance – Experimental evidence in rat and man
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