ROTHAMSTED
RESEARCH

Rothamsted Research
Harpenden, Herts, AL5 2JQ

Telephone: +44 (0)1582 763133
Web: http://www.rothamsted.ac.uk/

Rothamsted Repository Download

Graham-Bryce, I. J. 1965. Diffusion of cations in soils - Plant nutrient supply and movement. *Technical report - IAEA .* (48), pp. 42-56.

TECHNICAL REPORTS SERIES No. 48

Plant Nutrient Supply and Movement

JOINT FAO/IAEA DIVISION OF ATOMIC ENERGY IN AGRICULTURE

INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1965

PLANT NUTRIENT SUPPLY AND MOVEMENT

The following States are Members of the International Atomic Energy Agency:

AFGHANISTAN
ALBANIA
ALGERIA
ARGENTINA
AUSTRALIA
AUSTRIA
BELGIUM
BOLIVIA
BRAZIL
BULGARIA
BURMA
BYELORUSSIAN SOVIET SOCIALIST REPUBLIC
CAMBODIA
CAMEROON
CANADA
CEYLON
CHILE
CHINA
COLOMBIA
CONGO, DEMOCRATIC REPUBLIC OF
COSTA RICA
CUBA
CYPRUS
CZECHOSLOVAK SOCIALIST REPUBLIC
DENMARK
DOMINICAN REPUBLIC
ECUADOR
EL SALVADOR
ETHIOPIA
FINLAND
FRANCE
FEDERAL REPUBLIC OF GERMANY
GABON
GHANA
GREECE
GUATEMALA
HAITI
HOLY SEE
HONDURAS
HUNGARY
ICELAND
INDIA
INDONESIA
IRAN
IRAQ
ISRAEL
ITALY
IVORY COAST
JAPAN
KENYA
REPUBLIC OF KOREA
KUWAIT
LEBANON
LIBERIA
LIBYA
LUXEMBOURG
MADAGASCAR
MALI
MEXICO
MONACO
MOROCCO
NETHERLANDS
NEW ZEALAND
NICARAGUA
NIGERIA
NORWAY
PAKISTAN
PARAGUAY
PERU
PHILIPPINES
POLAND
PORTUGAL
ROMANIA
SAUDI ARABIA
SENEGAL
SOUTH AFRICA
SPAIN
SUDAN
SWEDEN
SWITZERLAND
SYRIA
THAILAND
TUNISIA
TURKEY
UKRAINIAN SOVIET SOCIALIST REPUBLIC
UNION OF SOVIET SOCIALIST REPUBLICS
UNITED ARAB REPUBLIC
UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
UNITED STATES OF AMERICA
URUGUAY
VENEZUELA
VIET-NAM
YUGOSLAVIA

The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world".

Printed by the IAEA in Austria
November 1965

TECHNICAL REPORTS SERIES No. 48

PLANT NUTRIENT SUPPLY AND MOVEMENT

REPORT OF A PANEL ON THE
USE OF ISOTOPES AND RADIATION IN PLANT NUTRIENT SUPPLY
AND MOVEMENT IN SOIL SYSTEMS,
CONVENED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND THE FOOD AND AGRICULTURE ORGANIZATION
OF THE UNITED NATIONS
AND HELD IN VIENNA, 9-13 NOVEMBER 1964

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1965

International Atomic Energy Agency.
Plant nutrient supply and movement. Report of a Panel on the Use of Isotopes and Radiation in Plant Nutrient Supply and Movement in Soil Systems, convened by the IAEA and the FAO ... Vienna, 9-13 November 1964. Vienna, the Agency, 1965. 160 p. (IAEA, Technical reports series no. 48)

621.039.85
631.81
581.13

PLANT NUTRIENT SUPPLY AND MOVEMENT, IAEA, VIENNA, 1965
STI/DOC/10/48

FOREWORD

The application of research to specific, practical problems is often preceded by efforts aimed at more fundamental ones. To help solve both types of problem in agricultural research, radiation and radioisotopes are widely used.

The International Atomic Energy Agency supports research contracts, panels, symposia and planning meetings concerned with the whole range of such investigations. Among the activities sponsored by the Joint FAO/IAEA Division of Atomic Energy in Agriculture is "A Co-ordinated Programme on Plant Nutrient Supply and Movement in Soil Systems". It covers some of the basic aspects of soil-plant relationships, and under its aegis contracts have been awarded and meetings held.

A meeting of the contractors and invited participants was held in Vienna from 9 to 13 November, 1964, to discuss the results reached under specific contracts and some related scientific topics. This publication contains the papers presented at the meeting; they give the results, obtained by using isotopes, of some basic research on soils.

CONTENTS

OPENING ADDRESS

H. SELIGMAN
DEPARTMENT OF RESEARCH AND ISOTOPES,
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, AUSTRIA

Most of you know that the bulk of the work supported by Agency research contracts in the field of agriculture is devoted to practical problems of soil fertility and fertilizer utilization. Among these are the co-ordinated programmes concerned with rice and maize fertilization, the former now in its third year. These programmes have the objective of obtaining information of immediate practical value to the food supply and the economy of the developing countries.

Despite the emphasis given by the Agency to this practical field experimentation, it is obvious that any long-term programme of soil fertility research must also take into account the fundamentals of plant nutrient supply and movement. Thus a large gap exists between the present methods used for predicting the response of a crop to fertilizer on any given soil and fundamental knowledge in soil physics, chemistry and biology. Only when precise determinations can be made of the quantity of ions in the soil solution, the adsorption complex, and the rate at which the exchange processes occur, will it be possible to develop a scientific basis for the evaluation of the nutrient status of soils and to make efficient fertilizer recommendations.

Study of these processes, and others, such as ion movement as affected by water flow and diffusion phenomena, have been carried out on a very limited scale by individual scientists in widely separated institutes. Comparative lack of progress in this field is, at least in part, due to the absence of co-ordinated planning and exchange of information among scientists working on these problems, and it is for this reason that this meeting has been organized by the Agency.

From the research point of view a co-ordinated research contract programme on plant nutrient supply and movement has already been initiated and at present there are six contractors. An essential feature of the programme is co-ordination, and this Panel partly represents the second planning meeting of these contractors. The discussions will, however, have wider scope, as other acknowledged specialists in the subject are participating in this Panel.

It is hoped that at this meeting you will hear something of the latest research being carried out in the field and that afterwards in the discussions you can establish the major gaps that exist in our knowledge. It is hoped, too, that you will be able to make some positive contribution to our present programme by making recommendations to guide us in our future planning and work.

ION UPTAKE IN THE SOIL-PLANT NUTRIENT SYSTEM

M. FRIED
JOINT FAO/IAEA DIVISION OF ATOMIC ENERGY IN AGRICULTURE,
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, AUSTRIA

From the standpoint of practical agriculture, the inorganic nutrition of plants essentially concerns the uptake of nutrient ions from the soil-plant system.

As long as the plant is alive and its roots are in the soil, the soil-plant system with regard to inorganic nutrition is an open system in which ions are continuously removed from the system at one end (the soil) and accumulated at the other end (the plant) as shown in Eq.(1):

$$\mathrm{M(soil)} \rightleftharpoons \mathrm{M(solution)} \rightleftharpoons \mathrm{M(plant\ root)} \rightleftharpoons \mathrm{M(plant\ top)} \qquad (1)$$

The movement of ions from soil to plant top has been written as an equation not only to emphasize that all the processes taking place are physical-chemical processes but to suggest that knowledge of the concentrations of the reactants and the rate constants of the processes gives a rather complete description of the overall process with the concomitant potential of process regulation.

Energy must be supplied to the system for the ion accumulation process to continue. In higher plants this energy comes from the absorption of quanta of light energy from the sun. To understand fully the process of inorganic nutrition from the soil-plant system one must also understand this energy process (photosynthesis). For living higher plants this energy process is quite capable of changing the concentration of reactants and the magnitude of the rate constants (as might other factors in the environment); yet the physical-chemical description of the overall process will not normally change.

In an open system, such as that described in Eq.(1), the amount of ion accumulated in the plant top in a given short unit of time will equal the net loss of ion from the soil. When all the intermediate reactions are occurring at the same rate, none of the reactants are changing in concentration and $dMi/dt = 0$. The system is then considered to be in a steady-state condition.

Ion uptake is a continuous dynamic process and all the reactions suggested and implied in Eq. (1) are going on all the time. To solve the kinetic equation, even involving only two consecutive reactions, is extremely complex. Reactions involving more than two steps lead to yet greater difficulties. Practical solutions normally necessitate certain approximations. The steady-state approximation is one of the most useful. The ion uptake process may be treated as a steady-state system which reacts to changes in concentration of one of the reactants, or of one of the rate constants, by the necessary adjustments in all other reactions, to result in a new steady-state level.

The individual reactions making up this continuum of ultimate accumulation of an ion initially present in the solid phase can be studied individually. But their significance to the accumulation process cannot be evaluated without consideration of the rest of the continuum.

Equation (1) describes the uptake of nutrient ions by the plant as a sequence of reactions which can be described in the quantitative terms of physical chemistry. The first term in this sequence is M(soil) which refers primarily to adsorbed ion insofar as the next term in the sequence M(solution) is concerned. However, over a long period of time minerals containing nutrient ions can be a further source of supply, as can organic matter if it is decreasing in amount over the years. In the absence of plant roots the concentration of a nutrient ion depends upon the nature of the reaction between the ion in solution and ion in the solid phase, and the quantitative descriptions available for describing this relationship need elucidation. They include, in addition to the concentration, a capacity factor and an apparent dissociation constant. However, the nutrient ion, after it is in solution, must traverse a physical distance in order to reach the ion-accumulating mechanism in the plant. This movement must take place either by diffusion or by bulk movement with the water phase.

Under ordinary transpiration conditions bulk movement can account for the movement of most nutrient ions. Should this bulk movement actually result in more ions reaching the root than are taken up by the plant, then diffusion gradients are set up away from the plant. Also, since water is not always moving, all ions at times move to the root under the driving force of diffusion.

It would appear that for most nutrient ions the concentration of the ion in the soil solution is the concentration most common to the root surface, and ion uptake rates should be predictable upon this basis. However, phosphate and, under low transpiration conditions or very low potassium concentration in the soil solution, potassium, may not reach the root surface at the concentration in the soil solution but at some lower concentration. The prediction, and the possible modification of this concentration is not at present possible due to lack of sufficient experimental information.

Even with phosphate, and under the special conditions mentioned, potassium, bulk movement and diffusion determine the concentration that reaches the root but the relative importance of these two mechanisms is not known and thus the relative importance of soil solution concentration as compared to diffusivity is not known. Since both mechanisms are affected by the same factors, the concentration gradient on the one hand and the amount of ion moved by bulk movement on the other hand, and the capacity factor determining the distance of movement necessary by either mechanism, there are certain experimental difficulties that have not yet been resolved.

Once the ion reaches the ion-accumulating surface of the root it is either accumulated by the root or passes into the xylem, through a step requiring metabolism, from whence it is translocated to the tops. This active ion-accumulation process can be described in the normal physical-chemical sense by three constants, ΣR, the total amount of a specific carrier, k_2, a specific reaction rate constant, and K_m, a constant which relates the concentration of the solution bathing the root to the amount of ion which would be attached to a given amount of total carrier. The nutrient ion which reaches the xylem probably went through a prior active step; it is not normally the ion which was previously accumulated by the root, although it can be. This ion is then translocated to the top of the plant where it is removed by the cells and utilized in the metabolic system.

This overall picture of ion uptake in the soil-plant system may be summarized by the following equation, Eq. (2), where M is the ion and R refers to carrier:

$$\begin{tikzcd}
 & \text{M(organic matter or minerals)} \arrow[dl, shift left, "\text{slow}"'] \arrow[dr, shift left] & & & \text{M(in xylem)} \arrow[r, dash, "\text{transpiration}"] \arrow[d, shift left] & \text{M(in shoot)} \\
\text{M(adsorbed)} \arrow[ur, shift left] \arrow[rr, rightleftharpoons] & & \text{M(soil solution)} \arrow[ul, shift left] & \text{M(root absorbing surface)} \arrow[r, rightleftharpoons] & \text{M(R)} \arrow[u, shift left] \arrow[r, rightleftharpoons] & \text{M(accumulation in root)}
\end{tikzcd} \tag{2}$$

In this continuum the rate-limiting step under steady-state conditions is probably the active accumulation step that occurs in the root of the plant although the rate limiting step undoubtedly differs for different ions. In this case all the reactions before this step are going on at approximately the same rate and are essentially at a pseudo-equilibrium. Since this is a metabolic process occurring in the root, ion uptake should be directly responsive to the concentration at the ion-accumulating surface and be markedly affected by temperature changes in the soil.

In addition to these concentrations and temperature functions any internal plant factors that result in higher carrier concentrations and higher turnover rates would markedly affect ion uptake. Of course, at the extreme, the continuum may be broken by a moisture content low enough to give discontinuity in the solid-liquid-plant system, thus preventing any ions from reaching the root; indeed another prime candidate for the rate-limiting step for some ions is the movement to the root surface.

The above brief glance at the soil-plant system as a whole can set the framework for the discussions to follow. They deal primarily with individual reactions within the framework. But their interpretation can only have validity when viewed as a part of the overall system.

TOWARD A CONNECTION BETWEEN IONIC EQUILIBRIUM AND IONIC MIGRATION IN CLAY GELS

H.C. THOMAS
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA,
N.C., UNITED STATES OF AMERICA

To point out some of the inherent limitations to the meaning of most, if not all, of the fundamental work on ion-exchange and ionic diffusion in soils, I would like to start by developing very briefly a thermodynamic formalism for handling ion-exchange on clays. There are differences of opinion as to the best ways of expressing these ideas, but this does not matter so much as long as we keep clearly in mind the distinction between the results of our experimental work and the results of our mental work. Particularly amongst soil scientists in my country there seems to be a tendency toward forcing experimental results to fit formulas derived from highly idealized models. There is certainly no objection to this if it is taken as an aid to visualizing complex processes, and if one is not too serious about it and end in vain attempts to prove that such-and-such an ion-exchange formula is "correct" or that such-and-such an idea about the structure of an interface must surely give the correct explanation of some very complex effect, such as diffusion. I am sure we will get ahead faster if we stick as closely as possible to paths indicated by carefully planned and objectively interpreted experiments; trying to recognize the large areas where theory does not fit simply because it is fundamentally inadequate.

What I propose to discuss now has no theory in it whatsoever. It is merely a scheme for formulating in a fairly general manner a class of experiments of real importance in our work. Furthermore, there is nothing new in what comes next; most of those present at this meeting are completely familiar with it.

When one studies ion-exchange phenomena on large beads of, say, Dowex 50×8, there need be little discussion as to what is the object of the study. With a pair of forceps and a bit of blotting paper one can do a fair job of characterizing the "ion-exchanger phase". We must do something much more elaborate with a clay mineral. Any separation process of which I am aware leaves us in real doubt as to whether the material separated is in fact the material we have studied. It is necessary to define the exchanger phase for a clay mineral in terms of some measurement that can be made without disturbing the system under study. This can undoubtedly be done in a variety of ways. I wish to point out the consequences of defining the composition of the clay phase, insofar as cations and water are concerned, as excesses over the total anion content of the system. This scheme will certainly not be satisfactory in every case, but at least for clays of fairly high exchangeable cation content, because the anion is known to be repelled from the surfaces, it has the advantage of supplying us with positive numbers for the ions of most interest. If, then, we suppose that we are dealing with a chromatographic column of definite material content, say for a barium-sodium-water-montmorillonite system, the <u>defined</u> contents of the clay phase (moles) are:

$$n_{Ba}^{\sigma} = n_{Ba} - n_{Cl}\frac{m_{Ba}}{m_{Cl}}, \quad \text{and} \quad n_{H_2O}^{\sigma} = n_{H_2O} - n_{Cl}\frac{55.51}{m_{Cl}}$$

$$n_{Na}^{\sigma} = n_{Na} - n_{Cl}\frac{m_{Na}}{m_{Cl}},$$

where n = mole in adsorbed phase, and
σ = clay phase

The m's are the molalities in the exterior equilibrating solution, that is, the concentrations of the solution fed to the column.

This method also serves to define the volume of the clay phase, its entropy, and its other extensive thermodynamic properties:

$$V^{\sigma} = V - n_{Cl}\frac{V_m}{m_{Cl}}, \quad S^{\sigma} = S - n_{Cl}\frac{S_m}{m_{Cl}},$$

where V = volume, and
S = entropy,

with V_m and S_m (per kilo of water) again referring to the exterior solution.

At least in principle we have a means of measuring all the properties of a clay-ion-water system, but, it is to be noted, only in one equilibrium state. When the system is carried to another state, we have no immediate assurance that our defined excess quantities will behave in a manner reasonable for a bulk phase. It is possible that a surface excess concentration might take on a negative value. We have only one course: we assume that our excess quantities define a "sensible" bulk phase, carry out as many experiments as we can and search for inconsistencies in the results. In some cases, of course, we do get sensible results. This is in part true because we have selected systems for investigation where such results might be expected.

Everyone does the development of formal thermodynamics in equivalent ways up to a certain point; then arbitrary choices become possible and the arguments start as to whose choice is the best. Almost everyone, for example, looks for an equilibrium constant expression. The very existence of such an expression depends on whether one can observe experimentally a definite stoichiometry in the defined clay phase. In terms of our defined excess quantities is there such a relation as:

$$\alpha, \, dn^{\sigma}_{Ba} + \alpha_2 \, dn^{\sigma}_{Na} = 0.$$

Chloride ion cannot enter in the system we discuss; it is defined away. If we find such a relation with $\alpha_1 = 2$ and $\alpha_2 = 1$, we say "this is sensible, and merely means that the clay carries a definite number of negative charge sites". We must, however, look for this relation experimentally and not be too surprised if it fails to appear. Some of the sites may be occupied by hydrogen ion; and if one does not greatly enlarge his study, he will find α's variable and indeed difficult to interpret. We are, in fact, bothered with the meaning of just such a case in connection with the zeolite clinoptilolite.

If we do find a definite stoichiometry, we can proceed to write an equilibrium constant expression governing the transfer of ions between exterior solution and defined clay phase. It is here that arise all sorts of variations in expression according to the tastes of the workers. All the final expressions should at least be interconvertible if nothing fundamental is left out by assuming too specific a model. One form of the result is

$$\frac{(N_{Ba} f_{Ba})\,(\gamma_{Na} m_{Na})^2}{(N_{Na} f_{Na})^2\,(\gamma_{Ba} m_{Ba})} = K^{Ba}_{Na}(P, T),$$

where N = equivalent fraction,
f = activity coefficient of ion in adsorbed state,
γ = activity coefficient of ion in solution,
K = equilibrium constant, and
P, T = pressure and temperature.

In this we assume that "sensible" stoichiometry has been established. If it has not, such an expression does not apply and its use may be quite meaningless.

A remark or two about some of the quantities in this expression may be in order. The N's mean equivalent fractions and constitute a natural, though not necessary, choice for the stoichiometry assumed established. It turns out that, for a highly idealized "clay", about which one can make theoretical calculations, the clay phase activity coefficients, the f's, then have their simplest forms. Even for this idealization the f's depend on the composition of the exchanger. In any case, the f's can be determined from experiment. They do not have the nature of individual ion activity coefficients but refer to a neutral combination of ion and clay. They must appear in any complete formula whatever the choice of units in which we express clay composition. Their absence would imply that we know, or assume, the exact form for the free energy expression of the clay-ion system. Generally this is a very large assumption indeed.

It is to be noticed that the effect of water is implicit in the activity coefficients; it has not been neglected. If we write

$$K_c = \frac{N_{Ba}\,(\gamma_{Na}\, m_{Na})^2}{N_{Na}^2\,(\gamma_{Ba}\, m_{Ba})} = \frac{f_{Na}^2}{f_{Ba}}\, K_{Na}^{Ba}(P, T),$$

where K_c = an equilibrium constant defined as the equation,

then it can be shown that

$$\left(\frac{\partial \ln K_0}{\partial \ln a_{H_2O}}\right)_N = 2\left(\frac{\partial\, n_{H_2O}}{\partial N_{Ba}}\right)_{a_{H_2O}},$$

where a_{H_2O} is the water activity according to the usual definition, in terms of vapour pressures of solution and solvent. Professor Laudelout is responsible for the above formula. We hope to exploit it in the near future.

Another point to be noticed is that, regardless of the complexity of the system, if it is "sensible" in the sense we imply, the value of the true equilibrium constant should be independent of the presence of other ions in the clay. Dr. K.B. Deshpande, in our Laboratory, is just now finishing some work on a three-ion system (Ba, Cs, Na montmorillonite) in which this is nicely demonstrated. His excess quantities have, in fact, been determined on the basis of the weight gain of chromatographic columns, not strictly as above described. In the case of a high capacity montmorillonite the difference is within experimental error. This procedure does, however, constitute the definition of another bulk clay phase. In Fig. 1 are shown his

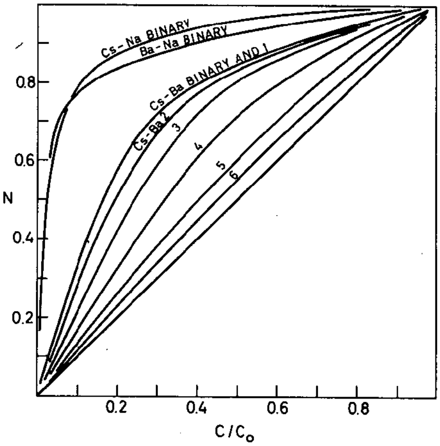


Fig. 1

Exchange isotherms for Ba-Cs for increasing sodium content (K.B. Deshpande)

exchange isotherms for Ba-Cs for increasing sodium content. From these data, in the usual manner, the average values of the $\ln K_c$ have been calculated

$$\ln K_{Ba}^{Cs}(P, T) = 1 + \int_0^1 \ln K_c \times dN_{Cs} \ .$$

These are given in Table I. We feel that the agreement between these quantities does show that we can sensibly calculate a standard free energy corresponding to definite phases for the reaction

$$BaM_2 + 2\ Cs^+ \rightleftharpoons 2\ CsM + Ba^{++} .$$

Perhaps the most significant and important result of equilibrium studies of this type is this: if they are carried out at different temperatures, we can deduce from them a heat of exchange for a pair of ions in a clay phase at a given composition

$$\frac{\partial \ln K_c}{\partial T} = \frac{2\,\bar{L}_{Na}^{\sigma} - \bar{L}_{Ba}^{\sigma}}{RT^2} ,$$

where T = absolute temperature,
R = gas constant, and
L = enthalpy of ion at adsorbed state,

the L's being referred to solution standard states. It must be remarked at once that very accurate work is required to produce reliable results for these heats. It seems probable that the direct calorimetric approach may

TABLE I

TERNARY ION EXCHANGE EQUILIBRIA
Na-Cs-Ba-Montmorillonite

	(30°C)		
	Eq. per cent Na in solution	Min. per cent Na on clay*	K^{Cs}_{Ba}
Binary	0	0	6.10
1 **	60	3.9	6.04
2	70	5.0	5.99
3	80	9.9	5.88
4	90	16.9	5.94
5	95	32.1	5.99
6	99	65.6	6.11

$-\Delta G^\circ = 3.62$ kcal/mole Ba

* The Na uptake of the clay varies very little with Cs/Ba.
** No. of isotherm in Fig. 1.

be better. We do no such work in our laboratory, and I again refer you to Professor Laudelout and others who are competent in calorimetry.

At best we can get only the difference of a pair of heats from exchange data. To connect such results with the energies of activation for a corresponding diffusion process is the announced topic of this paper. Let me continue to avoid it by describing to you first some of our work on diffusion. The extent of the project proposed will become more apparent.

THE DIFFUSION EXPERIMENT

Evidently in any soil system of practical interest there are always several mobile chemical components of importance. The study of diffusion in polycomponent systems is an extremely large and complex endeavour. For example, in an isothermal ternary liquid system there is a total of four diffusion coefficients to be measured. As a purely practical matter we must severely limit the scope of the experiments attempted. Perhaps the ultimate simplification is the study of isotopic diffusion in systems at chemical equilibrium. In our work at the University of North Carolina we have found that even this relatively simple experiment is sufficiently difficult to carry out with any degree of accuracy. We are now only in our first year of experiments on clay systems, and it will be some time before we make connection with really practical problems.

Let me describe our experiment and show you some recent results, as yet unpublished, which demonstrate what can be done in measuring isotopic diffusion in gels of the well-known substance, agar. This work might be called preliminary to the matter of interest here; that is, the study of clay systems.

In principle the experiment is quite simple. The gel is brought to equilibrium with a given solution, and, within the gel one of the chemical species present in gross amount is marked with a radioactive tracer. The nature of our equipment, and especially the design of the diffusion cell, is such that we are limited to the use of gamma emitters. This, however, leaves us many systems available for study, but unfortunately we cannot do experiments directly with calcium and only with much more difficulty with potassium. We are using instead barium and caesium.

The radioactive gel is confined behind a thin membrane permeable to water and to all the other chemical species present, except the matrix of the gel itself. For this membrane we use a thin unwaterproof cellophane. The gel, in a metal container of exactly known depth, is placed in the well of a scintillation counter. Over the exterior of the membrane passes a rapid flow of non-radioactive solution, the solution which is in chemical equilibrium with the gel. Diffusion of the tagged species takes place through the membrane, and as time passes we measure the amount of radioactivity left in the gel.

The experiments require some hours; we are now fortunately equipped with a recording spectrometer which prints on paper tape the results of the counting.

The computation of a diffusion coefficient from the results of an experiment is done by the method of least squares. So much arithmetic is required that the experiment would be useless without a high-speed electronic computer. Some four or five minutes of computer time are required for each experiment. This is five to seven dollars at the rates we are charged — no small item when a busy man does fifty or sixty experiments in a month.

We have now convinced ourselves that we can determine self-diffusion coefficients in agar and in clay gels with an accuracy approaching one per cent. As will be seen, a smaller accuracy would leave us little to discuss, and any improvement in the experiment will indeed be welcome. Let me show you some results obtained by Dr. Laird Slade with sodium and caesium chlorides in agar gels.

Figure 2 shows the course of a single experiment in which the ratio of the counting rate of the gel to its initial value is plotted against the square root of the time. To a rough first approximation, near the central portion of the experiment, this curve is a straight line. If one wants only a 10% accuracy in D, a straight edge and a piece of graph paper are all that is required. The difficulty is that one never knows just where to start and where to stop his straight line, and then its slope, which determines D, remains uncertain. Only with a digital computer is it possible to do real justice to the experiment.

Table II shows the results obtained with two different gels and several kinds of cellophane. Each value of D is the result of an experiment in which perhaps 50 to 100 counts were made.

The degree of precision attainable in the experiment is here apparent. In the theory of this experiment we assume a straight-line gradient in the confining membrane, and it is necessary then to show that the diffusion coef-

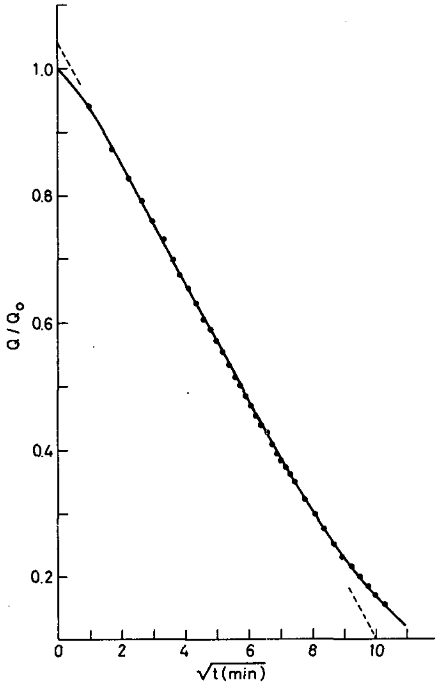


Fig. 2

Diffusion experiment, 0.05 M NaCl

• Experimental

—— Computed

ficients for the gels are independent of the nature and thickness of the membrane. Part of the evidence for this is in Table II.

The most interesting feature of Dr. Slade's work is contained in his study of the dependence of the diffusion coefficient on the agar content of the gel. To within the precision of the experiment Slade found that his observed values of D were linear with the weight per cent of agar in the gel and so he was able to extrapolate to zero agar content, that is, to the pure aqueous solution of the concentration in question. Figure 3 shows such an extrapolation, with the precision of the observed values of D indicated. Table III shows the results of these extrapolations for his most dilute solutions, where the extrapolated results might be expected to agree with the limiting equation in terms of ionic conductances. As can be seen, we do get this agreement for sodium and caesium. Such a simple extrapolation is not possible with divalent ions; we are now investigating cobalt and barium. These ions apparently interact much more strongly with the gel. With them agar behaves as a clay gel behaves with sodium.

It is interesting to see what these results for sodium and caesium mean in terms of the formation factors of the gels. If the agar offers only a mechanical obstruction to the motion of an ion, lengthening the diffusion path by a

TABLE II

SELF-DIFFUSION COEFFICIENTS OF $^{22}Na^+$ IN 0.0100 M NaCl AT 25°C

Agar (wt. %)	D × 10^5 (cm^2/s)	ξ (cm)	$\left(\frac{\Sigma\delta^2}{m}\right)^{\frac{1}{2}} \times 10^3$
EXPT. Cello.	1.249	0.0115	1.29
	1.255	0.0081	1.29
300-PUD Cello.	1.244	0.0130	1.51
	1.249	0.0118	1.25
300-NR Cello.	1.239	0.0081	1.46
	1.245	0.0088	1.13
	1.246	0.0116	1.35
	1.253	0.0094	1.20
	1.249	0.0106	1.15
	1.244	0.0115	1.17
	1.248	0.0095	1.30
	1.240	0.0109	1.41
	1.252	0.0092	1.51
	1.249	0.0108	1.29
300-GF Cello.	1.245	0.0103	1.51
	Av.(15): 1.247 ± 0.004		
2.0% Agar EXPT. Cello.	1.227	0.0084	1.68
	1.221	0.0087	1.51
	1.231	0.0068	1.26
	1.207	0.0081	1.72
300-PUD Cello.	1.222	0.0166	1.37
	1.215	0.0168	1.34
	1.238	0.0161	1.42
	1.242	0.0168	1.39
	1.227	0.0154	
300-NR Cello.	1.206	0.0130	1.35
	1.212	0.0118	1.51
300-GF Cello.	1.204	0.0132	1.55
	1.212	0.0131	1.61
	Av.(13): 1.220 ± 0.010		

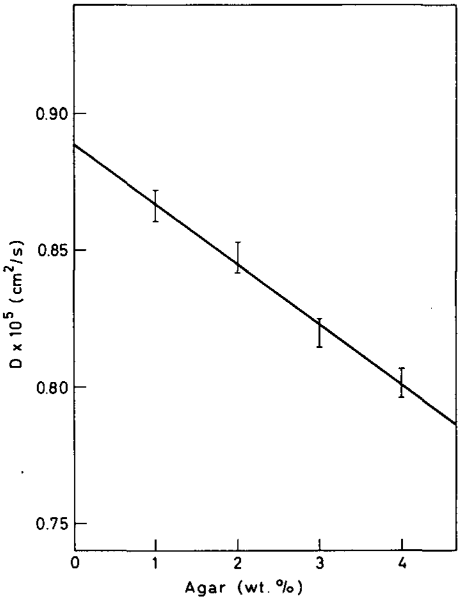


Fig. 3

Dependence of D on agar gel content. 0.050 M NaCl 10°C

TABLE III

COMPARISON OF RESULTS AT 0.0010 M SODIUM AND CAESIUM WITH RESULTS FROM A LIMITING LAW

	$D \times 10^5$ (cm²/s)		
	Experimental	Calculated	
0.0010 M $^{22}Na^+$	1.321	1.326	25°C
	0.8871	0.8810	10°C
0.0010 M $^{134}Cs^+$	2.012	2.041	25°C
	1.410	1.420	10°C

factor $\sqrt{F}$, we can get the formation factor directly from the extrapolated values of D, say D(0):

$$F = D(0)/D.$$

If the weight fraction of agar, w, is proportional to the volume fraction, and in addition is small, we must have

$$(F - 1)/w = (kv)\,(1 + w + \ldots) \approx kv$$

where k depends on the geometry of the gelled agar "molecule" and v is its specific volume.

Since F does not differ greatly from unity for these gels, this is a rather stringent test. For sodium and caesium (for which the F-factors are indistinguishable) we get:

Agar (%)	1	2	2.5	3	4
			(10°C)		
F	1.026	1.052	1.059	1.086	1.105
(F-1)/w	0.026	0.026	0.024	0.029	0.026
				(Av. 0.026)	
			(25°C)		
F	1.026	1.057	1.052	1.090	1.110
(F-1)/w	0.023	0.029	0.021	0.030	0.027
				(Av. 0.026)	

It is further found that when the heats of activation are calculated these prove to be independent of agar content.

It thus seems quite clear that at least for these two ions the idea of a purely mechanical barrier to diffusion is adequate to account for the results in the agar gels.

We need a much more complex formalism to describe the results when definite interaction takes place with the surface. This is the case which Dr. Adrien Cremers, from Louvain, is now treating by measuring diffusion coefficients in gels of Camp Berteau montmorillonite.

Perhaps the whole significance of these experiments lies in the possibility of a study by this means of a true surface diffusion coefficient. By "true" I mean here a coefficient defined in an operational manner, so that eventually it will be possible to attack the results theoretically, or, more optimistically, so that eventually the results may become guides in the development of theory.

We need first of all the formation factor for the clay gels and suspensions. The determination of these formation factors has been carried out by Professor Laudelout and Dr. Cremers, essentially by measuring the conductance of the gels at high-salt content where the surface conductivity is negligible and where the effect of the clay particle is wholly mechanical. A similar experiment might be done by diffusion measurements, but the amount of work involved would be almost prohibitive.

For our definition of surface diffusion coefficient we also need the values of diffusion coefficients in pure water solutions.

When an observed gel diffusion coefficient is multiplied by the appropriate form factor, we may imagine the result as giving the average D(0) for a fictitious gel in which all the surfaces are aligned in the direction of diffusive flow. Near such a surface we might have concentration profiles somewhat as depicted in Fig. 4.

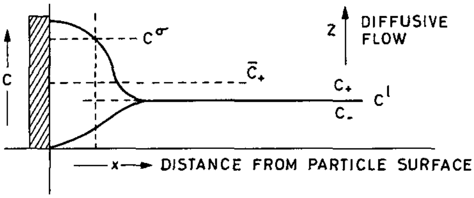


Fig. 4

Concentration profiles

Since we know nothing experimentally (and theoretically only for highly idealized systems) as to the actual shape of the concentration profiles, it is proposed to use an arbitrary but operational definition of the concentration of the ions assigned to the surface region. We might do this in terms of anion exclusion – as here shown – but in any case we are to use the same definition as is employed in ion-exchange experiments on the same system. Then with n^σ and n' the number of moles of ions in surface region and in solution, we have for the "aligned" gel

$$n^\sigma = x^\sigma c^\sigma, \; n^1 = x^1 c^1$$

and

$$n^{\text{total}} = \bar{c} L$$

for L the average half distance between the aligned surfaces and

$$L = x^\sigma + x^1.$$

The total diffusive flux is thus given by

$$-JL = D(0)L \frac{\partial(\bar{c}\theta)}{\partial Z} = D^\sigma x^\sigma \frac{\partial(c^\sigma\theta)}{\partial Z} + D^1 x^1 \frac{\partial(c^1\theta)}{\partial Z}$$

with θ the fraction of ions tagged, constant in the x-direction,

J = flux, and
Z = distance.

We get for the explicit definition of the surface region diffusion coefficient D^σ

$$D(0) = D^\sigma X^\sigma + D^1 X^1$$

with $X^\sigma = n^\sigma/n^{\text{total}} = 1 - X'$ the fraction of ions defined by the convention of the ion-exchange experiment to be in the surface region.

It is to be reiterated that this approach is meaningful only if we can find

$$D(0) = F\,D_{\text{gel}} \text{ (measured)}$$

that is, if we can by some means determine the formation factor for the system under study.

In the above $\bar{c}$ is some average concentration which gives the total ion content of the gel. In the aligned gel all the c's ($\bar{c}$, c^σ, c^l) are constant, in the Z direction at least up to the boundary of the gel. Under these conditions the value of $\partial\theta/\partial Z$ is independent of x, and there results the above expression for D(0).

It is important to notice that we have here made essential use of chemical and isotopic equilibrium. No examination has been made of the enormous difficulties which arise in non-steady systems. It seems probable, however, that even these severe limitations leave us much of interest to learn about the motion of ions near surfaces.

I should now like to show you results obtained by Dr. Cremers during the past six or eight months. He has measured self-diffusion coefficients for sodium, at two concentrations of sodium chloride, at 25°C and 35°C, for five different weight percentages of the montmorillonite. His experimental results and values of surface diffusion coefficients are given in Table IV. Surface region coefficients have been calculated on the basis of an exchange capacity of the clay taken to be 1.00 meq/g and using solution coefficients from two sources, either from extrapolations of our work with agar or by computation from Onsager's formula involving ionic conductances. He used formation factors supplied by his own work in Louvain.

Perhaps the most uncertain number that goes into this calculation is the value of the solution coefficient. There are serious discrepancies when one considers how the error is magnified in the calculation of D^o. Table V gives some comparisons. At 35°C "agar values" were obtained by extrapolation of results obtained at 10°C and 25°C. This is another uncertain procedure. Neither is it known how reliable the Onsager equation is at these concentrations.

Table VI compares the values of D^σ obtained by these two routes.

So many uncertainties remain in the work at this stage that it is somewhat presumptuous to attempt any calculation of quantities related to the activation process. We have nevertheless done so, and one very interesting point seems at least partly established. If we use the equation of Eyring to describe the diffusion coefficient

$$D^\sigma = \lambda^2 \frac{kT}{h} \exp\left(\frac{T\Delta S^\ddagger - \Delta H^\ddagger}{RT}\right)$$

where λ = jump distance,
R = Boltzmann's constant,
h = Planck's constant,
$\Delta S^\ddagger$ = activation entropy,
$\Delta H^\ddagger$ = activation enthalpy, and
$\Delta G^\ddagger$ = activation free energy,

and if we assume that the "jump distance" λ is independent of temperature, we can calculate the free energy of the activation process

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger,$$

TABLE IV

SELF-DIFFUSION OF SODIUM IN MONTMORILLONITE SUSPENSIONS

(D' from Onsager Equation)

Clay (%)	X^σ	F	D(obs'd) × 10^5		$D^\sigma \times 10^5$	
			(25°C)	(35°C)	(25°C)	(35°C)
0.0107 M NaCl						
0.79	0.425	1.028	0.8325	1.039	0.240	0.299
			0.8327	1.055		
				1.070		
1.55	0.593	1.055	0.6370	0.798	0.225	0.291
			0.6314	0.803		
			0.6295	0.813		
2.15	0.669	1.077	0.5429	0.684	0.226	0.278
			0.5446	0.689		
			0.5389	0.679		
2.98	0.738	1.108	0.4784	0.582	0.253	0.288
			0.4782	0.584		
			0.4790	0.589		
3.71	0.779	1.135	0.4297	0.539	0.246	0.321
			0.4179	0.541		
			0.4262	0.553		
0.0537 M NaCl						
1.26	0.191	1.045	1.082	1.357	0.476	0.534
			1.080	1.348		
			1.083	1.364		
1.79	0.251	1.064	1.000	1.270	0.411	0.554
			1.001	1.272		
			1.002	1.280		
2.25	0.297	1.081	0.945	1.216	0.401	0.552
			0.944	1.198		
			0.946	1.213		

TABLE IV (cont'd)

Clay (%)	X^{σ}	F	D(obs'd) × 10^5		$D^{\sigma} \times 10^5$	
			(25°C)	(35°C)	(25°C)	(35°C)
0.0537 M NaCl						
2.67	0.334	1.097	0.8853	1.147	0.357	0.539
			0.8907	1.148		
			0.8885	1.159		
3.21	0.377	1.116	0.8348	1.104	0.350	0.533
			0.8353	1.079		
				1.082		
3.70	0.412	1.135	0.8206	1.023	0.409	0.483
			0.8144	1.015		
			0.8062			
4.32	0.450	1.159	0.7560		0.400	
			0.7696			
			0.7649			

TABLE V

SELF-DIFFUSION COEFFICIENTS FOR Na^+ IN WATER

M NaCl	D × 10^5			
	Agar extrapolation		Onsager calculation	
	(25°C)	(35°C)	(25°C)	(35°C)
0.0107	1.277	1.606	1.311	1.633
0.0537	1.282	1.604	1.284	1.626

and we get the following results:

$\Delta G^{\ddagger}$ (kcal/mole)

M NaCl	Agar	Onsager
0.0107	3.86	3.31
0.0537	6.05	4.60

TABLE VI

SURFACE DIFFUSION COEFFICIENTS OF Na+ "ON" CAMP BERTEAU

M NaCl	Montmorillonite $D^{\sigma} \times 10^5$			
	Agar extrapolation		Onsager calculation	
	(25°C)	(35°C)	(25°C)	(35°C)
0.0107	0.260 ± 0.014	0.332 ± 0.026	0.238 ± 0.011	0.295 ± 0.014
0.0537	0.407 ± 0.040	0.586 ± 0.037	0.400 ± 0.038	0.532 ± 0.024

In the first place it is at once apparent how strongly the results are affected by inconsistencies in the data. It is however interesting that whatever route we take for the calculation we find higher free energies of activation at higher concentrations.

We have at this point used up all our information and are uncertain that this result is in fact correct. It will be some time before we are in a position either to bolster or refute the above discussion.

In conclusion let me return for just a moment to the advertised subject of this paper. Is there a connection between

$$RT^2 \left(\frac{\partial \ln K_c}{\partial T}\right)_N - \Delta\bar{L}^1 = (\bar{L}^{\sigma}_A - \bar{L}^{\sigma}_B) - (\bar{L}^1_A - \bar{L}^1_B)$$

$$= (\bar{\bar{H}}^{\sigma}_A - \bar{\bar{H}}^1_A) - (\bar{\bar{H}}^{\sigma}_B - \bar{\bar{H}}^1_B)$$

and

$$-\Delta H^{\ddagger} = (\bar{\bar{H}}^{\sigma}_A - \bar{\bar{H}}^1_A{}^{\ddagger}) + (\bar{\bar{H}}^{\sigma}_B - \bar{\bar{H}}^1_B{}^{\ddagger}).$$

We might expect this to be so if the "activated state" for our defined surface diffusion corresponds to a pair of ions in an environment closely similar to that of the bulk solution. But we do not know that this is correct, and the answer to the question at present is certainly subject to experiment. The route seems to be through studies of self-diffusion.

A UNIFIED TREATMENT OF TWO ION-EXCHANGE FORMULATIONS COMMONLY USED IN SOIL SCIENCE

H. LAUDELOUT,
UNIVERSITY OF LOUVAIN, BELGIUM

The study of ion-exchange processes undoubtedly belongs to the very first attempts towards an understanding of some of the physical chemical processes which determine soil fertility. More than a hundred years have elapsed since the first studies on this subject were published by WAY [1] and interest in it has not abated since then. In spite of this, comparable quantitative data onexchange processes between cations of agricultural importance are still relatively scarce, this being due, among other causes, to the fact that empirical formulations of ion-exchange constants may differ considerably when applied to heterovalent exchange. It would thus seem desirable, before undertaking a compilation of the ion-exchange data to be found in the soil literature, to examine the possibility of reducing the formulations most used to a common expression.

It seems obvious that the common denominator to which empirical or semi-empirical formulations should be reduced must be the thermodynamic expression of the ion-exchange equilibrium constant, were it only for the reason that any two values of the equilibrium constants referring to the exchange between cations A and B or A and C, allow the calculation of a third equilibrium constant, that of the exchange between B and C. We may consider the displacement of sodium by potassium ions as an example of homovalent exchange and that of potassium by calcium ions as an example of heterovalent exchange.

These two exchange reactions may be written as

$$\text{Soil Na} + \text{K}^+ \rightleftharpoons \text{Soil K} + \text{Na}^+ \qquad (1)$$

$$2\ \text{Soil K} + \text{Ca}^{++} \rightleftharpoons \text{Soil Ca} + 2\text{K}^+ \qquad (2)$$

and for each of these a "selectivity coefficient". K_c may be defined by

$$K_c^{(1)} = \frac{N_K(\text{Na}^+)_{sol}}{N_{Na}(\text{K}^+)_{sol}}$$

$$K_c^{(2)} = \frac{N_{Ca}(\text{K}^+)^2_{sol}}{N_K^2(\text{Ca}^{++})_{sol}}$$

where the parentheses refer to activities in the equilibrium solutions and the N to the equivalent ionic fractions in the surface phase defined by the experimental method chosen for isolating the equilibrium solution.

It has been shown by GAINES and THOMAS [2] that the free energy of exchange between the two ions considered is very nearly given by the result of a graphical integration of K_c over the entire composition range of the surface phase

$$\Delta F_0^{(2)}/RT = -\ln K^{(1)} = -\int_0^1 \ln K_c^{(1)}\, dN_K$$

$$\Delta F_0^{(2)}/RT = -\ln K^{(2)} = 1 - \int_0^1 \ln K_c^{(2)}\, dN_K$$

where R is the gas constant, T the absolute temperature, ΔF_0 and K the free energy change and equilibrium constant respectively for the reactions considered.

The approximations involved in this calculation of ΔF_0 have been discussed [2]. They introduce a negligible error if the purpose of the calculation is to compare compiled data on ion-exchange processes in different soils and clays. The same can be said if we substitute on K_c the ratio of concentrations to the ratio of activities.

A correlation of two empirical ion-exchange formulations with the thermodynamic expression mentioned above is very easy.

If we take Gapon's [3] equation

$$K_G = \frac{N_{Ca}(K^+)_{sol}}{N_K(Ca^{++})^{\frac{1}{2}}_{sol}}$$

it can be seen that

$$K_G^2 = K_c^{(2)} N_{Ca}.$$

Taking the logarithms of both sides, multiplying by dN_K and integrating from $N_K = 0$ to $N_K = 1$, gives

$$2\int_0^1 \ln K_G\, dN_K = 1 - \int_0^1 \ln K_c^{(2)}\, dN_K = \ln K,$$

where use has been made of the fact that $dN_K = -dN_{Ca}$.

Twice the result of the graphical integration of the logarithm of Gapon's constant will thus give the thermodynamic exchange constant. It is necessary that K_G varies with N_K, and even though it may seem that K_G is constant over a fairly wide range of composition, this constancy cannot extend to the whole range of composition. Attempts to interpret changes in the value of K_G as due to the presence of a mixture of clays with different exchange properties are thus not warranted.

Another empirical formulation which has been fairly commonly used is that of VANSELOW [4].

It is usually written as follows:

$$K_V = \frac{[K^+]^2(Ca^{++}_{sol})}{[Ca^{++}](NH_4^+)^2_{sol}} \times \frac{1}{([K^+] + [Ca^{++}])}$$

in which the square brackets refer to the amounts of exchangeable cations. If we define the molar fraction by

$$X_{Ca} = \frac{[Ca^{++}]}{[Ca^{++}] + [K^+]} \qquad X_K = \frac{[K^+]}{[Ca^{++}] + [K^+]}$$

It is apparent that K_V is analogous to K_c since it takes the form

$$K_V = \frac{X_K^2(Ca^{++})_{sol}}{X_{Ca}(K)^2_{sol}}$$

and a thermodynamical treatment of the reaction on the basis of the molar fractions would be as easily feasible as on the basis of equivalent ionic fractions.

The activities would then be defined by

$$a^{ads}_{Ca^{++}} = X_{Ca^{++}} y_{Ca^{++}} .$$

In homovalent exchange this difference is of no importance, while in the case of heterovalent exchange a relation between K_c and K_V can easily be found. Since we have the following relationships between the molar fractions and the equivalent ionic fractions in the case of the K, Ca exchange

$$X_K = \frac{2N_K}{1 + N_K} \qquad X_{Ca} = \frac{N_{Ca}}{1 + N_K}$$

we obtain the following relation between K_V and K_c

$$K_V = K_c \frac{1 + N_K}{4} .$$

Taking the logarithms of both sides, multiplying by dN_K and integrating from $N_K = 0$ to $N_K = 1$ gives:

$$\int_0^1 \ln K_V \, dN_K = \ln K .$$

Graphically averaging $\ln K_V$ over the entire composition range will give the logarithm of the thermodynamic equilibrium constant. Since a fairly large number of data exist on the range of variation of K_V or K_G with composition of the surface phase it would not be very difficult to tabulate the corresponding thermodynamic constants. Since only a part of the composition range is generally covered by the experimental data, it should be necessary to use an extrapolation formula similar to the one proposed by THOMAS and GAINES [5] or to make use of semi-empirical relationships relating the change of activity coefficients in the surface phase with its composition. Further, the calculation of the electrical work involved in the exchange between mono- and divalent cations becomes possible on the basis of the diffuse double layer theory, since it has been shown by BOLT [6] that K_G could be calculated from this theory. This may help to extend heterovalent exchange correlations such as those which were found by MARTIN and LAUDELOUT [7] in the case of the uni-univalent exchange between the polarizability differences of the cations and their free energy and enthalpies of exchange.

REFERENCES

[1] WAY, J. T., J. Roy. Agric. Soc. Engl. 1850, 11, 313.

[2] GAINES, G. L. and THOMAS, J. Chem. Phys. 1955, 23,2522.

[3] GAPON, E. N., J. Gen. Chem. U. S. S. R. 1933, 3, 144.

[4] VANSELOW, A. P., Soil Sci. 1932, 33, 95.

[5] THOMAS, H. C. and GAINES, G. L., Clays and Clay Minerals, 2nd Conf. National Academy of Sciences Publ. 327 (1954) 398.

[6] BOLT, G. H., Soil Sci. 79 (1955) 267.

[7] MARTIN, H. and LAUDELOUT, H., J. Chim. Phys. (1963) 1086.

DISCUSSION

G. H. BOLT: The calculation of the standard free energy of exchange and the adsorbed-phase activity coefficients, as based upon the consideration of electrostatic interaction only, was performed recently for the case of mono-divalent exchange. The method consisted of

(a) calculation of the equivalent fraction monovalent adsorbed, by means of equations based on the Gouy-Chapman theory, using a range of values for the surface density of charge, the total electrolyte concentration and the ratio mono- to divalent ions in solution*;

(b) calculation of the functional relationship between the different K values (i. e. the K value based on the use of mole fraction adsorbed, K_M, the K value based on the use of equivalent fraction adsorbed, K_N, and the K value defined by the Gapon exchange equation, K_G) and the equivalent fraction adsorbed.

The outcome of the calculations set out in (b) above indicates that ΔF^0 (for the reaction proceeding from Ca-clay to Na-clay) varies from about -2 RT for a surface charge density of $10^{-6.5}$ meq/cm^2 at a total electrolyte level of 1 N to about -1.5 RT for the same charge density at 10^{-3} N; for

---

* BOLT, G. H. and PAGE, A. L., "Ion exchange equations based on double layer theory", Soil Science (June 1965) p. 357.

a charge density of 10^{-7} meq/cm^2 ΔF^0 varies from about zero to +RT at the above electrolyte levels**.

B. ULRICH: When calculating free energy from exchange data one should be aware of the fact that a measured exchange constant may reflect differently-bound fractions of cations, as shown by recent work of Bolt et al., Schoüenburg et al. and Beckett.

NEW TRENDS IN ION-EXCHANGE STUDIES ON SALINE AND ALKALI SOILS

I. SZABOLCS
RESEARCH INSTITUTE OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY,
HUNGARIAN ACADEMY OF SCIENCES
AND
K. DARAB
ISOTOPE LABORATORY, NATIONAL INSTITUTE FOR AGRICULTURAL
QUALITY TESTING, BUDAPEST, HUNGARY

From the beginning of this century, studies of ion-exchange processes in salt-affected soils, a term referring to both saline and alkali soils, have had an ever-growing importance.

Three general problems make the consistent study of these processes necessary in theory and in practice, and the same problems require the quantitative description and determination of the ion-exchange processes in salt-affected soils.

1. The first of these three problems comprises the evolution and genetics of the various kinds of salt-affected soils, e.g. the solonetz-forming process, in the course of which the adsorption of Na-ions on the soil colloids became dominant; the de-solonetzation in the opposite direction; the solid-forming process, etc. All these processes develop in the presence of various anions and cations, and the soil properties are also different depending on the environmental conditions.

The direction and rate of ion-exchange processes are also different and need positive investigation.

2. The second process, in which the ion-exchange phenomenon plays an important role and has special importance, is the interaction between water and soils in the course of irrigation. It is well known that both irrigation water and ground water have an influence on soil salinity and alkalinity. In

---

** Note added after the meeting:

It was decided that a comparison will be made between experimental data as obtained by Laudelout et al. and the above computed values as a joint project between Louvain University and Wageningen State Agricultural University. It is expected that the detection and interpretation of specific effects present, aside from the electrostatic effects, will thus become more straightforward. The results of the comparison will be published in due course.

the literature and in practice this interaction has been better elaborated than the other two mentioned in this paper. Theoretical and practical equations and formulas are available all over the world in countries interested in irrigation, concerning the amounts of irrigation water and the physical and chemical properties of soil and water in order to avoid the danger of secondary salinization and alkalization of soils.

This problem, however, makes further investigation necessary of the interaction between water and soil in relation to the wide variety of natural conditions and soil properties.

3. The third problem, which is especially important from the point of view of ion-exchange studies of salt-affected soils, is that of the reclamation of these soils.

A large proportion of salt-affected soils belongs to the solonetz type, or to types related to it. The practical method of reclamation of these soils is the exchange of the Na-ions adsorbed on the soil colloids by Ca-ions. This way the disadvantageous physical and chemical properties of these soils are ameliorated.

As is pointed out in the literature, this reclamation takes place more or less according to the laws of ion exchange. To estimate the necessary quantity of reclamation material and to select the material for the best effect, as much as possible about the ion-exchange processes taking place under the natural conditions of the soil in question should be known.

It is clear from the above that among soil cations Na-ions have a special importance as regards soil alkalization and salinization in the interaction between water and soil, and in the reclamation of alkali soils.

In the study of ion-exchange processes in salt-affected soils, any practical approach has to deal with the nature of Na-ions taking place in the process, the relationship with other ions, adsorbing materials and the conditions of the soil medium.

The Na compounds present in soils may be classified as follows:

(a) Primary minerals containing Na;
(b) Soluble Na salts in soils; and
(c) Na-ions adsorbed on the organic mineral complex of the soil.

Of these, the soluble Na salts and the so-called exchangeable Na-ions play a direct part in the formation of salt-affected soils and in the definition of their characteristics.

In soils where there is a considerable quantity of soluble Na salts, the low productivity of the soil is caused by the high concentration of Na-ions in the soil solution. Therefore the purpose of soil amelioration and the precondition of utilization is to leach out the Na salts from the soils.

In cases where the low productivity of the soil is caused by considerable saturation of the organic-mineral complex with Na-ions with consequent disadvantageous characteristic physical properties and water economy, the purpose of the amelioration is to decrease the absolute and the relative quantity of the exchangeable Na-ions.

Experimental data and practical experience gained in the course of studying the formation of sodic soils and their amelioration have also shown that it is advisable to make further distinctions within the above two groupings. One means of further differentiation is to take into account the kind of anions to which Na-ions are bound, causing alkalization [5, 6] . Accordingly, there are chloride-, sulphate- and carbonate-type saline soils. The considerable increase in the amount of soluble salts in the soil is generally a necessary phenomenon of chloride and sulphate salinization during the formation of solonchak-like and solonchak soils.

In many cases the formation of sodic soils is not coupled with a considerable increase in the amount of soluble salts in the soil. Much experience proves that, even in the case of a relatively low concentration of ions in the soil solution, the organic-mineral complex of the soil is saturated to a great extent with Na-ions [6, 12]. According to experimental data, in the presence of soda a total salt concentration as low as 0.05 N is quite sufficient to have the colloid-complex of the soil saturated with Na-ions to 60-70% of the total exchange capacity [6].

Amelioration of these soils also shows great variance. In the course of leaching chloride and sulphate solonchak soils, generally when decreasing the amount of soluble salts, the quantity of the soil's exchangeable Na-ions is also decreased, if the water used for leaching contains a low level of relative Na-ion concentration. With the leaching of so-called sodic solonchak soils of high salt content, however, the decrease in the amount of the soluble salts in the soil does not go together with a considerable decrease in the exchangeable Na-ions. The result of the leaching in this case, therefore, will be the solonchak-solonetz transformation. In the course of irrigation, even in the case of a relatively low level of salt concentration, the quantity of exchangeable Na-ions may increase.

This is why, in selecting a practical method of amelioration, differences must be made in handling the chloride and sulphate types and the sodic type of salt-affected soils.

In the course of irrigation it is not only the maximum permissible salt concentration of the irrigation water and the maximum permissible relative value of Na salts that are required, but also the maximal value of soda or that of Na salts capable of alkaline hydrolysis e.g. (soda, $NaHCO_3$, Na_2SiO_3) [9, 11].

This procedure is correct and necessary because in the presence of soda and other Na salts capable of alkaline hydrolysis certain changes take place, partly in the chemical composition of the soil solution and partly in the colloid-chemical state of the soil's organic-mineral complex. These changes are often not taken into account, or are taken into account only partially, by the theoretical and empirical equations interpreting the laws of ion exchange.

The effect of the soil solution's anions on the soil's saturation with Na and on the exchange of Na-ions may be traced back to several factors:

1. Difference in the average activity coefficient of Na salts bound to various anions.

The difference that originates in the activity coefficients can be already observed in the cases of Na-chloride and Na-sulphate. BABCOCK made certain calculations in this respect [2, 3].

2. Difference between the various solubilities of Ca compounds.

In respect of the chloride-sulphate type of salinization, this prevails primarily with higher concentrations, and the equilibrium solution takes into account the concentration of Ca-ions on the basis of the solubility of gypsum.

This is more important in respect of carbonates, where, especially in an alkaline medium, the Na-ion has an almost exclusive role in the soil solution.

An example of the chemical composition of a sodic solonetz profile's soil solution is given in Table I.

According to the data presented in Table I, at a total salt concentration of 17 meq/l the amount of the Na-ions reaches about 85% of the cations, and at a total salt concentration of 48 meq/l 97% of the cations are Na-ions. In cases like these, presumably the rate of the Na-ions' exchange adsorption is essentially a function of the sodium ions' concentration in the soil solution.

3. The changes in the pH value of the adsorbent soil-solution system and the colloid-chemical changes brought about by the former.

Many authors [1, 12] trace the strongly alkalizing effect of solutions containing soda to these latter factors.

If the pH value of the medium becomes alkaline it involves the following changes:

(a) The organic matter in the soil becomes soluble;
(b) It increases the degree of dispersion of the soil's mineral colloids; and
(c) It brings about a change in the colloid particles' surface charge.

At a relatively lower pH value, the latter two factors lead to a decrease in the relative quantity of the exchangeable Na-ions [4] through the increase of the adsorption capacity, under the same conditions. These include the same concentration of the solution and the same relative amount of the Na-ions in the liquid phase, provided that the surface charge changes solely in proportion to the colloid particles' degree of dispersion.

The organic colloid particles becoming soluble, the low solubility of calcium carbonate, and hence the vastly increased importance of the Na-ions in the soil solution, have an opposite effect. It is also probable that in a more strongly alkaline medium, where the pH value is over 8, the value of the surface charge increases to a higher degree than the value corresponding to the degree of dispersion, because of the adsorption of the OH^- ions [12].

The above processes show that in soils containing salts capable of alkaline hydrolysis, the adsorption of the Na-ions is very extensive, even in the case of relatively low concentrations; also, from the point of view of the soils' alkalization, the use of ground-water containing soda, or irrigation water containing Na salts capable of alkaline hydrolysis, is much more dangerous than the use of solutions which contain neutral Na salts.

There are relatively few numerical data characterizing the effect of anions, and especially that of Na salts, capable of alkaline hydrolysis. Therefore it seems highly advisable to extend studies concerning ion exchange in this direction.

The conditions of conducting the investigations are as follows:

1. The organic and mineral parts of the soil should be examined separately because the effect of the medium becoming alkaline manifests itself in different forms.
2. When examining the mineral part, it is practical to choose a model material of homogeneous composition on which the colloid-chemical effects appearing in alkaline medium can be clearly observed.

TABLE I

ANALYTICAL DATA OF THE SOIL-SOLUTION, THE AQUEOUS EXTRACT AND THE GROUND WATER OF KOPÁNCS-PROFILE No. 301

Depth	Humidity	HCO_3	CO_3	Cl	SO_4	Ca	Mg	Na
(cm)	(%)	(meq/l)						
		Analysis of the soil-solution						
0-10	23.4	3.456	0.29	10.32	6.74	5.78	1.94	19.61
10-20	22.4	2.279	-	6.12	0.54	1.85	0.48	14.32
20-40	24.9	3.755	0.26	27.38	0.39	1.18	0.63	46.45
40-60	24.4	6.501	1.64	15.40	0.79	1.21	0.57	33.15
60-80	21.5	2.260	-	48.80	9.39	1.57	1.13	75.65
80-100	20.6	1.878	-	68.74	70.26	4.35	2.67	136.87
	Dry residue %	Analysis of the aqueous extract (meq/100 g soil)						
0-10	0.192	1.154	-	0.280	0.345	0.714	0.394	0.771
10-20	0.229	1.412	-	0.360	0.545	0.229	0.197	1.891
20-40	0.376	2.288	0.152	0.480	1.218	0.209	0.098	3.679
40-60	0.311	2.476	0.132	0.760	1.279	0.124	0.139	4.252
60-80	0.460	2.158	0.210	1.040	2.372	0.334	0.156	5.080
80-100	0.523	1.800	0.210	1.560	4.027	0.499	0.222	6.666
		Water analysis (meq/l)						
		10.05	-	48.42	103.74	27.75	17.71	81.66

3. During the experiments, special attention should be paid to ensure that the ratio of the Na^+, Ca^{++} concentrations of the liquid phase is large, corresponding to the concentration conditions prevailing in the liquid phase of sodic soils.
4. In the course of the experiments it is necessary to watch the changes occurring in the system's colloid-chemical state, and in its surface charge, in a relatively wide range of concentrations.
5. Comparative experiments must be conducted with systems containing neutral Na salts. As the first step in the evaluation of the experimental data comparison should be made on the basis of an index proportional to the surface size of the adsorbent relating to the ion (sodium ion) in question.

The examinations were started by studying the physico-chemical and colloid-chemical processes taking place in the mineral part of the soil.

EXPERIMENTAL

In the authors' investigations, bentonite from Istenmező, Hungary, was used. According to chemical and mineralogical examinations (cations' adsorption capacity, composition of exchangeable cations, differential thermal-analysis, X-ray diffraction analysis) it contains Ca-montmorillonite in high purity.

1. Fractions smaller than 2 μm diam. were separated by sedimentation from a water-suspension of the material to be examined. The separated fraction was used partly in its natural condition in further investigations, and partly saturated with the corresponding cations.

2. Kinetic determinations in systems of bentonite-NaCl solution 1:5 aqueous suspension of the bentonite's separated fraction was used in the determinations by diluting it with Na-chloride solution of corresponding concentration, so that the ratio of the solid and liquid phases of the suspension was 1:10. For the kinetic determinations the suspension was labelled with ^{24}Na isotope; under constant mixing, samples were taken from the suspension at 2, 15 and 30 min respectively and at 1, 2, 4, 6, 24, 48, 96 and 120 h respectively. The samples were centrifuged immediately and the activity and total concentration of the Na-ion of the solution were determined (Table II). The activity of the solid phase plotted against time formed a graph sharply increasing at the beginning and then becoming flat. A similar graph was produced by the result of our kinetic determination carried out with soil-Na chloride solution in a similar arrangement (Fig. 1).

3. Examinations were conducted with systems containing neutral Na-salts, namely: Ca-bentonite - NaCl solution, and Ca-bentonite - Na_2SO_4 solution. In an arrangement identical with that of the kinetic determinations, the extent of the ^{24}Na isotope adsorption of these systems as a function of Na-ion concentration in the equilibrium state was determined. The ratio of the solid and liquid phases of the suspension was also 1:10. The initial concentrations of the solutions containing Na-ions were: 0.01 $\underline{N}$; 0.05 $\underline{N}$; 0.1 $\underline{N}$; 0.25 $\underline{N}$; 0.5 $\underline{N}$; and 0.75 $\underline{N}$ respectively. When a state of equilibrium was achieved samples were taken, the solid and liquid phases separated by centrifuging, and we determined the solution's ^{24}Na and ^{45}Ca activity, as well as the equilibrium concentration of the Na and Ca ions. From the values, the quantity of ^{24}Na adsorbed on the surface (Fig. 2), and the value of the distribution quotient of ^{24}Na isotope between the liquid and solid phases, (Table III), were calculated. The amounts of the exchangeable Na^+ and Ca^{++} ions were determined, and on the basis of the Vanselow equation the equilibrium constants were also determined. The data show that the isotope adsorption of the two systems, disregarding higher concentrations, were almost identical.

4. Experiments conducted with Na-salts capable of alkaline hydrolysis.

The experiments were conducted with bentonite - Na_2CO_3 solution systems, where the *initial concentrations* of Na_2CO_3 were as follows: 0.01 $\underline{N}$; 0.05 $\underline{N}$; 0.25 $\underline{N}$; and 0.5 $\underline{N}$.

The rate of swelling of the above systems was examined, together with the changes in the time of thyxotropic consolidation, the changes in its electrokinetic potential, depending on the Na_2CO_3 concentration, and the rate of the ^{24}Na adsorption on the solid phase as a function of the Na-ion concentration of the Na_2CO_3 solution.

(a) The experiments conducted show that the system's swelling ability grew in the Na_2CO_3 solution and gives a maximum value at an initial Na-ion concentration of 100 meq/l (Fig. 3).

TABLE II

THE ADSORPTION OF ^{24}Na ISOTOPE AND THAT OF THE Na^+ ION AS A FUNCTION OF TIME

Time (min)	Na^+ adsorbed as % of initial Na^+ conc.	Activity adsorbed as % of initial activity
2	16.55	8.05
15	17.05	18.85
30	18.10	22.30
60	19.50	24.60
120	19.40	25.35

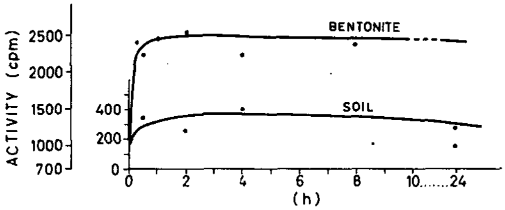


Fig. 1

Change in the adsorption of ^{24}Na plotted against time in systems of bentonite - 0.05 N NaCl and soil - 0.05 N NaCl. The scale from 700 to 2500 refers to bentonite and the scale from 0 to 500 refers to soil.

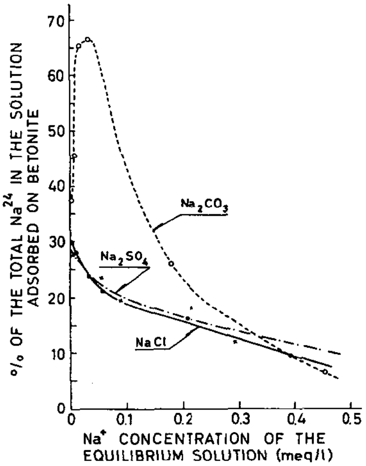


Fig. 2

The activity taken up by bentonite in the percentage of the initial activity as a function of the equilibrium Na concentration in systems of bentonite - NaCl solution, bentonite - Na_2SO_4 solution and bentonite - Na_2CO_3 solution.

TABLE III

RATIO OF THE ^{24}Na ACTIVITY OF THE EQUILIBRIUM SOLUTION AND OF THE BENTONITE'S SURFACE AS A FUNCTION OF THE EQUILIBRIUM SOLUTION'S IONIC STRENGTH IN SYSTEMS OF BENTONITE - NaCl SOLUTION AND BENTONITE - Na_2SO_4 SOLUTION

Ionic strength of equilibrium solution (mol/l)	Activity of solution Activity of surface NaCl (ml/g)	Activity of solution Activity of surface Na_2SO_4 (ml/g)
0.01	0.235	0.275
0.02	0.26	0.285
0.05	0.335	0.338
0.1	0.42	0.415
0.2	0.49	0.44
0.3	0.62	0.56
0.4	0.775	0.735

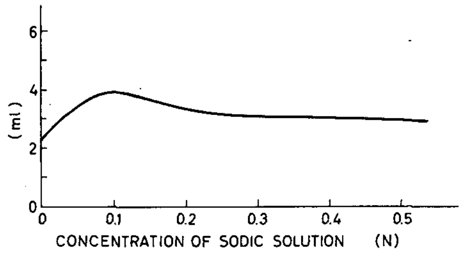


Fig. 3

Swelling of bentonite suspension

(b) The time of the thyxotropic consolidation of these same systems considerably decreased due to the effect of the Na_2CO_3 solution: it reached the minimum at an initial Na-ion concentration of 100-500 meq/l, then it rapidly increased with further increase in the concentration (Fig. 4). Between 100 - 500 meq/l the system showed a characteristic reopexy.

(c) Similarly the electro-kinetic potential values determined on the basis of electroforetical migration velocity also reached the maximum with the increasing Na_2CO_3 concentration (Table 4).

(d) To determine the rate of ^{24}Na adsorption on the solid phase in systems of bentonite - Na_2CO_3 solution, experiments were carried out in a similar manner as with systems of bentonite - NaCl solution and bentonite - Na_2SO_4 solution.

The experimental data obtained show (Fig. 2) that while in systems containing neutral Na-salts the quantity of ^{24}Na adsorbed by the bentonite was

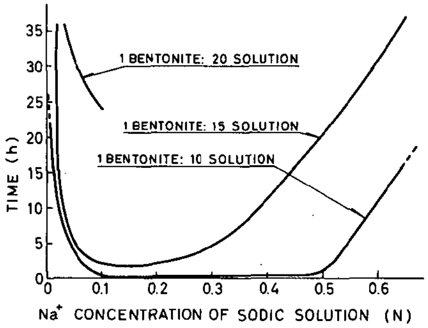


Fig. 4

Time of the thyxotropic consolidation of bentonite suspensions treated with Na_2CO_3 solutions of different concentration

TABLE IV

THE DEPENDENCE OF THE ELECTRO-KINETICAL POTENTIAL (S POTENTIAL) UPON THE CONCENTRATION OF THE Na_2CO_3 SOLUTION, ON THE EDGE SURFACE OF BENTONITE SUSPENSION – Na_2CO_3 SOLUTION (1 : 100)

Concentration of Na_2CO_3 solution (N)	Electroforetic migration velocity (cm/s)	Electrokinetic (S) potential (mV)
0	0.000467	25.6
0.005	0.0008	44.2
0.01	0.00113	60.8
0.05	0.00115	63.0
0.1	0.00122	66.4
0.25	0.00102	55.6
0.5	0.00095	51.9
0.75	0.00088	48.1

almost identical, as a function of concentration it decreased to an ever greater extent. In the bentonite-Na_2CO_3 solution system the quantity of ^{24}Na isotope adsorbed by the bentonite increased at the beginning with the concentration of the Na-ions, and it reached maximum values at a Na-ion concentration of 50 meq/l. A similar picture is obtained when plotting the isotope's distribution quotients against the equilibrium ^{24}Na concentration in the solution.

DISCUSSION

From the graphical evaluation of data relating to the kinetics of the sodium isotope adsorption in the system of bentonite-NaCl solution (Fig. 1), three part processes can be distinguished. They seem to satisfy the formal kinetic equation applied by L. IMRE [7] to describe the processes taking place on the surface of a crystallized solid system which is in equilibrium with its saturated solution:

$$x_t = A_0 - /A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_3 e^{-k_3 t},$$

where x_t = the amount of isotope taken up by the absorbent till t, point of time.

A_0, A_1, A_2, A_3 = constants

k_1, k_2, k_3 = rate constants of the part processes.

Constants ($k_1 = 1.9$ min^{-1}; $k_2 = 0.362$ min^{-1}; $k_3 = 0.0253$ min^{-1}), determined by graphical evaluation, show that the part processes proceeded with essentially different velocity. The first part process occurs in the first 12-15 min, the second, marked by k_2 rate constant, ends in the 1.5 - 2 h of the examination, and the third process is a very slow one.

After two hours the amount of ^{24}Na adsorbed on the surface (Table II) was 6% higher than the amount of sodium ions exchanged. If it is considered that, in the second period, between 15 - 120 min, around 7% of the total activity of the solution came to the surface, the second part process, marked by k_2 rate constant, seems to be identical with the isotope exchange.

When plotting the logarithm of the quantity of the bentonite's exchangeable Na-ions as a function of the logarithm of the solution's initial Na-ion concentration, a linear logarithmic relation is obtained for the first two hours' period, which seems to satisfy the isotherm by Freundlich (Fig. 5),

$$x = K C^p$$

where K and p are constants (the numerical value of K = 0.142 and that of p = 1.14). Thus the amount of the adsorbed Na-ions is in proportion to the initial concentration of sodium ions in the solution.

The isotope exchange characteristic of the second phase seems to be supported by the fact that, when plotting the isotope's distribution quotient between the liquid and solid phases against the Na-ion concentration of the K_2 process, a linear relation is obtained (Fig. 6):

$$\frac{S_1}{S_0 - S_1} = \frac{C}{A},$$

where S_1 = the amount of ^{24}Na in the solution in equilibrium with the $S_0 - S_1$ = the amount of ^{24}Na on the surface. C = the Na-ion concentration of the solution in the second process (equilibrium sodium ion concentration).

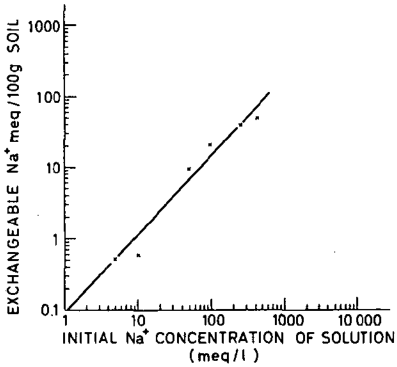


Fig. 5

Amount of exchangeable Na^+ ions of bentonite plotted against the initial concentration of Na^+ ions

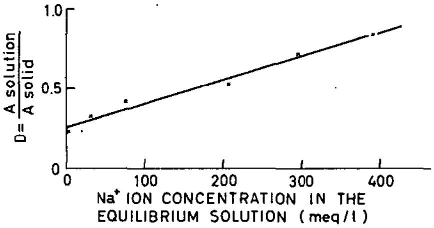


Fig. 6

Distribution quotient of ^{24}Na between the solid and liquid phases as a function of the Na^+ ion concentration relating to the second part process

The slope of the line gives the isotopically-exchangeable surface size relating to ^{24}Na. It is the first part process, however, which exercises influence on the precision of the determination.

It is apparent from the above that the first two part processes of the kinetic process may be characterized by cation exchange and by isotope exchange and it seems that, considering the very low velocity of the third reaction stage, the state of the isotope exchange near the equilibrium in an analogous system is achieved in about 2 h, and that the value of the isotope's distribution quotient is the measure of the surface size exchangeable with the given isotope.

To clarify the character of the third phase further examinations would be necessary. This, however, was not the aim of the authors' experiments.

The effect of anions in systems containing neutral Na-salts.

According to the data of the authors' comparative examination of systems of bentonite-NaCl solution and bentonite-Na_2SO_4 solution, the adsorption of the ^{24}N isotopes was nearly the same in both systems, which indicates that the nature of the process is essentially the same in the presence of either anion.

A slight deviation was shown in the degree of isotope adsorption, which was always slightly higher in the case of a bentonite-Na_2SO_4 solution system than in the case of a bentonite-NaCl solution system. This deviation increased parallel with the increase in Na^+ ion concentration in the equilibrium solution. Accordingly, the distribution quotient of ^{24}Na is smaller between the solution and the surface of the adsorbent in the case of solutions of greater ionic strength (Table III).

Considering that the appearance of the isotope adsorption graphs is the same, the nature of the process is also the same, and it is therefore probable that the small deviation originates in the difference between the average activity coefficients and can be eliminated by taking the activity coefficients into account. This is indicated by the fact that the average value of the equilibrium constants, calculated on the basis of Vanselow's equation with respect to the average activity coefficients, showed good agreement in both systems. It was 0.0253 in the bentonite-NaCl solution system and 0.0258 in the bentonite-Na_2SO_4 solution system. It must be noted, however, that in the calculations only those data were taken into account where the ionic strength of the solution, in equilibrium with bentonite, was less than 0.5 mol. This was because, in the case of solutions of higher concentration, it would be necessary to deal with deviations caused by the different solubility of $CaCl_2$ and $CaSO_4$ formed in the course of exchange. The colloid-chemical experiments carried out in a bentonite-soda solution system show clearly that the adsorbant's colloidic characteristics markedly changed in the presence of Na_2CO_3. The experimental data obtained this way are in accordance with the experimental data published by ANTIPOV-KARATAEV [1]. He treated the horizon A of a chernozem soil with soda solution and examined the changes in the system's degree of dispersion, swelling ability, and in the amount of soluble humus. On the basis of his experiments Antipov-Karataev found that, along with an increase in the concentration of Na_2CO_3, the amount of the particles smaller than 1 μm diam. also increased. The experimental data, in accordance with the above data in the literature, clearly show that along with an increase in the solution's Na_2CO_3 concentration, the colloid particles' degree of dispersion also increases, as well as their swelling ability, while their colloid-chemical status undergoes a change, with the time of thyxotrope consolidation lessening. The electro-kinetic potential of the bentonite-Na_2CO_3 solution changes parallel with the colloid-chemical change of state.

The change in the degree of dispersion and in the electro-kinetic potential involves a change in the size of the surface exchangeable with Na-ions. This fact is supported by the authors' isotope adsorption experiments carried out in a system of bentonite-Na_2CO_3 solution.

When comparing the data of these determinations (Fig. 2) with the data of determinations carried out in systems containing neutral sodium salts, it appears that, while in the latter systems the amount of ^{24}Na isotope bound by the adsorbent was nearly the same, in systems containing Na_2CO_3 solutions the nature of isotope adsorption was definitely different. In this case the amount of ^{24}Na bound by the bentonite increased first, along with the increase in the Na-ion concentration of the Na solution, and it reached maximum value at a Na^+ ion concentration of about 50 meq/l. This considerable adsorption of ^{24}Na seems to support the previous assumption, namely, that a change in the degree of dispersion and in the surface charge of a system brings about an increase in the surface exchangeable with sodium ions. This is one of the main factors causing the sodium ions' extensive adsorption in alkaline medium.

The precise measurement of the above correlations and the numerical determination of the effects of the different factors is a further task to be carried out in the future.

REFERENCES

[1] ANTIPOV-KARATAEV, I.N., Melioracija szoloncov v S.S.S.R., Ak. Nauk. S.S.S.R. (1953).

[2] BABCOCK, K.L., "Theory of the chemical properties of soil colloidal systems at equilibrium", Hilgardia 34 11 (1963) 417-542.

[3] BABCOCK, K.L. and SCHULZ, R.K., "Effect of anions on the sodium-calcium exchange in soils", Soil Sci. Soc. of Am. Proc. 27 6 (1963).

[4] PRATT, P.F., WHITTIG, L.D. and GROVER, B.L., "Effect of pH on the sodium-calcium exchange equilibria in soils", Proc. Soil Sci. Soc. of Am. 26 3 (1962) 227-230.

[5] DARAB, K., Talajgenetikai elvek alkalmazása az Alföld öntözésénél. OMMI Genetikus talajtérképek, Ser.1 4 (1962) Budapest.

[6] DARAB, K. and SZABOLCS, I., "Types of secondary salinization of soils in the irrigated zones of the region of the Great Hungarian Plain", 7th Int. Congr. of Soil Science, Madison, Wisc. USA VI 17 (1960).

[7] IMRE, L., Z. Phy Chem. A. 153 (1931) 262.

[8] IMRE, L., Neuere prinzipielle Bemerkungen zur heterogenen Reaktions-Kinetic, Kolloid Zeitschrift B.131 1 (1953) 21-38.

[9] MADOS, L., Az öntözővizek vizsgálata és minősitése, Mezőgazd. Kut. XII 121 (1940).

[10] MOLNÁR, F., MÁTÉ, F. and KENDE, I., "A talaj $^{32}PO_4^{3-}$ felvételének kinetikájához", Agrokémia és Talajtan Tom.6. 3 211-222 (1957).

[11] RICHARDS, L.A., Ed., "Diagnosis and improvement of saline and alkali soils", USDA Handbook No.60 (1954) Gov. Print. Off., Washington, D.C.

[12] SOMMERFELD, T.G., "Effects of anions in the system on the amounts of cations adsorbed by soil materials", Proc. Soil Sci. Soc. Am. 26 (1962) 141-143.

MOBILITIES OF CATIONS IN SOILS AND CLAYS AT VERY LOW MOISTURE CONTENT

J. CHAUSSIDON
INSTITUT NATIONAL DE LA RECHERCHE AGRONOMIQUE
STATION CENTRALE D'AGRONOMIE, VERSAILLES, FRANCE

Very often the cation exchange capacity of a soil depends more upon organic matter than upon inorganic colloids. It is not known what happens to the soil organic matter at very low moisture contents, but it is almost certain that very complex denaturation phenomena affect the ability of the product to bind ions so that study of cation mobilities is very difficult.

When considering the mechanism of cationic mobility, practically all questions which arise may be inferred from the state of adsorbed water. Water determines the electrical work required to remove a cation from the close vicinity of lattice oxygens, through its dielectric constant. It determines the geometry of the diffusion path. It determines the properties of the cation itself towards a migration process, if we assume, as in the case of solutions, that hydration is a factor governing diffusion.

This is why the study of cationic mobility is a difficult matter. If systems are investigated of rather high water content colloidal effects, such as tortuosity, axial ratios of particles, etc., must be taken into account. If systems of low water content are investigated the problem of the solvent state of these conditions arises.

Many highly qualified researchers have worked on the question of water and it would not be of interest to abstract what has been published [1, 2]. However, it may be useful to make some elementary remarks concerning what can be imagined when speaking of low water content.

Consider an expanding lattice clay, such as a montmorillonite, for which the hydration phenomena are very important (referred to in this paper as Camp Berteau montmorillonite, of which there is good knowledge of surface areas, crystallography data, etc.). The minimum homogeneous hydration state for such a clay is one layer of water molecules on the external surface and one layer intercalated between the platelets. Assuming a coverage of 11 Å^2 per water molecule, that is 66 m^2/18 mg, it is seen that this coverage corresponds to a content of 11%:

$$18\left(\frac{80}{66} + \frac{645}{2\times66}\right) = 18(1.21 + 4.89) = 109.8 \text{ mg } H_2O/g.$$

It is then evident that, chemically speaking, this content cannot be considered as a very low water content. This is the first difficulty as, if it is not admitted that a difference of scale in appreciation of water content may exist, investigation must be made of systems which are mixed layers and in which ionic mobility involves at least two distinct phenomena, such as migration in the presence of solvent and solid state diffusion. It is considered by the author that the scales used to define the water content are different for a clay and for a current chemical product.

Even so some things still remain difficult. In the case of potassium montmorillonite X-ray data and water adsorption isotherms show that a 12.5 Å rational spacing is obtained for a P/Po value of the order of 0.8, which corresponds to a water content of 6 H_2O mM/g. As the exchange capacity of this material is 1 meq/g this means that, statistically, 6 H_2O molecules must be found around 1 cation. Taking into account the size of the water molecule, it is difficult to place 6 H_2O molecules around 1 cation in a plane configuration. It is almost possible, but the packing having to be considered for two consecutive oxygen planes, which limit the interlayer space, 12.5 Å instead of 15 Å is obtained for the basal reflection. It is then evident that for 12.5 Å the hydration of interlayer and external cations is not the same.

Chemical and crystallographic analyses of Camp Berteau montmorillonite show that statistically one finds 0.72 K atom per unit cell. As one unit cell contains two hexagonal holes, there is 0.36 K atom per hexagonal hole, that is about one cation every three holes. This statistical repartition is favourable to a type-3 symmetry which leads to the assumption that interlayer K atoms are surrounded by 3 H_2O molecules. It is then easily observed that, under these conditions, a 12.5 Å structure is realized in which:

(1) Protons are equally distributed as to their distance from the lattice oxygen atoms;

(2) Water molecules are bound to the exchangeable cation by one free orbital of the water oxygen atom, the other being engaged in a bond with a proton of the neighbouring water molecule;

(3) Water molecules keep a rotational degree of freedom through liberation of the dipolar moment axis, which would give to the interlayer spacing a "dynamic" definition.

Moreover it must be pointed out that this configuration is not in contradistinction to the well-known turbostratic arrangement of montmorillonite since, as MERING and OBERLIN have shown [3], in Camp Berteau Montmorillonite "the particle is an ordonnated association of primary platelets, with a mutual orientation defined by a rotation of k × 60°, this orientation being held in a thick pseudocrystal".

The direct consequence of such a state of affairs is that some water must be repelled towards the external surface. In the case considered above, a very simple computation shows that the external surface must be covered by about three layers of water molecules. It might be argued that such a configuration is not thermodynamically stable. In fact, for potassium montmorillonite the plot of d ool spacings against water content does not exhibit a very wide plateau around 12. 5 or 15 Å values. It is then possible that these spacings are interesting for crystallography because they correspond to a series of rational reflections, but that they are not correlated to a particularly stable thermodynamic arrangement. A stable arrangement seems realized with an intercalation of 3-in water layers between the platelets. A rational basal spacing of 17. 5 Å is effectively observed for systems ranging from 4% clay suspensions up to solid samples containing at least 65% clay.

MERING and PEZERAT [4] have investigated the position of exchangeable cations close to the oxygen planes, under a vacuum or in the 12. 5 Å state. For sodium and caesium they showed that in the hydrated case atoms stay "inside" the hexagonal holes. It may be presumed that this is also the case with K ions under the same conditions, but it may be questioned whether this is still true when the hydration layer thickness increases. It is possible to remove, by ion exchange, K ions of a K clay, in conditions where the ratio clay/liquid is at least equal to the minimum value where a 17.5 Å rational spacing is still observed. This implies that the 3-in water layers between the platelets are not a barrier preventing ions from diffusing, and then the ability of external cations to move might not be precluded for a 12.5 Å hydration state.

It is possible to discuss this question in the same way for systems equilibrated with very low relative humidities. When outgassing a K montmorillonite at room temperature up to a vacuum of 10^{-6} Hg mm, it was observed that nitrogen and water adsorption isotherms enable surfaces to be computed which are only half the external surface. This has been interpreted as being due to the presence of residual water, the properties of which have been extensively investigated by various workers [5, 6, 7]. This residual water amounts to 1. 2%, and, for the K clay, the comparative studies of hydration isotherms and d ool against P/Po plots ensure that

(1) this water is located upon external surfaces; and

(2) up to P/Po = 0.3, water molecules hydrate only the external surface.

When distributing the number of residual and newly-adsorbed water molecules per cation, at P/Po = 0, 6 H_2O per ion is found and at P/Po = 0.3, 12 H_2O per ion is found.

Then there is the question of whether in this range of hydration external cations can move or not. It is difficult to answer for P/Po = 0, but at P/Po = 0.3 the situation is no worse than it is for internal cations located in 7.5 Å-thick interlayer spacing, for which the hydration number is not greater than 9.

It is somewhat disappointing to see that experimental data are not very numerous in the literature. However, among others, the following may be mentioned: LOW [8, 9, 10] who has developed several studies on ionic migration either by diffusion or by electrical conductivity measurements, MORTLAND [11, 12], who measured the self-diffusion of radioisotopes, CREMERS [13] in Laudelout's laboratory, who determined the electrical conductivity of suspensions and gels, and PONCELET [14], in Fripiat's laboratory, who measured the dielectric properties of Na and Ca clay pellets in the low-moisture content range. At present, in Versailles, Mamy and Weiler are applying dielectric relaxation measurements to K clays, especially, over the whole range of water content.

Chemical determinations of ionic diffusion enabled Husted and Low to say that below a water content of 25%, no cationic diffusion occurs. In a recent paper, Oster and Low were able to determine activation energies for ion movement in Li, Na, and K clays, at three different hydration levels. The "low" moisture content refers to systems in which the percentages of water are: 18.3% for Li clay, 15.2% for Na clay and 10% for K clay. If the measured electrical effects are really to be attributed to cation movement, it seems that the first given limit of 25% is over-estimated. This conclusion would agree with Mortland's results, which show that Na ion diffusion is still appreciable in a 100%-clay sample on an oven-dry basis. Mortland does not give any indication as to the exact water content of the clay at this stage, but it is presumably close to the "residual water" state, for which we have seen that as much as 6 H_2O molecules are still statistically present around an external cation.

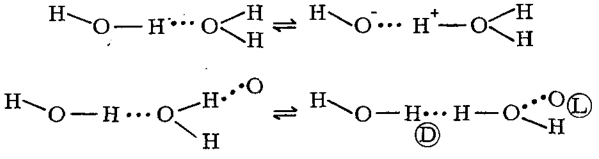
Fripiat and Poncelet have recently studied the hydration of montmorillonite by entropy measurements and electrical conductivity. They showed, firstly, that if σ is the specific conductivity, for a given frequency there is a linear correlation between $\log \sigma$ and the number of charge carriers. Secondly, it is experimentally observed that if $\log \sigma$ is plotted against the number of adsorbed water molecules a linear correlation is obtained. The validity of this result for K clays at 30°C, from P/Po = 0 up to P/Po = 0.95 was checked for frequencies ranging from 0.1 kHz to 20 kHz. For these hydrations plots were made of several linear parts. The only interpretation is that the charge carrier is hydrated with a constant hydration number within certain ranges of relative humidities. From this result it is impossible to infer that the charge carrier is a cation or, for instance, a proton which comes from the dissociation of residual water. It can only be noted that STAMIRES [15], working in the same way on zeolites, concludes that these plots are characteristic for cationic conductivity.

A difficulty follows from the examination of Cremers's experiments performed in Professor Laudelout's laboratory. It was observed that, in the adsorbed state, limiting conductivities of exchangeable alkaline ions depend upon the crystallographic radii and not upon the hydrated radii. Laudelout's conclusion is that, in the adsorbed state, ions move in a dehydrated state even in gels which are highly hydrated. This is evidently in contradistinction to results which have been noted previously. There is no decisive explanation of this, but it is questionable whether these results clash with the others as much as it appears at first sight.

It seems well-established that, if regular water has, within a short distance from a central (reference) molecule, an arrangement which looks like the tetrahedral arrangement of ice, dissolved cations bring to this structure modifications which depend at the same time upon the size and charge of the ions. GURNEY [16] classified ions in water structure as disrupting, inactive, or structure-forming, according to these two parameters. This concept agrees with and explains various anomalies of electrolyte solutions. When considering solutions of alkaline ions it is clear that the only parameter to be taken into account is the size, because all the ions bring the same charge. In the adsorbed state the constancy of charge may be queried. The largest ions cannot make their way into the hexagonal holes like the smaller ones, and it is not impossible that, with a large cation, a residual interlayer positive charge still exists, more important than with a small cation. Then, two "opposite" parameters (size and charge) increase jointly, and the resultant effect may reverse properties usually found in solution. If, as Gurney says, the behaviour of a "structure-former" is favoured both by a small size and a large charge, it could occur that in the adsorbed state Cs is more a structure-former than Na because of the residual charge, and in spite of the larger size. Then the limiting cationic conductivity of Cs would be smaller than that for Na. If this schematic outline proved to be sound, it would be an implicit argument for ionic hydration. It may be noted that a very similar explanation has been given in different terms by FRIPIAT et al. [7], to explain differences in exchange selectivities between ion exchange resins and clays.

However, the problem of the charge carrier in low-moisture-content systems is not solved. DUCROS et al. [17], working with nuclear magnetic resonance measurements, showed that for a Na montmorillonite containing 14% water, the width of the resonance line of hydrogen was small at high temperatures and increased by a factor of six from -100°C to -200°C. He attributed this phenomenon to high mobility of protons with an activation energy of 2 kcal/M. However at low-water content (5%), the width of the resonance line does not differ more than 3-4 G from room temperature down to -200°C. He considers then that proton diffusion is hindered, and that protons are either motionless or moving around preferential sites which could be the exchangeable cations. This does not disagree with the fact that chemical transformations of adsorbed molecules due to residual water are only noticeable at very low moisture content, but this is not in full agreement with a protonic conductivity theory in weakly-hydrated systems. Explanations given by Ducros suggest more a group of H_2O molecules rotating around a cation than an atmosphere of dissociated protons.

GRANICHER et al. [18] has postulated that in an ice-crystal network, two types of defects could be present: translational defects due to a translation of proton along the O—H bond direction, and orientational defects due to a rotation of water molecule around an O—H bond.



The first case only involves a real ionization of water molecule with proton transfer, because of the displacement of the co-ordination link. The translational defect has an activation energy of 0.33 eV, whereas the orientational defect has an activation energy of 0.5-0.6 eV. As dielectric absorption of ice occurs at low frequencies, these defects can be studied easily with a current impendance bridge. The author recorded the hertzian spectrum of various montmorillonite samples in a frequency range from 0.1 kHz to 20 kHz, for temperatures which vary from 130°K to room temperature; K clays have been investigated both at low-moisture content and as pastes. Recently two Na samples, the concentrations of which are 35% and 20%, have also been studied.

In the range of temperatures and frequencies used experimentally, two types of dielectric effects are found: a dielectric relaxation of water and a free charge carrier conductivity which appears as a background all the more intense as the water content is high.

For K montmorillonites, the activation energy of the dielectric relaxation is 11 kcal/M on average.

For Na montmorillonites besides, a dielectric absorption with $E_A = 7$ kcal/M = 0.3 eV is found.

If an attempt is made to correlate these results with Granicher values, it is seen that the activation energies would correspond to orientational defects due to a rotation of water molecules and, the case of Na-clays excepted, no absorption due to translational defects is detectable.

The activation energy of 0.3 eV found in the Na sample at temperatures between 240 and 263 deg K could be compared with the values given by Granicher for translational defects, that is, water ionization. Taking into account the difference in temperatures, this is perhaps not in contradistinction to Ducros's results.

For potassium the situation is different: a free carrier conductivity is observed, and only activation energies of orientational defects are obtained. The protonic conductivity might then be questioned and these results show, at least, that more experiments are needed before reaching any final conclusion.

This paper is devoted mainly to the state of water rather than cationic mobility itself. It is difficult to separate these two topics and, as a consequence, it may appear that direct methods, such as ion diffusion measurements, do not have the same power of explanation as more sophisticated ones, which theoretically provide information on cation and solvent. Unfortunately these latter are seldom unequivocal, and this is why any real progress must involve close connection between them.

REFERENCES

[1] LOW, P. F., Advances in Agronomy 13 (1961) 269.
[2] TORRENCE MARTIN, R., Clays and clay minerals, 9th Conf. (1960) 28.
[3] MERING, J. and OBERLIN, A., Bull. Groupe Fr. Argiles XIV (1964) 147.
[4] MERING, J. and PEZERAT, H., Bull. Groupe Fr. Argiles X (1958) 25.
[5] MORTLAND, M.M., FRIPIAT, J.J., CHAUSSIDON, J. and UYTTERHOEVEN, J., J. phys. Chem. 67 (1963) 26.
[6] CALVET, R., CHAUSSIDON, J., HELSEN, J. and FRIPIAT, J.J., Nature 196 (1962) 161.
[7] CALVET, R., CHAUSSIDON, J., CLOOS, P., de KIMPE, C., FRIPIAT, J.J., GASTUCHE, M.C., HELSEN, J., JELLI, A., LEONARD, A., PONCELET, G. and UYTTERHOEVEN, J., Bull. Groupe Fr. Argiles XIV (1964) 59.
[8] HUSTED, R.F. and LOW, P.F., Soil Sc. 77 (1954) 343.
[9] LOW, P.F., Soil Sc. Soc. Am. Proc. 22 (1958) 395.
[10] OSTER, J.D. and LOW, P.F., Soil Sc. Soc. Am. Proc. 27 (1963) 369.
[11] LAI, T.M. and MORTLAND, M.M., Clays and clay minerals, 9th Conf. (1960) 229.
[12] LAI, T.M. and MORTLAND, M.M., Soil Sc. Soc. Am. Proc. 25 (1961) 352.
[13] CREMERS, A., Electrical conductivity of clay gels, Dr. Thesis, Louvain Univ. (1964).
[14] PONCELET, G., "Etude de l'eau adsorbée par les montmorillonites, par des mesures d'entropie et de conductivité électrique", Dr. Thesis, Louvain Univ. (1964).
[15] STAMIRES, D.N., J. chem. Phys. 36 (1962) 3174.
[16] GURNEY, R.W., Ionic Processes in Solution. McGraw Hill, London, N.Y. (1953).
[17] DUCROS, P. and DUPONT, M., Bull. Groupe Fr. Argiles XIV (1964) 99.
[18] GRANICHER, H., JACCARD, C., SCHERRER, P. and STEINEMANN, A., Disc. Farad. Soc. 23 (1957) 50.

DIFFUSION OF CATIONS IN SOILS

I. J. GRAHAM-BRYCE
ROTHAMSTED EXPERIMENTAL STATION,
HARPENDEN, HERTS., UNITED KINGDOM

INTRODUCTION

The rate at which nutrients move through soil can possibly limit their availability to plants; in some cases this movement is mainly by diffusion. Several studies of cation diffusion in soils have been reported (e.g. GRAHAM-BRYCE [1, 2], PATIL et al. [3], EVANS and BARBER [4], PLACE and BARBER [5]). For soils or similar materials, the most easily interpreted diffusion measurements relate to self-diffusion which can be studied when a concentration gradient of radiotracers is set up in a system where the non-radioactive ions are uniformly distributed. In this paper a method of determining self-diffusion coefficients for cations is described and previously published results obtained by this method are reconsidered together with some unpublished data. The role of cation diffusion in plant nutrient supply is discussed in the light of these results.

DETERMINATION OF SELF-DIFFUSION COEFFICIENTS

Fick's Law of Diffusion can be solved to give diffusion coefficients for many boundary conditions corresponding to both steady-state and transient experimental systems. Although steady-state experiments are easier to analyse mathematically, they are difficult to set up, particularly with unsaturated soils, so transient systems have an advantage. Because diffusion in soils is slow and the root mean square displacement of the diffusing ions is proportional to $\sqrt{\text{time}}$, the distances over which diffusion is measured must be small for experiments not to take unduly long periods. Also, it is desirable to study diffusion under different soil conditions (for example different compaction or moisture content). The diffusion coefficients discussed here were determined by a method designed to meet these requirements (SCHOFIELD and GRAHAM-BRYCE [6]). The basic model for this method consists of two similar cylindrical sections of soil, prepared in the same way except that one contains uniformly-distributed radiotracers of the ion being studied. When two such sections are placed in contact, the tracer ions diffuse from the labelled to the unlabelled soil and the value of the coefficient of diffusion (D) can be obtained from the quantities of radioactivity in the two layers after a suitable time interval by applying the appropriate solution of Fick's Law:

$$Q/Q_\infty = 1 - 8/\pi^2[e^{-Bt} + e^{-9Bt}/9 + e^{-25Bt}/25 + \text{etc.}]$$

where

B = $D\pi^2/4L^2$,

L = Length of soil section,

Q = Quantity of radioactive ions that has diffused across the boundary in time t, and

Q_∞ = Quantity of radioactive ions that would diffuse across the boundary in infinite time, i.e. half the total quantity of radiotracers present in the two sections.

When Q/Q_∞ is less than 0.5, the system approximates to one of infinite length and the simpler relationship

$$Q/Q_\infty = 2/L\sqrt{Dt/\pi}$$

can be used.

In practice it is difficult to place two thin sections of soil firmly in contact so that the boundary is sharp and to separate them precisely for analysis at the end of the experiment. With sections so large that errors at the boundary can be neglected, experiments take a long time to complete. However, the pattern of diffusion in the model is such that the tracer concentration at the boundary becomes half the initial value in the labelled soil as soon as transfer to the unlabelled section starts, and it remains at this value throughout the period that the sections are in contact. When a permeable ion-exchange material in equilibrium with this boundary concentration is inserted between the sections, the effect on the movement of the tracer is negligible, provided that diffusion through the material is fast enough and the exchange capacity of the material large enough relative to the soil. Permaplex ion-exchange membrane satisfies these conditions. The membrane is thin, but makes a sufficiently rigid barrier between the sections. Keeping the layers separate in this way facilitates removal for analysis and the dimensions of the sections are precisely defined, so that thin layers can be used and results obtained quickly. To set up the experiment,two aliquots of air-dry soil converted to the appropriate ionic form are shaken individually in excess of the pore solution to be used for the diffusion measurements, together with a membrane disc. Radioactive tracers of the ion under study are included with one aliquot. The membrane discs are cut to fit brass cylinders (length 0. 5 in, diam. 1 in) used for diffusion measurements. After equilibration the two discs are removed and held in contact until the radioactive ions are uniformly distributed as a result of diffusion - this takes about 24 h. Either of these discs can then be used to separate the soil layers in the diffusion cylinders; the other is kept to check so that the disc in the cylinder does not gain or lose radioactivity during the experiment. The soil suspensions are centrifuged, and the soils removed and adjusted to the desired moisture content before packing into the diffusion cylinders, where labelled and unlabelled soils are separated by the membrane disc. The cylinders are closed by air-tight lids and kept at constant temperature for a suitable time, after which the soil sections are removed and the radiotracers extracted for liquid counting.

In soils, sources or sinks for the diffusing ions could interfere with the simple diffusion pattern, so that diffusion coefficients calculated as described from Fick's Law would change with time. However the experimental results discussed here followed the theoretical predictions and constant diffusion coefficients were obtained.

DIFFUSION IN HOMOIONIC SOILS

Table I shows self-diffusion coefficients for several cations in homoionic forms of a Lower Greensand soil.

In general these diffusion coefficients are approximately one hundredth of the corresponding values in aqueous solution. As in ion exchange resins, KITCHENER [7], monovalent ions diffuse faster in soil than divalent ions, possibly because the divalent ions retain their hydration spheres more firmly, or because they have a greater affinity for the exchange sites.

DIFFUSION IN SOILS CONTAINING MIXED EXCHANGEABLE CATIONS

In practice ions diffuse in heteroionic soils. Two of the most important nutrient cations are K and Mg; their diffusion coefficients in the presence of other ions, particularly Ca, are therefore of interest - K^{42} has a very short half-life, so Rb was studied instead. Because Rb^+ and K^+ are both

Table I

SELF-DIFFUSION COEFFICIENTS (D) IN HOMOIONIC FORMS OF A LOWER GREENSAND SOIL*

Diffusing ion	Composition of equilibrium soil solution	$D \times 10^7$ (cm^2/s)
^{42}K	[KCl] = M/500	2.2
^{86}Rb	[RbCl] = M/500	1.7
^{28}Mg	[$MgCl_2$] = M/100	0.77
^{89}Sr	[$SrCl_2$] = M/100	0.21

* At 37% volumetric moisture content (pF2). Bulk density 1.6 g/ml. Temperature 21°C. Values of D are the means of 9 determinations.

monovalent cations of similar size, the effects of soil conditions on their diffusion coefficients should be similar, although their behaviour will not be identical (cf. FRIED et al. [8]). Lower Greensand soil prepared in equilibrium with two different mixtures of Rb and Ca was used. The activity ratios in the equilibrium soil solutions were

(i) $\{Rb\}/\sqrt{\{Ca\}} = 0.014$;* this corresponds to the ratio $\{K\}/\sqrt{\{Ca\}}$ in the equilibrium soil solution for the natural soil. Two solution concentrations were used: [$CaCl_2$] = M/5, M/500;

(ii) $\{Rb\}/\sqrt{\{Ca\}} = 0.001$. This value was chosen to represent levels of $\{K\}/\sqrt{\{Ca\}}$ below which uptake of K by plants would be reduced by Ca antagonism. [$CaCl_2$] in this solution was M/500.

For Mg one heteroionic soil was investigated. The composition of the equilibrium soil solution was $\{K\} : \sqrt{\{Ca\}} : \sqrt{\{Mg\}} = 0.0025:1:0.2$, [$CaCl_2$] = M/100. Self-diffusion coefficients for Rb and Ca in these mixed soils are given in Table II.

In these heteroionic soils, values of D_{Rb} are intermediate between those for monovalent ions and divalent ions alone in homoionic soils (Table I) and for the two cases where [$CaCl_2$] = M/500, D_{Rb} is smaller in the soil containing the larger proportion of Ca. The presence of the slow moving divalent ion seems to have a considerable retarding effect on Rb. D_{Mg} was unaffected by the presence of other ions in the soil studied; Mg diffuses more slowly than Rb in homoionic soils and it was present in much greater proportion than Rb in the soils referred to in Table II, so that the smaller effect of Ca is understandable. The effect of soil solution concentration on D_{Rb} indicated by the first two results in Table II will be discussed later.

Diffusion in soil is slower than in aqueous solution because of two factors: first an electrical factor associated with the charges on soil particles, and secondly a geometrical factor due to the longer path and smaller cross-section available for diffusion in a porous medium than in free solution. The electrical factor will be considered first; the geometrical factor

---

* $\{M\}$ *denotes the activity of ionic species M.*

TABLE II

SELF-DIFFUSION COEFFICIENTS FOR Rb AND Mg IN HETEROIONIC FORMS OF A LOWER GREENSAND SOIL*

Diffusing cation	Composition of equilibrium soil solution		$D \times 10^7$ (cm^2/s)
^{86}Rb	$\{Rb\}/\sqrt{\{Ca\}} = 0.014$,	$[CaCl_2] = M/5$	1.2
^{86}Rb	$\{Rb\}/\sqrt{\{Ca\}} = 0.014$,	$[CaCl_2] = M/500$	0.8
^{86}Rb	$\{Rb\}/\sqrt{\{Ca\}} = 0.001$,	$[CaCl_2] = M/500$	0.6
^{28}Mg	$\{K\} : \sqrt{\{Ca\}} : \sqrt{\{Mg\}} = 0.0025 : 1 : 0.2$	$[CaCl_2] = M/100$	0.8

* At 37% volumetric moisture content (pF2). Bulk density 1.6 g/ml. Temperature 21°C. Values of D are the means of 9 determinations. $\{M\}$ denotes the activity of ionic species M.

will be discussed in more detail in connection with effects of moisture content.

The predominantly negative charges on soil particles influence ion movement by their interaction with water, which increases viscosity near the surfaces, and their interaction with the charges on the diffusing ions in the exchange phase. The geometry of the diffusion path for ions within the exchange phase also differs from those in free pore solution. When this difference in path and the increased viscosity are allowed for, the electrical factor should not affect diffusion rates, provided the fields from the fixed charges overlap sufficiently to be continuous in the direction of diffusion. Only where there are gaps would additional energy be required for forward movement.

Diffusion within the exchange phase was studied by measuring D_{Rb} in heteroionic soils of the same activity ratio but with different soil solution concentrations (Table II). The diffusing ions in solution are in equilibrium with those in the exchange phase at all points in the system because ion-exchange is a fast process relative to diffusion. A decrease in solution concentration will therefore increase the proportion of diffusing ions in the exchange phase and so increase the contribution of these ions to the apparent diffusion coefficient. For the soils in Table II the relative quantities of ions in solution and exchange phases (calculated on the basis of volumetric exchange capacities) were approximately equal for $[CaCl_2] = M/500$ and 100 to 1 for $[CaCl_2] = M/5$. If the energy barriers for diffusion in the exchange phase are so great that the exchangeable ions can be regarded as stationary, a large difference in diffusion coefficients will be observed at these two concentrations, whereas if the exchangeable ions diffuse at the same rate as those in free solution, allowing for the different diffusion path and for increased viscosity, concentration will affect D much less. (The effect of concentration on aqueous self-diffusion coefficients is of minor importance in this range). The effect of concentration shown in Table II does not suggest

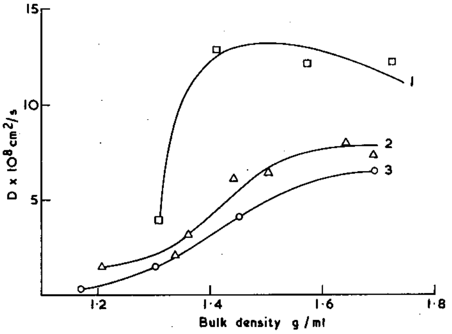


Fig. 1

Effect of compaction on D_{Rb} in Lower Greensand soil

1. $\{Rb\}/\sqrt{\{Ca\}} = 0.014$, $[CaCl_2] = M/5$
2. $\{Rb\}/\sqrt{\{Ca\}} = 0.014$, $[CaCl_2] = M/500$.
3. $\{Rb\}/\sqrt{\{Ca\}} = 0.001$, $[CaCl_2] = M/500$.

[By courtesy of Journal of Soil Science 14 (1963) 191]

that the exchangeable ions are stationary; it appears that they diffuse within the exchange phase, although at a slower rate than in free solution. A similar conclusion has been reached in studies of counter ion diffusion in other ion-exchange materials such as clays (e.g. LAI and MORTLAND [9, 10], BLOKSMA [11]) and resins (e.g. JAKUBOVIC et al. [12, 13], LAGOS and KITCHENER [14]). These results do not indicate how far the slower diffusion in the exchange phase depends on geometrical and viscosity effects or on energy barriers associated with discontinuities in the overlap of the electrical fields from fixed charges. However the effect of compaction on D_{Rb}, discussed in the next section, suggests that the continuity of the exchange phase affects the diffusion rate, particularly for concentrations where a large proportion of the ions are restricted to the exchange phase.

EFFECT OF COMPACTION

Figure 1 summarizes the effects of compaction on D_{Rb} in the three heteroionic soils referred to in Table II; the soil moisture tension was adjusted to pF2 (corresponding to 37% volumetric moisture content) before the diffusion cylinders were packed, and different bulk densities were produced by packing increasing weights of the moist soil into the cylinders and compressing to a constant volume.

For the soil in which $\{Rb\}/\sqrt{\{Ca\}} = 0.014$, $[CaCl_2] = M/5$, (curve 1) D_{Rb} rises rapidly as the compaction is first increased, after which there is little change on further compression. The initial rise may be explained by the establishment of a continuous aqueous diffusion pathway as the water-filled pore space increases, air pockets are removed and the crumbs are pressed into contact. However, compression also increases obstruction by the solid particles; the flat portion of the curve may be attributed to the increasing obstruction by the solid particles balancing the further removal of air pockets and increase in water-filled pore space once continuity has been established. As compaction increases, the pores become saturated and solution is expelled. The increasing obstructional effect is no longer balanced and diffusion coefficients fall. The reliability of values for diffusion coefficients obtained at these large bulk densities is doubtful however, because some soil solution is expelled, so they are not presented in detail. When the soil solution is more dilute (curve 2), D_{Rb} increases more gradually on compression and the curve does not show a plateau in the range of compaction studied. The difference from curve 1 may be related to the greater proportion of ions in the exchange phase at the smaller concentration. With the dilute solution the continuity of the liquid network is less important because it affects a smaller proportion of the ions, and the sharp rise coinciding with the establishment of continuity is therefore not observed. At this concentration the increased contact of the solid surfaces on compression assumes greater significance, for it results in a greater overlap of electrical fields from the fixed charges and permits more continuous movement in the exchange phase, which contains a larger proportion of the diffusing ions. The electrical double layer will also be thicker in the more dilute solution, and this may increase the importance of movement in the exchange phase. The greater continuity of the exchange phase (together with that of the aqueous system as with concentrated solutions) appears to outweigh the obstructional effect, so that no plateau is observed. Curve 3 for $\{Rb\}/\sqrt{\{Ca\}} = 0.001$, $[CaCl_2] = M/500$ is similar to curve 2 over the whole range of compaction, but lies below it as would be expected from the greater proportion of Ca in the system.

The effects of compaction on D_{Rb} can be compared with results for self-diffusion in Bentonite reported by LAI and MORTLAND [10], where the activation energy for cation diffusion decreased with increasing clay content. This was attributed to the "hopping distance" between clay plates becoming smaller as the clay content increased.

EFFECT OF TEMPERATURE

The effect of temperature on diffusion can also be discussed in terms of the electrical factor. Table III shows the effect of temperature on D_{Rb} at two bulk densities in one of the soils previously described.

Temperature has a much greater effect at the smaller bulk density. Activation energies calculated from the Arrhenius type of equation are 3.4 kcal/mole at 1.64 g/ml bulk density and 16.9 kcal/mole at 1.34 g/ml. The first value is very close to that for diffusion in water, whereas the second clearly implies some form of energy barrier. If, as suggested in discussing the effects of compaction, the solid particles are well separated at small bulk densities, there will be discontinuities in the exchange phase and ions will have to leave the double layers to diffuse through the soil. Activation energy will be required to cross the gaps. For soil which is more compressed the electrical fields from neighbouring charges overlap sufficiently for uninterrrupted movement in the exchange phase, and the ac-

TABLE III

EFFECT OF TEMPERATURE ON D_{Rb} IN LOWER GREENSAND SOIL*

Bulk density (g/ml)	Temp. (°C)	$D_{Rb} \times 10^8$ (cm^2/s)
1.34	3.5	0.28
1.34	21.0	1.8
1.64	3.5	5.8
1.64	21.0	8.1

* $\{Rb\}/\sqrt{\{Ca\}} = 0.014$, $[CaCl_2] = M/500$. Each value is the mean of 9 determinations.

tivation energy is correspondingly less. The value for the activation energy at the smaller bulk density appears large when compared with values reported for clays (e.g. LAI and MORTLAND [9, 10], WALKER [15]) or ion exchange resins (MEARES [16]), and some other factor (for example some aspect of microbial activity*) may also be involved.

EFFECT OF MOISTURE CONTENT

The path for the diffusing ions is modified by the changes in compaction described above - the geometrical factor may also be altered by changing the soil-moisture content. Figure 2 shows the relationship between D_{Rb} and moisture content for the heteroionic form of the Lower Greensand soil ($\{Rb\}/\sqrt{\{Ca\}} = 0.014$, $[CaCl_2] = M/500$). Measurements were made at three bulk densities (1.36, 1.7 and 1.95 g/ml) over a range of moisture content from the air-dry condition to roughly field capacity. The temperature was 21°C.

The effect of moisture content was similar at the three compactions. At small moisture contents diffusion was extremely slow and diffusion coefficients were smaller than 10^{-9} cm^2/s. As the soil was made more moist, D increased rapidly over the range 5-15% moisture content depending on compaction, followed by a more gradual increase as more water was added. Except at very small moisture contents, where results are less reliable because of unavoidable errors in counting the small quantities of radiotracers crossing the boundary, values of D increased with compaction at all moisture contents.

It is apparent from Fig. 2 that D_{Rb} is not linearly related to moisture content in these soils over the whole range studied and an equation of the form $D/D_0 = a\theta + b$ (where D_0 = diffusion coefficient in free solution, θ = moisture content and a, b = constants) does not apply. For a porous solid

---

* I am indebted to Dr. B. Ulrich for this suggestion.

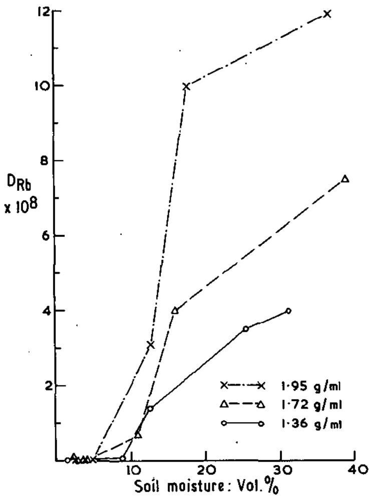


Fig. 2

Effect of moisture content on D_{Rb} in Lower Greensand soil

of length L, the theoretical relationship $D/D_0 = (L/L_e)^2 f$ (where L_e is the length of the effective diffusion path and f is a factor allowing for the non-uniform cross-section of the pores) may be derived for diffusion coefficients calculated as described here, assuming no electrical interaction with the diffusing ions (cf. PORTER et al. [17]). However, although results by Porter et al. show that $(L/L_e)^2 f$ is linearly related to moisture content for chloride diffusion, there seems no theoretical reason why this should be expected over a large range of moisture content in all cases of diffusion in systems of irregularly shaped crumbs which are themselves porous even in a sieved soil. Figure 2 suggests that there are several distinct phases in the relationship between diffusion coefficient and moisture content corresponding to diffusion in different pore systems. When the saturated soil is dried, the largest pores, which are mostly between the crumbs, empty first (phase 1). On further drying water is lost from the crumb pores whose geometry is likely to differ from that of the intercrumb pores, so that in this second phase the relation between D and moisture content differs from that in phase 1. If clay plates are arranged in packages in the crumbs, this could give rise to a third phase at smaller moisture contents and a further corresponding change of slope.

The large increase in D over the 5-15% range of moisture content probably corresponds to phase 2. At smaller moisture contents the path for the diffusing ions would be very tortuous because only the clay packages, many of which must be isolated, would contain water. In phase 2, the establishment of a continuous aqueous network from crumb to crumb through their points of contact would reduce tortuosity considerably, leading to the rapid increase in D. Once this continuity has been established, adding more moisture apparently decreases tortuosity less and the slope decreases again in phase 1. The changes of slope shown by the curves in Fig. 2 may thus be related to the structure of the soil. Because soil structure varies widely, it seems unlikely that there is a unique relationship between ionic diffusion coefficients and moisture content in different soils. Also, results obtained in the laboratory are likely to depend on the method of packing and compacting the soil. This interpretation of the shape of the moisture content/diffusion coefficient curves is similar to that proposed by CURRIE [18] for gaseous diffusion in wet granular materials.

The possibility that moisture content and diffusion coefficient are related by a simple power law fitting the equation $D/D_0 = \eta\theta^{\sigma}$ (where η and σ are constants) was tested by plotting the results on a log-log basis. This type of equation has been applied with moderate success to gaseous diffusion in porous media (e.g. BUCKINGHAM [19], MILLINGTON [20], CURRIE [18]), but Fig. 3 shows that, for the results obtained in this work, it holds over only a limited range of moisture content.

In discussing these effects of moisture content, the electrical factor has been assumed to be constant and only variations in the geometrical factor have been considered. However as the volume of pore solution increases, wider pores are filled and the proportion of ions in free solution increases compared with those in the exchange phase. Consequent changes in the electrical factor will complicate interpretation of the effects of moisture content.

DIFFUSION IN DIFFERENT SOIL TYPES

The results discussed above were all obtained with the Lower Greensand soil that contains little clay. D_{Rb} was also determined under standard conditions in eight other widely different soils. The results (Table IV) indicate limited variation of D_{Rb} in the different soils.

The correlation of these values with soil properties, such as pH, cation exchange capacity, exchangeable K in the natural soil, clay content and volumetric moisture content was tested, but no simple relationship was found. This is not surprising because the value of the diffusion coefficient is controlled by both electrical and geometrical properties for which there can be no simple parameter.

ROLE OF DIFFUSION IN PLANT NUTRIENT SUPPLY

It is tempting to use the values for diffusion coefficients given here to assess the importance of diffusion in transporting nutrients to plant roots. This can be done only with many reservations. The results presented here are for self-diffusion whereas in practice nutrients are transported along a concentration gradient so that diffusion coefficients would not be constant. Further, because of the selective uptake or rejection of components of the soil solution by plant roots the composition of the solution around the root is likely to differ greatly from that in the bulk of the soil. In this situation inter-diffusion and mutual diffusion will modify diffusion coefficients in a manner difficult to predict. The presence of a sink for the diffusing ions (e.g. fixation of K) or the release from fixed forms, or from primary

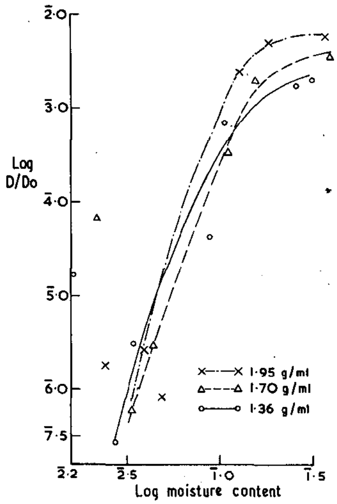


Fig. 3

Logarithmic diffusion/moisture content relationships for Lower Greensand soil

TABLE IV

SELF-DIFFUSION COEFFICIENTS FOR Rb
IN DIFFERENT SOILS AT 21°C

Soil	$D \times 10^8$ (cm^2/s)
Lower Greensand	7. 1
Lower Lias (Banbury loam)	13. 6
Middle Lias (Banbury loam)	5. 6
Upper Lias (Banbury loam)	8. 1
Gault clay	8. 8
Oxford clay	11. 6
Calcareous grit	15. 5
Red tropical clay	13. 7
Kilberanga	9. 3

* Bulk density 1. 7 g/ml. Moisture tension pF 2. $\{Rb\}/\sqrt{\{Ca\}} = 0.014$, $[CaCl_2] = M/500$. Values of D are the means of three determinations.

minerals by weathering, would also disturb diffusion. In this work diffusion coefficients were constant with time indicating that irreversible or slowly reversible processes were not significant, or that their effects remained constant over the period of measurement, but the cylinders were small and the experiments brief so that slow processes are unlikely to have been apparent. A few results suggest that exchange diffusion coefficients are smaller than those for self-diffusion. For example, CHENG [21] reported values of the order of 10^{-9} cm^2/s for the exchange diffusion coefficient of Na in soil columns, the exact value depending on the exchanging cation. These exchange diffusion coefficients decreased with time; a similar result was found by HESLOP and BLACK [22] for phosphate. Heslop and Black attributed this slowing to adsorption and fixation of the diffusing phosphate. A further major difficulty in applying these results to natural soils is that the self-diffusion coefficients were determined with sieved soils. Although some small stable porous crumbs survive sieving, the pores will be arranged differently from a soil made up of natural aggregates.

In spite of these and other possible reservations, some general conclusions about cation diffusion can be drawn and its contribution to nutrient supply indicated. The effect of moisture content on D is large and has been discussed. The importance of this factor has been reported in many other studies of cation and anion diffusion (HESLOP and BLACK [22], STEWART and ECK [23], CHENG [21], PORTER et al. [17], PATIL et al. [3], GRAHAM-BRYCE [1]). When compared with soil type, temperature etc., moisture content appears to be the factor that would influence D most under field conditions. In this work, D decreased rapidly on drying at moisture tensions in the region of the permanent wilting point. Nutrient cations cannot therefore be transported to the root by diffusion when mass flow in the transpiration stream is not also able to operate. For some nutrients selective rejection when the plant is taking in water causes the ion to accumulate in the root zone, when it will diffuse away from the root rather than towards it.

The role of diffusion in nutrient transport can be estimated by calculating the ionic flux to an idealized cylindrical root assuming a constant diffusion coefficient. The condition of a constant concentration at the root surface, or of a constant rate of uptake is imposed. Analogous problems have been solved for heat flow and the corresponding mathematical treatments may be applied. Assuming constant surface concentration, the appropriate equation is (CARSLAW and JAEGER [24]):

$$F = \frac{4b\,D(C_0 - C_r)}{a^2} \int_0^\infty \frac{e^{-Du^2t/a^2}}{u[J_0^2(au) + Y_0^2(au)]}$$

where

F = flux of ions in meq/unit area root surface/s
C_0 = concentration in bulk of soil in meq/ml
C_r = concentration at the root surface in meq/ml
b = ratio of exchangeable to solution ions
D = diffusion coefficient in cm^2/s
J_0 and Y_0 = Bessel functions
t = time in s
a = radius of root.

One of the principal objections to the use of this type of equation is that the value to use for C_r, or for the rate of uptake by the plant, is not known and cannot be measured in conditions wholly free from the effects of film diffusion, even with well-stirred culture solutions. For the equation given, however, if uptake at the root surface is not rate-limiting for the overall nutrient supply, C_r will probably be small in comparison with C_0 and its value will have little effect on the flux. This condition will be assumed here. To calculate the flux of K and Mg diffusing to the root the following representative values may be inserted into the flux equation:

$a = 0.05$ cm (BOULDIN [25], OLSEN et al. [26])
$b = 100$ (estimated from data given by REITEMEIER [27])
$C_0 = 4$ ppm K, 24 ppm Mg
$D_K = 1.0 \times 10^{-7}\ \mathrm{cm^2/s}$
$D_{Mg} = 8 \times 10^{-8}\ \mathrm{cm^2/s}$.

Inserting these values, the calculated flux at the root surface changes with time, as shown in Figs. 4 and 5. Curves for two values of the surface concentration are plotted - 1 ppm and 0.1 ppm; values of C_r less than 0.1 ppm give curves which are almost identical with those for 0.1 ppm. The total quantity of ions transported in time t may be found by graphical integration of $\int_0^t F\,dt$, i.e. from the areas under the curves. For the curves in Fig. 4 this gives 2.9×10^{-3} meq K transported per unit surface area in 70 h when $C_r = 1$ ppm, and 3.7×10^{-3} meq when $C_r = 0.1$ ppm. For Mg the corresponding figures are 5.1×10^{-2} meq and 5.43×10^{-2} meq. Bouldin has estimated that 1 g of roots has a surface area of approximately 40 $\mathrm{cm^2}$ and if 10% of this area is active in uptake, then diffusion could supply $1\text{-}1.5 \times 10^{-2}$ meq K per g of roots in 70 h and approximately 0.2 meq Mg in the same period. These estimates do not allow for possible overlap of the volumes of soil in which ions diffuse to adjacent roots, or for the effects of root hairs.

These calculations are subject to many assumptions and reservations, so that they can be regarded as giving only the order of magnitude of the quantities of ions which can be transported. The curves in Fig. 4, however, indicate the pattern of nutrient supply by diffusion and points of practical usefulness are suggested by the flux equations. If rate processes such as transport by ionic diffusion limit the availability of nutrients, then many of the analytical methods (such as equilibrium extractions) used in advisory work appear to have little theoretical justification and their success, if any, seems fortuitous. The dynamic approach, however, supports some of the established methods. Flux equations, such as that given here, indicate that the total flux over a given time is proportional to $C_0 \times b$, provided D is constant and C_r small enough to be neglected. $C_0 \times b$ is a measure of the exchangeable ions, so that when diffusion is the major method of transport (such as seems likely for K) the supply to the root will depend on the quantity in exchangeable form. Measurement of the exchangeable ions could thus be used to assess availability in soils where diffusion coefficients were similar. These nutrients may be contrasted with those for which mass flow is the dominant method of transport, for example Mg. For these ions, the quantity transported is given by the product of the concentration in the soil solution and the rate of mass flow. If the soil solution is well buffered so that the nutrient concentration remains effectively constant during uptake,

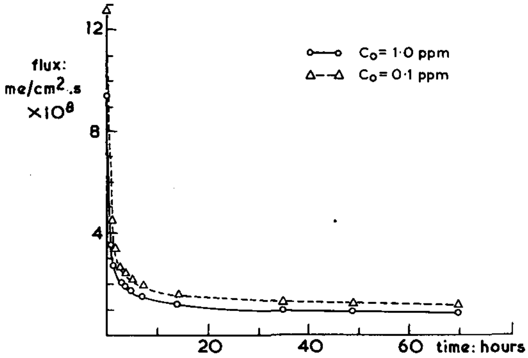


Fig. 4

Change of ionic flux with time for diffusion of K to a cylindrical root, radius 0. 05 cm, with fixed surface concentrations (C_0) of 0. 1 and 1 ppm

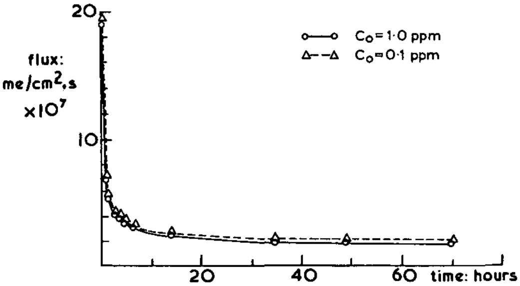


Fig. 5

Change of ionic flux with time for diffusion of Mg to a cylindrical root, radius 0. 05 cm, with fixed surface concentrations (C_0) of 0. 1 and 1 ppm

and if uptake by the plant is directly related to this intensity, the concentration in the soil solution flowing to the root would give a measure of the availability. It will be fortunate if the assumptions on which these conclusions are based prove to be justified in practice, because measurements of ionic movements in soil are time-consuming and could not easily be made part of routine analysis.

SUMMARY

The rate at which a nutrient diffuses through soil may possibly limit its availability to plants. In this paper some previously published self-diffusion coefficients (D) for cations in soil are reconsidered together with some unpublished data. The self-diffusion coefficients were measured by determining the quantities of radiotracers diffusing from labelled to initially unlabelled soil sections through suitably prepared ion exchange membrane barriers. Diffusion coefficients in soil were found to be approximately 10^{-2}

of the values in aqueous solution; this is attributed to geometrical and electrical factors. In homoionic soils, monovalent ions diffuse faster than divalent ions and in soils containing both monovalent and divalent ions, diffusion coefficients for monovalent ions are reduced. Effects of soil solution concentration, compaction and temperature on D_{Rb} suggest that cations diffuse in the exchange phase although more slowly than in free pore solution, and that diffusion in the exchange phase is affected by the extent to which the electrical fields from the fixed charges overlap. Moisture content has a large effect on D_{Rb} and would probably be the most important factor affecting diffusion in the field. It is suggested that there are several phases in the relationship between diffusion coefficient and moisture content, corresponding to diffusion in different pore systems. The effect of soil type was investigated by measuring D_{Rb} in eight widely different soils under standard conditions. No simple relationship with any of the soil properties measured was found. Estimation of the quantities of K and Mg supplied to a cylindrical root under idealized conditions are calculated by means of a flux equation. On the basis of the dynamic picture of nutrient supply, methods of assessing nutrient availability are discussed.

REFERENCES

[1] GRAHAM-BRYCE, I. J., J. agric. Sci. 60 (1963) 239.

[2] GRAHAM-BRYCE, I. J., J. Soil Sci. 14 (1963) 188.

[3] PATIL, A. S., KING, K. M. and MILLER, M. H., Canad. J. Soil Sci. 43 (1963) 44.

[4] EVANS, S. D. and BARBER, S. A., Soil Sci. Soc. Amer. Proc. 28 (1964) 53.

[5] PLACE, G. A. and BARBER, S. A., Soil Sci. Soc. Amer. Proc. 28 (1964) 239.

[6] SCHOFIELD, R. K. and GRAHAM-BRYCE, I. J., Nature (Lond.) 188 (1960) 1048.

[7] KITCHENER, J. A., in Modern Aspects of Electrochemistry. No. 2, (O'M. Bockris, J. Ed.) Butterworths Scientific Publications, London (1959) p. 144.

[8] FRIED, M., HAWKES, G. and MACKIE, W. Z., Soil Sci. Soc. Amer. Proc. 23 (1959) 360.

[9] LAI, T. M. and MORTLAND, M. M., Soil Sci. Soc. Amer. Proc. 25 (1961) 353.

[10] LAI, T. M. and MORTLAND, M. M., Clays and Clay Minerals 9 (1962) 229.

[11] BLOKSMA, A. H., J. Colloid. Sci. 12 (1957) 40.

[12] JAKUBOVIC, A. O., HILLS, G. J. and KITCHENER, J. A., J. Chim. Phys. 55 (1958) 263.

[13] JAKUBOVIC, A. O., HILLS, G. J. and KITCHENER, J. A., Trans. Faraday Soc. 55 (1959) 1570.

[14] LAGOS, A. E. and KITCHENER, J. A., Trans. Faraday Soc. 56 (1960) 1245.

[15] WALKER, G. F., Nature (Lond.) 184 (1959) 1392.

[16] MEARES, P., J. Chim. phys. 55 (1958) 273.

[17] PORTER, L. K., KEMPER, W. D., JACKSON, R. D. and STEWART, B. A., Soil Sci. Soc. Amer. Proc. 24 (1960) 460.

[18] CURRIE, J. A., Brit. J. appl. Phys. 12 (1961) 275.

[19] BUCKINGHAM, E., U. S. Dept. Agric. Bureau of Soils Bull. No. 25 (1904).

[20] MILLINGTON, R. J., Science 130 (1959) 100.

[21] CHENG, C.-Y., Ph. D. thesis, University of Illinois (1960).

[22] HESLOP, J. M. and BLACK, C. A., Soil Sci. 78 (1954) 389.

[23] STEWART, B. A. and ECK, H. V., Soil Sci. Soc. Amer. Proc. 22 (1958) 260.

[24] CARSLAW, H. S. and JAEGER, J. C., Conduction of Heat in Solids (2nd Ed.) Oxford University Press (1959) p. 336.

[25] BOULDIN, D. R., Soil Sci. Soc. Amer. Proc. 25 (1961) 476.

[26] OLSEN, S. R., KEMPER, W. D. and JACKSON, R. D., Soil Sci. Soc. Amer. Proc. 26 (1962) 222.

[27] REITEMEIER, R. F., Adv. in Agronomy 3 (1951) 113.

IONIC MIGRATION IN SOILS AND CLAYS

C. DAKSHINAMURTI
DIVISION OF AGRICULTURAL PHYSICS,
INDIAN AGRICULTURAL RESEARCH INSTITUTE,
NEW DELHI, INDIA

Migration of ions in soil to plant roots takes place either by the viscous movement of the soil solution through the pore space, or by ionic diffusion. As long as there is drainage viscous flow is possible, but when once the drainage stops ionic diffusion alone migrates the ions. The amount of the nutrient ion that diffuses at a given temperature in a soil depends upon the soil structure and the moisture condition.

In free liquids, or in straight uniform channels, the diffusing ions are not obstructed in the course of their migration along the direction of measurement. In such cases the whole fractional area of the cross-section will be effective. But in a bed of soil where the channels bend round corners, forming twists and constrictions, the quantity of the ion diffused falls short of the expected value and the decrease in the ion diffused in such cases should be attributed to the twists and constrictions. The effective fractional areas obtained under different conditions of compaction give a measure of the effect of twists and constrictions on the migration of ions in each case.

EFFECTIVE FRACTIONAL AREAS

The tortuosity experienced by the migrating ions should be the same for a bed of inert materials, whether the migration is recorded by diffusion measurements or by electrical conductivity.

Diffusion experiments were carried out under conditions of constant total ionic concentration, following the treatment of EINSTEIN [8]. The amount, q, of ions that diffuse across area A in time τ is related to the diffusion coefficient, D, and the root mean square displacement of an individual ion, $\overline{\Delta x}$ by the equation

$$\sqrt{\frac{\pi}{2}} \times \frac{q}{C_B A} = \sqrt{2D\tau} = \overline{\Delta x} \qquad (1)$$

where C_B is the concentration of the ions at the boundary. In the case of porous beds where f is the fractional area of cross-section, C_B is related to the concentration of the electrolyte C_0 by the equation

$$C_B = \frac{f}{1+f} \times C_0. \qquad (2)$$

If q, A, f and C_0 are measured D is obtained by combining equations 1 and 2. If D is known C_B can be calculated in an unknown porous bed and the effective value of f can then be obtained by using Eq. (2).

TABLE I

FRACTIONAL AREAS CALCULATED FROM DIFFUSION AND CONDUCTIVITY MEASUREMENTS IN INERT MATERIALS AND CLAYS

Material	Diffusion measurements				Conductivity measurements	
	Experiments made (No.)	f_{Br^-}*	$f_{NH_4^+}$	Porosity (P)	Porosity (P)	$f_{cond.}$
Glistening dew	6	0.289	0.327	0.366	0.367	0.290
Glistening dew and glass beads	2	0.179	-	0.236	-	-
Sand	2	0.273	0.291	0.352	0.352	0.269
Bentonite	4	0.808	0.970	0.996	0.996	0.836
Rothamsted subsoil clay	4	0.790	-	0.909	0.909	0.790
Kaolin	4	0.462	-	0.716	-	-

* f = fraction

(After Schofield and Dakshinamurti, 1948)

Table I gives the fractional areas calculated from diffusion and conductivity measurements in inert materials and clays. Electrical conductivities were measured, using a cell with parallel rectangular electrodes.

For a bed of coarse particles, there is no doubt that the ratio f/P is simply an indication of the twists and constrictions in the water channels. The ratios obtained in Table I for the kaolin and subsoil clay are readily interpreted in this way. In the case of bentonite, however, it will be seen that f conductivity is 0.836 while f_{Br^-} is only 0.808. This difference is outside the experimental error and should be due to the excess of cations balancing the negative charges on the particles. The kaolin and the subsoil clay also give rise to additional conductance that can be observed in very dilute salt solutions, but which would not give rise to significant differences in Table I. The 0.91% suspension of bentonite in N/10 KBr is a thixotropic gel, and has a conductivity 16% less than that of the salt solution. The particles, although they occupy only 0.4% of the total volume, consist of plates only 10 Å thick. The weak rigidity of the gel and the hindrance to ionic migration could both be due to the existence of a network in which the particles tend to adhere by their edges.

The relative conductivity of bentonite suspension in potassium bromide solutions at different concentrations is given in Table II. In a solution con-

TABLE II

RELATIVE CONDUCTIVITY OF BENTONITE SUSPENSIONS IN POTASSIUM BROMIDE SOLUTIONS AT DIFFERENT CONCENTRATIONS

Normality of electrolyte	Weight of Bentonite (%)	Relative conductivity
0. 1	0. 91	0. 836
0. 05	1. 14	0. 924
0. 0333	0. 76	0. 974
0. 025	0. 57	1. 028
0. 0167	0. 38	1. 026
0. 0125	0. 27	1. 037
0. 0083	0. 19	1. 033

(After Schofield and Dakshinamurti, 1948)

taining N/40 KBr, or less, the bentonite is deflocculated, and the suspension exhibits no rigidity. Measurements of electrical conductivity, recorded in Table II, show that the adding of bentonite to these solutions produces a net increase of about 3% in the conductivity. Evidently the positive contribution made by the electrophoresis of the negatively-charged particles and the opposite migration of the corresponding excess of cations, more than offsets the obstruction caused by the bentonite particles when they are separated from one another.

The low ionic migration in the suspensions of bentonite in N/10 KBr, when first observed, seemed to point to an increase in the viscosity of the water. When, however, no such effect was apparent in N/40 KBr, this idea was abandoned. It is hardly conceivable that a drastic change in the viscosity of water could occur in the stronger, but not in the weaker, salt solution. There is thus no escape from the conclusion that this bentonite reduces the conductivity of N/10 KBr mainly by a process of obstruction due to the manner in which the particles are linked in the thixotropic gel.

These results throw light on the formation of gel structure. The existence of long-range forces of attraction is usually attributed to be the cause of thixotropy. Clay particles which repel each other, due to their negative charges, are surrounded by an atmosphere of cations in the electrolyte. Between any two such clay particles parallel to each other, there would be a layer of increased anion concentration due to negative adsorption (SCHOFIELD, R.K.,[10]). Thus the clay electrolyte system might be considered as concentrated groups of opposite charges. If the electrolyte concentration is such as to balance or overcome the repelling forces between the charged atmospheres of two clay micelles, the gel structure would form and would immobilize the fluid. Under these conditions it is likely that a central anionic concentration might repel the clay particles so as to form the end-to-end network suggested earlier (SCHOFIELD and DAKSHINAMURTI, [10]).

ISOCONDUCTIVITY VALUE AND CATION EXCHANGE CAPACITY

With decreasing concentrations of the electrolyte used, the rigidity of the gel is lowered; and below a critical concentration the clay suspension deflocculates and increases the conductivity of the electrolyte in which the clay is suspended. At a critical concentration value of the electrolyte the conductivity of the clay electrolyte system remains constant with increasing quantities of clay added to the system (Dakshinamurti, 1948). This critical concentration is termed the "Isoconductivity Value" of the clay.

The isoconductivity value is not influenced by the valency of the cation of the electrolyte, as was noted with calcium chloride and potassium bromide in a large number of samples studied. Further, a linear relationship between the cation exchange capacity of the clay and the isoconductivity value was observed for clays separated from soils of different origin as well as for pure clay minerals (DAKSHINAMURTI, [3]). Recently this technique has been extended for the determination of the cation exchange capacity of soils as well (CHANDOOL, [2]).

All the clays studied were first converted, as required, into calcium or potassium clays. The homoionic clay so prepared was suspended in a calcium chloride solution of a concentration suitable for the formation of a thixotropic gel. By repeated washings, the clay was brought into equilibrium with the electrolyte under study. The conductivity of the gel so formed (Cg) was compared with that of its equilibrium electrolyte solution (Ce). The ratio of the conductivities (Cg/Ce) is termed the relative conductivity of the clay electrolyte system. At each concentration of the electrolyte the relative conductivity values for different percentage weights of the clay were determined. As the concentration of the electrolyte decreased, the rigidity of the gel also decreased. The results obtained for Kaolin are given in Fig. 1.

At any one concentration of the electrolyte studied, the relative conductivity values were found to be proportional to the percentage clay content and, as expected, the line connecting different points passed through unit relative conductivity value with zero clay. Decrease in the concentration of the electrolyte used would tend to make the lines more and more horizontal to the percentage weight axis. At a concentration called the isoconductivity value, the relative conductivity value was 1.0 with all the percentage weights of the clay studied. For concentration of electrolytes lower than the critical concentration the relative conductivity value worked out to be greater than 1.0. Under these conditions the clay would dissociate.

The relative conductivity values obtained from Fig. 1 for constant weight of kaolin, say ten percent, were plotted in Fig. 2 against their respective electrolyte concentrations. For all electrolyte concentrations above the critical value the relative conductivity was found to vary directly with the concentration of the electrolyte. The isoconductivity value is found to be

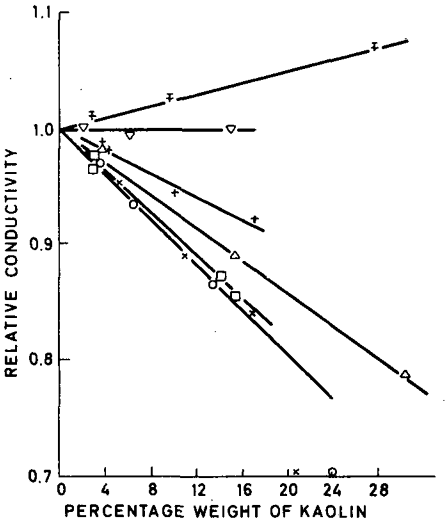


Fig. 1

Relative conductivity of kaolin calcium-chloride system at various concentrations of the electrolyte
Normality of calcium-chloride solution

×	0.1	△	0.01	∓	0.00125
○	0.05	+	0.005		
□	0.02	▽	0.0025		

(After Dakshinamurti, [3])

a linear function of the cation exchange capacity of the clay, irrespective of the type and size of clay particles studied (Fig. 3).

The isoconductivity values for a large number of clays separated from soils of four major groups in India viz., Black cotton soils, alluvial soils, laterite soils and hill soils, were determined by Chandool in our Laboratory and further established this linear relationship.

The technique developed for clays has recently been extended by Chandool to determine the isoconductivity values of soils as well. The procedure used in this case is the same as that for clays. In the case of soils, however, the relative conductivity values obtained for 30% weight of soil were taken instead of 10% weight preferred in the case of clays. This is only for practical convenience, as the soil electrolyte system could not be kept homogeneous during the period of study and is not so convenient to handle with low concentrations of soil. In spite of varying proportions of clay and inert material present in the different soils studied, the isoconductivity value was found to be a linear function of the cation exchange capacity. The results recorded for both clays and soils are given in Fig. 4.

It is gratifying to note that the isoconductivity values obtained for clays and soils, when plotted against their respective cation exchange capacity values, fall on the same straight line passing through the origin.

Isoconductivity value determines the limiting concentration of the electrolyte above which the charged particles of a system get immobilised, due to the interaction of the ionic concentrations between clay particles, and

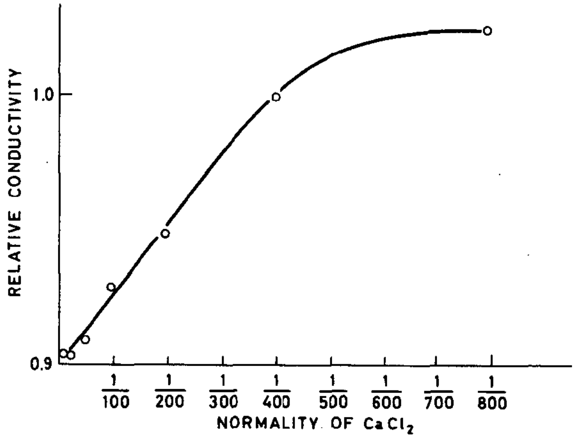


Fig. 2

Relative conductivity of 10% kaolin calcium-chloride system

(After Dakshinamurti, [3])

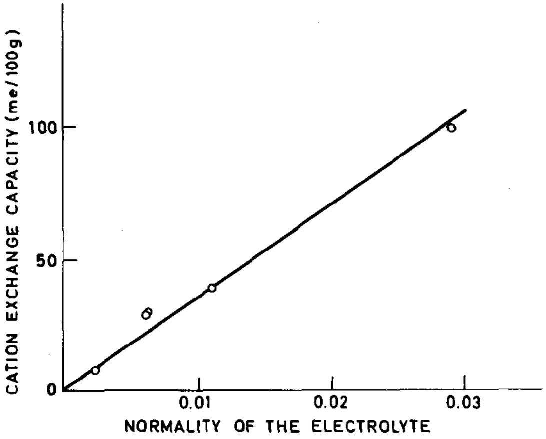


Fig. 3

Relation between cation-exchange capacity of clays and the iso-conductivity value of clay-electrolyte systems

(After Dakshinamurti, [3])

below which dispersion results. The most probable explanation may be the double-layer formation and interaction between clay plates. The surface conductance should also play a role, in that the excess cations in the diffuse layer (Stern) might contribute to the conductivity by easily rolling over the plates, the isoconductivity value that determines the ionic excess in that

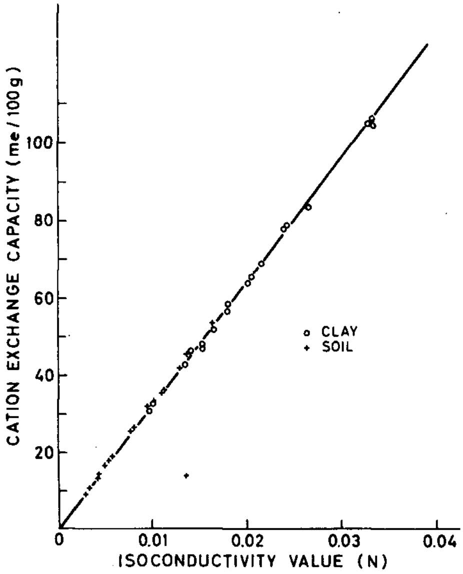


Fig. 4

Relation between cation-exchange capacity of soils and clays and the respective iso-conductivity value of their electrolyte systems

(After Chandool, [2])

layer becoming a function of the cation exchange capacity. Although it is possible to work out the distribution of ion concentrations between particles of known surface charge density placed in an electrolyte of known concentration, experimental measurements using more sensitive techniques are likely to throw more light on clay-electrolyte interactions.

DIFFUSION IN SOILS

As long as the porous beds are saturated, the conditions are similar to those described above. In actual field conditions, however, except under water-logged soils the soil pore space contains partly liquid and partly air. The distribution of the pore space between liquid and air for a given porous bed, depends upon the suction applied to the soil in removing the moisture. With increase in suction, the liquid in larger pores gets emptied, leaving the more tortuous, finer, pores filled up. In the three-phase system of the soil, the air and the solid material can be assumed to act together in forming the twists and the constrictions in the channels. Diffusion measurements of bromide ion under such conditions are recorded in Table III.

The results recorded at the three different suction pressures applied, indicate that the bigger pores that are emptied in the beginning effectively reduce ionic migration, but do not proportionately seem to reduce the total pore space filled by the liquid. At a suction of 7. 5 cm, applied bromide

TABLE III

EFFECTIVE FRACTIONAL AREAS CALCULATED FROM DIFFUSION MEASUREMENTS IN WOBURN SOIL

T (d)	Suction pressure (cm Hg)	A (cm^2)	Porosity of air (P(air))	Porosity of liquid (P(liquid))	q/C_0 for bromide	f_{Br^-}	$\frac{f_{Br^-}}{P(liquid)}$
1.0	25.1	33.03	0.293	0.174	0.37	0.015	0.085
1.0	25.1	17.69	0.212	0.179	0.26	0.020	0.109
1.0	13.5	33.03	0.298	0.174	0.90	0.040	0.228
1.0	7.5	33.03	0.224	0.244	1.76	0.071	0.294
1.0	7.5	17.69	0.223	0.238	0.71	0.054	0.225

(After Dakshinamurti, 1955)

ion contained in 1.76 ml of liquid diffused in one day. For the same quantity of ion to diffuse at suction values of 13.5 cm and 25.1 cm, the time required works out to be about 3 d and 23 d respectively. This rapid decrease in the amount of ion diffused with increase in applied suction is important for understanding the movement of salts in soils. The diffusion measurements thus indicate that at high values of applied suction the migration of ions due to diffusion is practically negligible.

EFFECTIVE POROSITY

Tortuosity, which is mainly due to the twists and constrictions in porous beds, should be the same for either the movement of gas molecules through gas-filled pores, or the migration of ions by diffusion when the pores are completely filled up with an electrolyte, or for conductivity measurements. The effective fractional areas of cross-section worked out by these methods are the same as the effective porosity of the medium. The data for actual and effective porosity values collected for inert and active materials are given in Table IV and Fig. 5.

The results show good accord between the observations of Penman, obtained by measuring gaseous diffusion, and those of the present author measured by ionic diffusion. Throughout the region of porosities studied, they fall on a smooth curve which tends to reach a value $P_{eff} = 1$ as would be expected when $P = 1$. The line drawn to a porosity value of about 0.65 shows a tortuosity factor $a = P_{eff}/P = 0.70$. Above the value of $P = 0.65$ the course of the curve changed, suggesting a change from the non-colloidal to the colloidal size of the particles that constitute the porous bed; in the former the electrolyte fills the porous bed, while in the latter the solid is suspended in the electrolyte.

TABLE IV

EFFECTIVE POROSITY VALUES OBTAINED WITH INERT AND ACTIVE MATERIALS FROM DIFFUSION MEASUREMENTS

Materials	By ionic diffusion		By gaseous diffusion			
			Penman		Bavel	
	P	P_{eff}	P	P_{eff}	P	P_{eff}
Sand			0.372	0.245	0.415	0.244
	0.35	0.267	0.378	0.252	0.355	0.205
	0.352	0.270	0.381	0.252		
			0.155	0.109		
Glistening dew	0.366	0.289				
	0.368	0.299				
	0.378	0.299				
Glistening dew and glass	0.271	0.193	0.185	0.151	0.250	0.125
	0.237	0.178	0.397	0.319		
Kaolin	0.716	0.46	0.772	0.598		
	0.715	0.46	0.782	0.600		
Bentonite	0.996	0.807				
	0.997	0.840				
	0.995	0.790				
	0.995	0.80				
Rothamsted subsoil clay	0.909	0.79				
	0.859	0.67				
	0.896	0.75				
Kieselguhr			0.844	0.677		
			0.924	0.805		
			0.93	0.815		
			Penman		Flegg	
Soils						
pF 2.53	0.174	0.015	0.518	0.298	0.55	0.35
	0.179	0.020	0.518	0.304	0.65	0.37
pF 2.26	0.174	0.040	0.547	0.346	0.48	0.30
pF 2.01	0.244	0.471	0.55	0.358	0.61	0.38
	0.238	0.054			0.64	0.36
					0.55	0.35
					0.65	0.38

(After Dakshinamurti, 1959)

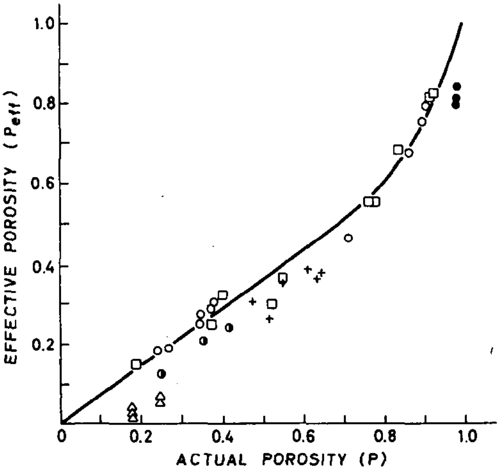


Fig. 5

Actual and effective porosities of porous beds composed of particles of different sizs and shapes

Author's results: ○ △ ●
Bavel's results: ◐
Penman's results: ☐
Flegg's results: +

(After Dakshinamurti, [4])

In soil under different suction pressures the points fall very much below the expected value. Here the air and the solid material are assumed to act together in the formation of twists and constrictions of the water channels. Porosities of the same value as those recorded in the suction experiments were also obtained in the regularly packed inert porous beds of spherical particles, but in these instances the effective pore space values measured were of the expected magnitude. In soils subjected to a high suction force, the larger pores through which the ions could migrate with ease are devoid of liquid, leaving only the smaller pores which are filled with liquid. Effective porosity apparently depends not on total porosity but on the size distribution and shapes of pores.

A second set of points which do not fall in line belong to bentonite, which formed a thixotropic gel with a porosity about 0.996. In such cases it is the structural arrangement of the 10 Å-thick bentonite plates that is responsible for the high value of tortuosity. The tortuosity factor also depends upon the size of the pores. A relationship should therefore exist between the tortuosity factor and the pF value. Between the pF values 2.0 and 2.5 studied, this relationship seems to be approximately linear (Fig. 6).

SOIL SOLUTION

It has been suggested that ionic diffusion plays an important role in the extraction of soil solutions by the displacement method, but no satisfactory evidence has ever been established. The water channels in the soil,

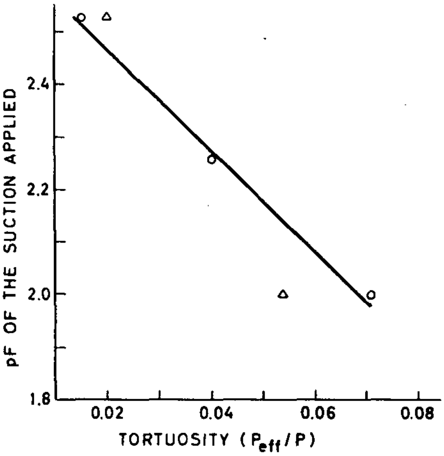


Fig. 6

Tortuosity factor for ionic mobility as a function of the p^F values in soils

○ large-size containers
△ small-size containers

(After Dakshinamurti, [4])

though quite irregular may, to a first approximation, be treated as irregular capillaries. Streamline flow of one liquid displacing the other is shown in Fig. 7.

Study of the flow of electrolytes, one (sodium nitrate) displacing the other (sodium bicarbonate) in capillary tubes, under different velocities within the limits of streamline flow, indicated that the volume, V_{L_b}, of the liquid, L_b, that gets displaced as the displacing liquid moves through the tube of length L, can be calculated from the geometry of the tube and the flow pattern, as given by

$$V_{L_b} = \frac{\pi}{2} R^2 \left(2L - \frac{L}{n}\right),$$

where n represents the number of lengths of the tube over which the displacing liquid in the paraboloid is supposed to have been extended. If the boundary of the paraboloid is rigid the above equation should determine the amount of liquid L_b that is present in a known volume of liquid collected at the open end. When $n = 1$, i.e. the tip of the paraboloid, M, just touching the open end, half of the liquid L_b originally present in the tube should be displaced before the displacing liquid appears in the liquid collected.

Experimental results shown in Fig. 8 indicate that, up to a volume of liquid displaced equal to half the volume of the capillary tube (1.9 mm diam. and 100 cm long), there is a linear relation, as expected, between the total volume of the liquid collected and the volume of the sodium bicarbonate displaced. This is irrespective of the velocity of the flow within streamline limits. For greater volumes of the liquid collected, however, the curves for different velocities of flow spread out and the lower the velocity of flow,

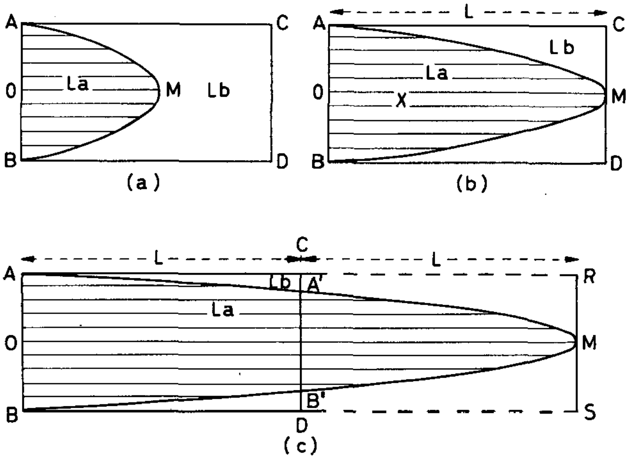


Fig. 7

Stream line flow through a narrow tube

(After Dakshinamurti, [6])

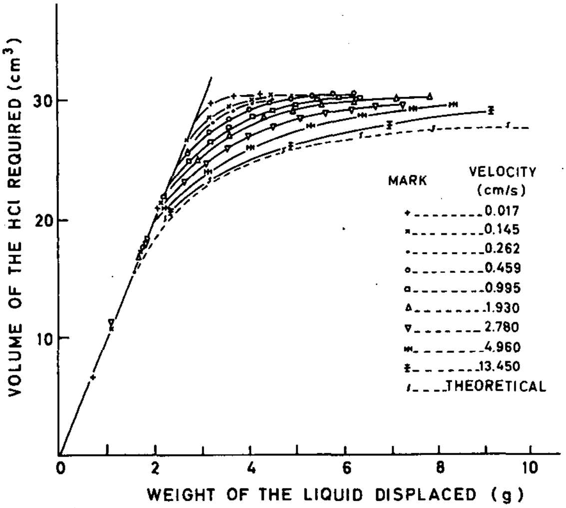


Fig. 8

Volume of the displaced liquid present in a known weight of the liquid collected at the open end for different velocities of flow

Length of the tube = 100. 0 cm. Diameter of the tube = 1. 98 mm.
Volume of HCl required to neutralize the $NaHCO_3$ solution completely filling the tube = 31. 10 cm^3

the greater is the sodium bicarbonate solution displaced. For the same weight of the liquid collected, the curve corresponding to a higher velocity of flow is closer to that drawn from geometrical considerations than the one corresponding to a lower value. With decreasing values of the velocity of flow, however, the linear part of the curve increased and at an average velocity of 0.017 cm/s studied, as high as 95% of the sodium bicarbonate solution originally present in the tube is displaced, before the sodium nitrate solution would flow out of the tube. This observation cannot be explained by Poiseuille's flow alone. This can be explained only as due to ionic diffusion between the two liquids inside the tube during the course of flow. At the common boundary of the paraboloid, bicarbonate ions diffuse towards the centre of the tube and thus pick up higher and higher speeds, while nitrate ions diffuse away from the centre losing their speed. The smaller the velocity of flow, the greater is diffusion.

It is possible to work out the order of the diffusion coefficients with this technique, as the parameters involved in these measurements work out to a non-dimensional constant K for each curve given by

$$K = \frac{D}{r^2} \times \frac{L}{V}$$

where D is the diffusion constant, r the radius of the tube and V the mean velocity of flow.

In a fairly uniformly packed soil, the diffusion measurements indicated that at high values of applied suction, the migration of ions due to diffusion is practically negligible. On the other hand, a study of the flow of liquids through narrow tubes showed that a Poiseuille flow coupled with diffusion is very effective for the movement of salts, while a Poiseuille flow alone was not so effective. This explains the principle behind the results obtained by LAWES, GILBERT and WARINGTON [9] with drainage solutions. In one of their experiments, where air-dried arable soil was wetted from the top, they observed that 75% of the diffusible salts were removed in about 50 cm^3 of the drainage water. The soil in that case contained some moisture and the more easily soluble and diffusible salts are in the ionic form. As the water slowly percolates from the top these ions diffuse into the pore space, acquire greater speed and appear as if they were being pushed down by the percolating solution. Subsequent work of BURD and MARTIN [1] shows that water could be used to displace the soil solution by the process of percolation, and successive displaced solutions in the first few fractions collected had equal concentrations. The concentration thus measured in each case was the same as that of the liquid obtained without the use of displacing water. In all these cases ionic diffusion is responsible for the soil solution being displaced before the displacing liquid would appear.

Ionic Diffusion and Electrical Conductivity measurements thus open parallel lines of investigation for understanding the mobility of plant nutrients in soils. The conductivity methods, being expedient and accurate enough, might prove to be sensitive tools for exploring the various interactions not only in the soil-water system, but also in the soil-water-plant systems.

REFERENCES

[1] BURD, J.S. and MARTIN, J.C., "Water displacement of soils and the soil solution", J. Agric. Sci. 13 (1923) 265.

[2] CHANDOOL, D.E., "Electrical Conductivity and Cation Exchange Phenomena of Soil and Clay Systems" Ph. D. thesis of the Indian Agric. Research Institute, New Delhi (1964).

[3] DAKSHINAMURTI, C., "Studies on the conductivity of clay systems", Soil Sci. 90 (1960) 302-5.

[4] DAKSHINAMURTI, C., "Effective porespace measurements in porous media by ionic diffusion", Soil. Sci. 88 (1959) 209-12.

[5] DAKSHINAMURTI, C., "Ionic diffusion in soil", Proc. Nat. Acad. Sci. (India) 24 (1955) 25-27.

[6] DAKSHINAMURTI, C., "Role of ionic diffusion in soil solutions", Proc. Ind. Acad. Sci. 35 (1952) 314-22.

[7] DAKSHINAMURTI, C., "Study of Ionic Migration in Clay Systems" Ph.D. thesis of the University of London (1948).

[8] EINSTEIN, A., "Über die von der molekular-kinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen". An. der Phys. 17 (1905) 549.

[9] LAWES, J.B., GILBERT, J.H. and WARINGTON, R., "On the amount and composition of rain and drainage waters collected at Rothamsted", J. Roy. Agric. Soc. 17 (1881) 241.

[10] SCHOFIELD, R.K. and DAKSHINAMURTI, C., "Ionic diffusion and electrical conductivity in sands and clays", Discussions, Faraday Soc. 3 (1948) 56-61.

DISCUSSION

H. LAUDELOUT: The existence of an isoconductivity value may be demonstrated in the following way:

If we split quite formally the measured conductivity, K_g, of the clay gel imbibed by an electrolyte solution of conductivity K_1 into two terms:

$$K_g = \frac{K_1}{F} + \Delta\lambda,$$

thereby defining the contribution $\Delta\lambda$ of the surface phase to the conductivity of the gel, F is a factor (> 1) by which the conductivity of the solution is reduced due to the presence of a solid matrix.

If λ_s is the surface conductance, S_u the surface per unit volume and φ the porosity we have

$$Fk_g - K_1 = \lambda_s \frac{S_u}{\varphi} .$$

At the isoconductivity point $K_g = K_1 = K_{iso}$

$$K_{iso} = \frac{\lambda_s S_u}{(F-1)\varphi} = \frac{2.5\ \lambda_s S_0(1-\varphi)}{(F-1)\,\varphi},$$

where S_0 is the specific surface (per g) of the solid matrix. K_{iso} will be independent of the porosity if $F-1$ has the form

$$F - 1 = k\frac{1-\varphi}{\varphi} .$$

This is precisely the form of Burger's equation (Phys. Zeitsft 20 (1919) 73) which has been found to be valid even in the case of montmorillonite gels (Cremers and Laudelout, to be published).

The correlation between K_{iso} and the base exchange capacity (BEC) follows if we replace S_0 by BEC/σ where σ is the surface charge density. Thus

$$K_{iso} = \frac{2.5\,\lambda_s}{k\sigma}\ \mathrm{BEC},$$

which ensures a correlation between K_{iso} and the BEC, provided the variations in the three parameters λ_s, k and σ have a tendency to compensate one another.

DIFFUSION OF PHOSPHATE TO PLANT ROOTS

D. G. LEWIS
DEPARTMENT OF AGRICULTURAL CHEMISTRY, WAITE INSTITUTE,
UNIVERSITY OF ADELAIDE
AND
J. P. QUIRK
DEPARTMENT OF SOIL SCIENCE AND PLANT NUTRITION,
INSTITUTE OF AGRICULTURE,
NEDLANDS, UNIVERSITY OF WESTERN AUSTRALIA, AUSTRALIA

Following suggestions of earlier workers, SCHOFIELD [1] has stressed the necessity of considering both capacity and intensity factors when assessing the availability of plant nutrients. Plant growth, however, is a dynamic process in which ion-transport phenomena are involved, both within the soil and within the plant. A number of workers, including FRIED and SHAPIRO [2, 3, 4], BARBER [5], OLSEN et al. [6], LEWIS and QUIRK [7], and GRAHAM-BRYCE [8] have stressed this fact and have made diffusion measurements. Diffusion measurements of cations (Rb and K) have also been made by KLUTE and LETEY [9], WALKER and BARBER [10], SCHOFIELD and GRAHAM-BRYCE [11], and GRAHAM-BRYCE [12].

If one refers specifically to anions, $H_2PO_4^-$ and NO_3^- represent extremes. This may be seen by reference to Table I, where the mean velocity of diffusion is represented for three different levels of phosphate and for chloride.

For anions where reaction with soil colloids is very limited, the ideas on diffusion in inert granular materials, as discussed by MILLINGTON and QUIRK [13, 14], apply. These authors have used probability of continuity in preference to the tortuosity concept which was proposed by KOZENY and CARMAN [15]. This method has been used extensively by oil industry research workers and, recently, by PORTER et al. [16]. The model used by Millington and Quirk allows ready consideration of ionic and gaseous diffusion for partially-saturated media.

TABLE I

DIFFUSION COEFFICIENT AND MEAN VELOCITY OF PHOSPHATE IONS IN SEDDON POT SOILS ($\bar{v} = 2D$)

Added phosphate	Self-diffusion coefficient	Mean velocity
(µg P/g soil)	(cm^2/d)	(mm/d)
100	0.1×10^{-4}	0.04
300	0.36×10^{-4}	0.08
1000	3.4×10^{-4}	0.26
Chloride	0.46*	6.5

* Predicted [13]: 0.44 cm^2/d.

The authors have measured diffusion coefficients of phosphate and have adopted a model root system to analyse diffusive flux. The flux to the model system has been compared with uptake by wheat plants. As our approach is different in some respects from BOULDIN [17] and OLSEN et al. [6], a brief summary of this is given. The results will be published in greater detail.

The accumulation of phosphate by wheat plants has been followed as a function of time over a complete growth cycle, and the rate of uptake compared with a computed uptake if diffusion alone contributed. The soil used for both pot experiments and laboratory studies was the Seddon sandy loam for which some data on phosphate retention have been obtained by KANWAR [18]. Phosphate additions of 150, 300 and 600 µg P/g soil were made to bulk samples of soil by spraying on appropriate amounts of calcium phosphate solution, followed by drying and thorough mixing. Wheat plants were grown under conditions of controlled environment in small pots of these soils and the plant tops were harvested and analysed at intervals of two weeks from sowing to maturity (22 weeks). The rate of phosphate uptake was almost constant during the period of 2 to 12 weeks and the mean rates for the three phosphate levels were 2.7, 5.6 and 12.0 µg P/plant per hour.

For the calculation of phosphate supplied to the root by diffusion, a physical model was adopted in which the root was considered to be a cylindrical sink towards which phosphate ions would diffuse under the influence of a concentration gradient induced by active uptake at the root surfaces, i.e. flow would be radial at all times from an infinite unstirred medium of uniform initial phosphate concentration P_0. Since the concentration of phosphate near the root surface could not be measured, some estimate was necessary to enable mathematical calculations to be made. In this work the boundary condition imposed was that the phosphate concentration at the root surface decreased exponentially with time from the initial value P_0.

For this system a general diffusion equation can be written as follows, using cylindrical polar co-ordinates:

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

valid for

$$a \leqslant r \leqslant 0, \quad t \geqslant 0,$$

where

$C = C_{(r,t)}$ = concentration of phosphate for any time 't' at a distance 'r' from the centre of the root;

D = diffusion coefficient; and

a = root radius.

As no published data were available on the diffusion of phosphate in soil, experiments were carried out to evaluate the diffusion coefficient for Seddon soil using different levels of added phosphate. The techniques given by LEWIS and QUIRK [7] were used to determine the self-diffusion of P^{32} in samples of soil to which KH_2PO_4 solution had been added to give phosphate additions ranging from 100-2000 μg P/g soil. The soils were stored at 20% water content for seven days before the diffusion cells were assembled. The measured diffusion coefficient was calculated from the amount of P^{32} transported across the boundary for six days' contact. The calculated diffusion coefficients were very small, ranging from approximately 2×10^{-10} cm^2/s for the lowest addition to 4×10^{-8} cm^2/s after the addition of 2 mg P/g soil.

Over this range there was a very marked curvilinear relationship between diffusion coefficient and level of phosphate addition, which could be described approximately by

$$D = K P^2, \tag{2}$$

where

D = measured diffusion coefficient of the phosphate ion in the porous medium;

K = constant; and

P = concentration of added phosphate (μg P/g soil).

Since the measured diffusion coefficient is not constant, it is not possible to give a general solution to the diffusion Eq. (1) given above, but numerical solutions can be obtained for specific initial concentrations and prescribed boundary conditions.

On substituting relation (2) into Eq. (1) a non-linear equation results which, subject to the imposed boundary conditions, was solved by numerical methods (using an IBM1620) to give the change in concentration at any point out from the surface of the root with time. Calculations were performed for three levels of added phosphate (150, 300 and 600 μg P/g soil) and two different root dimensions (0.2 and 0.005 mm) corresponding to the observed radii of the main root and the root hairs. Subsequent integration of each set of results around the root axis gave the cumulative change in concentra-

TABLE II

PHOSPHATE UPTAKE RATES: COMPUTED AND MEASURED

	Phosphate addition (μg P/g soil)		
	150	300	600
Computed uptake (μg P/m per hour)			
for main root	0.074	0.33	1.57
for root hairs	0.0084	0.034	0.13
for proposed model root*	0.494	2.03	7.97
Measured uptake (μg P/plant per hour)	2.7	5.6	12.0
Required length of model root (m/plant)	5.5	2.8	1.5

* Model root proposed had 50 mm of root hair per millimetre of main root.

tion per unit length of root with time, i.e. the mass of phosphate which had moved from the soil to the root surface as a result of diffusion. The mean uptake rates for the different root dimensions at the three levels of phosphate are given in Table II.

To convert these data to total plant uptake a model of the nutrient absorbing root must be used. On the basis of microscopic observation of the root systems of wheat plants grown in the Seddon soil a model root was adopted, in which every millimetre of main root has 50 root hairs attached to it, each of an average length of 1 mm, i.e. each millimetre length of root is associated with 50 mm of root hairs. The total uptake rates per unit length of model root for each of the three levels of added phosphate are also given in Table II together with the mean uptake rate per plant determined in the pot experiment.

By comparing the computed rate of uptake per unit length with the measured uptake rate of the growing plant, the length of model root required to achieve the measured uptake can be calculated, assuming diffusive movement to the root surface to be totally responsible. The calculated lengths shown in Table II must be recognized as minimum values of activity absorbing root under ideal moisture conditions. The lengths required (2 to 6 m per plant) are not excessive and may be even less if the root hair numbers or lengths are greater than the estimates used. Field measurements of root lengths of wheat plants indicate values ranging from 32 m [19] to half a mile [20] when sown in drills, and up to 50 miles for isolated plants [20]. These suggest that the values obtained would represent only a small fraction of the total root system.

At maturity the plants in the uptake experiment had a root volume of 7 to 12 cm^3/plant which would correspond to 50 to 90 m of model root per plant. FAWCETT [21] conducted similar pot experiments and after six weeks' growth found oven-dry root masses of 0.67 g/plant, which would correspond to 15 to 17 m of model root. At the six-week stage, the plants would be absorbing phosphate at the mean rate given in Table II, so about 40% of the calculated length would need to be active at the lowest P addition or only 7% at the highest level. These results suggest that, for the ideal model systems considered, diffusion alone could supply the phosphate adsorbed by plants. In practice the conditions are less than ideal, e.g. where the water content is less than saturated it is probable that the diffusion coefficient would be lower. On the other hand, it is also likely that older tissue continues to be active in uptake, although perhaps not as efficiently as newer tissues near the root tip.

In the experiments discussed above, the diffusion coefficients were measured under saturated conditions. In the plant growth experiments the water content of the soil was maintained near to "field capacity". However, interesting differences in the effect of water stress on phosphate uptake have been noted by WATANABE et al. [22] and FAWCETT and QUIRK [23].

The application of the approach as outlined here to water and other nutrient fluxes should lead to a more satisfactory appreciation of the complex physical relationships which exist between the soil and plant-root systems.

The results given in Table III serve to illustrate the relative importance of the root as compared with its associated root hairs. This information, when coupled with autoradiographic observations, helps to define the region in the soil from which phosphate is drawn.

It is of some interest to note that, for the model root system, and a distance of exploitation of 0.1 mm from main root and root hairs, the volume of a soil is 1.82 cm^3/m so that, for a root length of 60 m, the volume of soil from which roots withdraw phosphate would be 110 ml. The plants were grown in pots containing approximately 600 ml of soil.

With a root hair density of 50 per mm of main root, it may be calculated that each root hair is associated with a cylinder of soil of radius 0.1 mm immediately adjacent to the main root.

Other experiments relating to the nature of the diffusion process lead to the tentative suggestion that

$$D_p = D_e \times R', \qquad (3)$$

where

D_p = diffusion coefficient for non-reacting anions, which is simply obtained from the diffusion coefficient in solution and the tortuous nature of diffusion path;

D_e = experimentally determined diffusion coefficient for phosphate;

$R' = \frac{\text{Labile } P^{31}}{\text{Solution } P^{31}}$ associated with a unit mass of soil;

or $R' = \frac{\text{Total } P^{32}}{\text{Solution } P^{32}}$ associated with a unit mass of soil.

On this basis it may be suggested that D_e combines intensity, capacity and transport factors. Data illustrating Eq. (3) are given in Table IV.

The results in Table IV imply that diffusion through solution rather than surface migration is the important process. The results, therefore, sup-

TABLE III

EFFECT OF RADIAL DISTANCE FROM THE SURFACE ON THE VOLUME OF SOIL SURROUNDING ROOTS AND ROOT HAIRS

R = Radial thickness of soil (mm)	V_1 = Volume surrounding 1 cm of root ($cm^3 \times 10^3$)	V_2 = Extra volume associated with root hairs ($cm^3 \times 10^2$)	V_2/V_1
0. 01	0. 16	0. 031	1. 9
0. 05	0. 86	0. 448	5. 2
0. 1	1. 89	1. 55	8. 2
0. 15	3. 06	3. 20	10. 4
0. 2	4. 40	5. 28	12. 0
0. 3	7. 54	10. 2	13. 5

Root diam. = 0. 5 mm
Length = 1 mm each

Root hair diam. = 0. 01 mm
Root hair population = 50/mm root

TABLE IV

RELATIONSHIP BETWEEN EXPERIMENTAL SELF-DIFFUSION COEFFICIENT AND SOLUTION PHOSPHATE

Added phosphate (μg P/g)	$R = \frac{\text{Total P}}{\text{Solution P}}$	D_e* ($cm^2/d \times 10^5$)	$D_e \times R$ (cm^2/d)
100	3570	1. 40	0. 05
300	7150	5. 23	0. 36
500	1515	13. 4	0. 20
750	664	36. 3	0. 24
1000	471	51. 0	0. 24
1250	190	76. 4	0. 15
1500	110	136. 0	0. 15
2000	58	332. 0	0. 19
		Mean	0. 20

* Conditions of experiment different from those in Table I with respect to diffusion period and time of storage.

port the basic assumption made by OLSEN et al. [6] in their analysis of phosphate flux to a root. It should be stressed, however, that more extensive experimental observations are required to verify Eq. (3).

REFERENCES

[1] SCHOFIELD, R. K., Soils Fertil. 18 (1955) 373-75.

[2] FRIED, M. and SHAPIRO, R. E., Annu. Rev. Pl. Physiol. 12 (1961) 91-112.

[3] FRIED, M. and SHAPIRO, R. E., Proc. Soil Sci. Soc. Amer. 20 (1956) 471-75.

[4] FRIED, M. and SHAPIRO, R. E., Soil Sci. 90 (1960) 69-76.

[5] BARBER, S. A., Soil Sci. 93 (1962) 39-49.

[6] OLSEN, S. R., KEMPER, W. D. and JACKSON, R. D., Proc. Soil Sci. Soc. Amer. 26 (1962) 222-27.

[7] LEWIS, D. G. and QUIRK, J. P., Trans. Comm. IV and V Int. Soc. Soil Sci. N. Z. (1962) 132-38.

[8] GRAHAM-BRYCE, I. J., J. Soil Sci. 14 (1962) 195.

[9] KLUTE, A. and LETEY, J., Proc. Soil Sci. Soc. Amer. 22 (1958) 213-15.

[10] WALKER, J. M. and BARBER, S. A., Science 133 (1961) 881-82.

[11] SCHOFIELD, R. K. and GRAHAM-BRYCE, I. J. Nature 188 (1960) 1048-49.

[12] GRAHAM-BRYCE, I. J., J. Soil Sci. 14 (1963) 188.

[13] MILLINGTON, R. J. and QUIRK, J. P., Trans. Faraday Soc. 57 (1961) 1200-07.

[14] MILLINGTON, R. J. and QUIRK, J. P., Nature 202 (1964) 143-45.

[15] CARMAN, P. C., Flow of Gases through Porous Media, ch. 2, Butterworth, London (1956).

[16] PORTER, L. K., KEMPER, W. D., JACKSON, R. D. and STEWART, B. A., Proc. Soil Sci. Soc. Amer. 24 (1960) 460-63.

[17] BOULDIN, D. R., Proc. Soil Sci. Soc. Amer 25 (1961) 476-80.

[18] KANWAR, J. S., Soil Sci. 82 (1956) 43-50.

[19] WEAVER, J. E., Amer. J. Bot. 12 (1925) 502-09.

[20] PAVLYCHENKO, T. K. and HARRINGTON, J. B., Sci. Agric. 16 (1935) 151-60.

[21] FAWCETT, R. G., Thesis, University of Adelaide (1960).

[22] WATANABE, F. S., OLSEN, S. R. and DANIELSON, R. E., 7th Int. Cong. Soil Sci. III (1960) 450-56.

[23] FAWCETT, R. G. and QUIRK, J. P., Aust. J. Agric. Res. 13 (1962) 193-205.

DISCUSSION

C. DAKSHINAMURTI: The phosphate content in the main root decreased with increasing time of diffusion. Is the blackening observed in the autoradiographs a real deficiency of phosphorus or photographic blackening due to excess of phosphorus?

DIFFUSION IN SOIL CRUMBS

S. LARSEN AND D. GUNARY
LEVINGTON RESEARCH STATION, IPSWICH, UNITED KINGDOM

INTRODUCTION

In a multi-component system matter can move as a result of mass-flow and by diffusion. In soil both means of transport occur, but while mass-flow is largely restricted to the coarse pores between the soil aggregates (crumbs), transport by diffusion prevails inside the soil crumbs where the media in which diffusion occurs (water and air) are held in the fine pores by capillary forces. A similar situation exists in compacted (structureless) soil but as soil with a crumb-structure is the normal and more favourable medium for plant growth, a discussion of diffusion in soil crumbs is desirable.

A. DIFFUSION COEFFICIENTS IN RELATION TO SPHERES

By diffusion we mean the process by which matter is transported from one part of a system to another as a result of the random thermal movement of molecules or ions. Characteristic of this type of transport is the fact that the amount of material transported is not proportional to the time elapsed but to its square root. In the transport of matter over long distances diffusion may be neglected but it becomes very important over distances of a few millimetres particularly from or to the surface of a porous solid in which mass flow of the external medium is retarded.

The diffusion coefficient, D, is defined by the following expressions:

Rate of transfer per unit area of section = $-D\ dC/dX$ where C is the concentration of the diffusion substance and X the space co-ordinate measured normal to the section, or

$$\frac{dC}{dt} = \frac{d^2C}{dX^2} \times D$$

where t = time.

These two expressions are usually referred to as Fick's first and second laws of diffusion. These equations are applicable to linear diffusion in one dimension. Considering radial diffusion in a sphere – and we shall for simplicity assume soil crumbs to be spherical – the diffusion equation takes the form

$$\frac{dC}{dt} = D\left(\frac{d^2C}{dr^2} + \frac{2dC}{rdr}\right),$$

where r is the radius of the sphere.

Putting $\mu = Cr$ we get

$$\frac{d\mu}{dt} = \frac{d^2\mu}{dr^2},$$

which is basically the same equation as for linear diffusion in one dimension, CRANK, [1].

B. DIFFUSION IN POROUS MEDIA

(i) Inert porous media filled with either liquid or gas

The diffusion in inert porous material is reduced by two factors compared with diffusion in a system consisting of liquid or gas only: firstly, the physical barrier provided by the skeleton of the porous solid through which molecules and ions cannot diffuse, secondly by the crooked shapes of the pores. A correction for the first factor is usually made so that the unit area of the section is reduced by the fraction of the total volume occupied by solid particles. Another way of allowing for the fact that only a fraction of the volume is available for diffusion is to express the concentration as unit amount per unit volume. This way expression of concentration will also allow for other obstacles, such as air pockets in capillaries, where a solute is diffusing in a solution.

The second factor - the so-called tortuosity factor - reduces the diffusion in soil by a factor of about 0.6. This was established in a water-saturated soil by PENMAN [6], who also showed that the factor was almost constant for a variety of soils.

(ii) Inert media filled with liquid and gas

The fine pores of a moist soil crumb are filled with water; bubbles of trapped air will, however, occur. Such bubbles provide an obstruction to diffusion in the liquid phase and reduce the tortuosity factor. Reduction of the moisture content will decrease the tortuosity factor, which becomes zero, before all moisture is removed, i.e. when continuous water-filled pores no longer exist. PORTER et al. [7] found that after a threshold moisture content was exceeded the tortuosity factor increases linearly with increased moisture content.

(iii) Diffusion in porous material which combines with the diffusing matter

When molecules and ions are sorbed by the surface of the solid skeleton of the porous material, diffusion can take place in the liquid, in the pores and along the surfaces, and in the solid.

It is reasonable to assume that the rate of diffusion in the liquid phase is much greater than the rates of diffusion on the surface and in the solids, and the only way in which the sorption can affect the rate of diffusion in the liquid phase is by influencing the concentration gradient. If the distribution between the three fractions is the same, regardless of the concentration in the liquid phase, the rate of diffusion will be unaffected. However, this is not so when ions are sorbed to solids in soil, as the proportion of ions in solution will increase as the saturation percentage of the sorption capacity increases. This sorption to the surface of the solids introduces a complication.

When self-diffusion is considered, i.e. diffusion of 'carrier-free' labelled atoms in the absence of a concentration gradient, the exchange of ions between the liquid and the solid phase is important, for this will cause a loss of the label and the apparent diffusion coefficient calculated by use of labelled ions will be vastly different from the diffusion coefficient calculated on the basis of a concentration gradient. Relative to the rate of diffusion in liquid the rate of isotopic exchange is not a slow process and the bulk of this exchange takes place within a few days. GRAHAM-BRYCE [2] was therefore not right when he stated: "The isotopic exchange between the different soluble and insoluble forms of soil P is a relatively slow process, so that it may be assumed that little exchange takes place during the 2 - 3 d period of the diffusion experiments".

Diffusion in the liquid phase of a porous body, where there is an equilibrium between the solid/liquid phase with respect to the diffusing components, may be compared with diffusion in a granule of a sparingly-soluble salt. Assuming this granule is surrounded with pure water, the rate of dissolution depends at time zero on the solubilization which is a chemical reaction. As the concentration around the granule builds up diffusion (assuming no stirring) of matter away from the surface, this becomes important and may be the factor limiting the rate of dissolution.

Let us assume that a sparingly-soluble salt is mixed with a fine powder, such as clay, and granules are made of the mixture. In a static system the dissolution of the sparingly-soluble salt will depend on diffusion of matter through the porous shell, formed after dissolution, and diffusion in the bathing solution. If fresh water is passed through a bed of such granules the diffusion in the porous shell should be the limiting factor.

Experiments with simplified soil granules of this type may provide a quantitative measure of transport of matter out of soil crumbs.

C. SPECIAL CONDITIONS IN SOIL CRUMBS

(i) The influence of biological activity on diffusion of ions in soil crumbs

An important aspect of soil is the activity of soil micro-organisms which consume oxygen and produce carbon dioxide. Renewal of oxygen and disposal of carbon dioxide are brought about by diffusion and mass flow. If we consider a soil in which the coarser pores between the crumbs are filled with air and the finer pores in the soil crumbs are filled with water (a condition which is approximated at 'field capacity') the two gases will be transported by mass flow and diffusion in coarser air-filled pores and by diffusion in the liquid in the finer pores of the soil crumbs. In this situation an accumulation of carbon dioxide will, as shown by GREENWOOD and GOODMAN

[3], occur towards the centre of the crumbs. It is well known that an increase of the carbon dioxide in neutral and calcareous soil increases the hydrogen ion concentration and the concentration of ions in solution. As the carbon dioxide concentration rises towards the centre of a soil crumb the concentration of ions will also rise, bringing about a concentration gradient. This will cause the ions to diffuse towards the surface of the crumbs and an accumulation will occur on or near the surface. This could be particularly important for ions of low mobility in soil, such as phosphate ions.

Phosphate deposited near to the surface of the crumbs would be, so far as uptake by plants is concerned, in a more favourable position than phosphate distributed throughout the crumbs; such migration of phosphate by diffusion could affect the phosphate uptake by plants, particularly in the early stages.

This hypothesis has the advantage that it can be tested by a relatively simple experiment in which phosphate uptake can be compared on soils receiving the following treatments:

(a) Wet to field moisture capacity for x months;

(b) Dry for 1 month, wet for x - 1 months; and

(c) Dry for 2 months, wet for x - 2 months, etc.

The experimental soil should have a crumb structure, be of neutral or alkaline reaction and phosphate should limit plant growth. The experiment would, of necessity, be in pots. If the hypothesis is supported, phosphate uptake should be greatest in treatment (a).

Supporting evidence for the hypothesis is given in some results by GUNARY [4] who investigated the diffusion of ^{32}P-labelled phosphate in soil crumbs. During perfusion of two soils with 0.01 M $CaCl_2$ he found little sign of migration of labelled phosphate placed on the surface of soil crumbs (Fig.1). In spite of that isotopic dilution as measured in the perfusing solution has gone on all the time and was approaching an equilibrium level (Fig.2). This can only mean that unlabelled phosphate had diffused from the centre of the crumbs towards the surface and into the perfusing solution.

It should be noted that the perfusing technique employed by GUNARY [4] ensured aeration of the solution and thus a low concentration of carbon dioxide outside the soil crumbs.

(ii) Diffusion of ions from surface to centre of soil crumbs

The concentration of ions in the soil solution outside the crumbs may be raised by application of fertilizer salt. In this situation a diffusion towards the centre of the soil crumbs will occur. This is of particular importance in relation to slow-moving ions, such as phosphate. Immediately after application the phosphate ions, of which the majority will be sorbed by the solid skeleton of the crumb, will be in a favourable position for absorption by plants. As time passes more and more phosphate will move towards a less favourable position at the centre of the crumbs. A consequence of this is that the 'positional' availability will decrease with time. Recently-applied phosphate will thus be better utilized by plants than phosphate which has been in the soil for some time although no 'fixation', i.e. transfer from available forms to unavailable forms, or chemical change, has taken place.

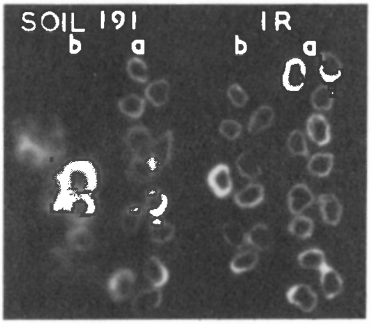


Fig. 1

Distribution of ^{32}P across sections of soil crumbs before (b) and after (a) perfusion

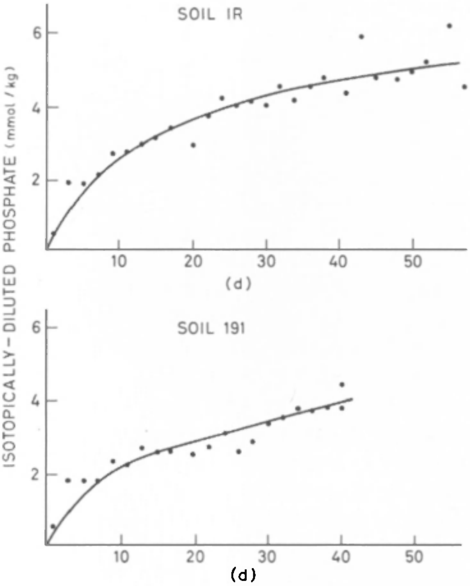


Fig. 2

Isotopic dilution during perfusion with 0.01 M $CaCl_2$ of crumbs of the two soils shown in Fig. 1. Soil IR is of basaltic origin with a large phosphate sorption capacity. Soil 191 is a culm measure clay.

In crop experiments with phosphate it is difficult to differentiate between the fall in availability and fall in accessibility. It is, however, relatively easy to devise an experiment in which allowance can be made for the former process. A determination of 'labile' phosphate by ^{32}P dilution would provide means for such an allowance.

(iii) Diffusion of ions to discrete spots within soil crumbs

During experiments in which the diffusion of ^{32}P from the surface to the centre of soil crumbs was followed, discrete spots of ^{32}P accumulation

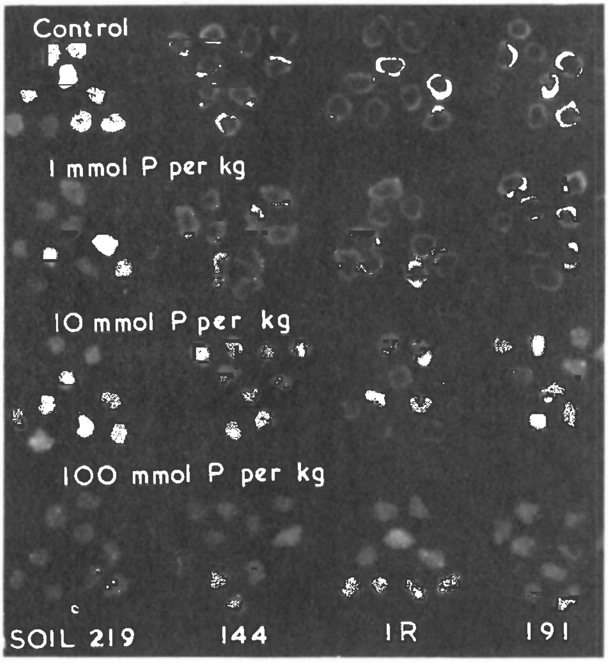


Fig. 3

Distribution of ^{32}P across sections of soil crumbs after four weeks' incubation in solutions of varying phosphate concentration. Zones of ^{32}P concentration can be seen in Soil 191 at the 10 mM phosphate level, and soil 219 at the 100 mM phosphate level.

within the soil crumbs have become apparent. An example of this is shown in Fig. 3 where ^{32}P has diffused, together with carrier phosphate, into crumbs of different soils. In the crumbs of soil 191 where 10 mmol of carrier phosphate was added, a good example of this ^{32}P accumulation can be seen. The simplest explanation is to assume that these zones coincide with zones which are highly active with respect to phosphate sorption. Such zones may well be small ion or manganese concretions which have formed within the soil crumbs. Micropedological techniques, together with radioautography, should assist in furthering our understanding of the nature of these phosphate-sorbing zones.

From this discussion it is apparent that diffusion of phosphate in soil crumbs may bring about changes in the phosphate status of soils to which phosphate has neither been added nor removed. How important this is has yet to be determined. It is, however, clear that a study of diffusion in soil crumbs may yield results and conclusions which may not be apparent from a study of diffusion in structureless soil.

REFERENCES

[1] CRANK, J., The mathematics of diffusion, The Clarendon Press, Oxford (1956).
[2] GRAHAM-BRYCE, I.J., "Self-diffusion of ions in soil II anions", J. Soil Sci. 14 (1963) 195-200.

[3] GREENWOOD, D.J. and GOODMAN, D., "Oxygen diffusion and aerobic respiration in soil spheres", J. Sci. Fd. Agric. 4 (1964) 579-588.

[4] GUNARY, D., "Behaviour of carrier-free phosphorus-32 in natural soil in relation to the measurement of labile soil phosphorus", J. Sci. Fd. Agric. 14 (1963) 319-324.

[5] HARTLEY, G.S., Herbicide behaviour in the soil I Physical behaviour and action through the soil. The physiology and biochemistry of herbicides (L.J. AUDUS, Ed.), Academic Press, London and New York (1964) 111-159.

[6] PENMAN, H.L., "Gas and vapour movements in the soil. The diffusion of vapours through porous solids", J. Agric. Sci. 30 (1940) 437-462.

[7] PORTER, L.K., KEMPER, W.D., JACKSON, R.D. and STEWARD, B.A., "Chloride diffusion in soils as influenced by moisture content", Soil Sci. Soc. Amer. Proc. 24 (1960) 260-263.

DISCUSSION

I.J. GRAHAM-BRYCE: The sentence quoted by Dr. Larsen was used in discussing apparent self-diffusion coefficients (D) for phosphate ions, calculated from the rate of transfer of radiotracers from soil sections labelled uniformly with ^{32}P to exactly similar sections initially without tracer, GRAHAM-BRYCE [1]. The labelled soils were prepared by shaking with solutions containing ^{32}P for five weeks, by which time the rate of further isotopic equilibration between the soil and the added tracer was negligible. The calculation of D requires knowledge of the fraction of the radiotracers initially present in the labelled section which has crossed the boundary between the sections in a given time. Three different soil extractants were used to obtain values for this fraction (i) M/100 $CaCl_2$, (ii) 0.2 $\underline{N}$ H_2SO_4, (iii) 2 $\underline{N}$ H_2SO_4 after ignition at 550°C. These extractants are of increasing effectiveness for soil P - the $CaCl_2$ solution removes only the relatively easily extracted phosphate (principally that in the soil solution) while the acid extractants will also remove solid phase phosphate. The value of the apparent self-diffusion coefficient calculated in this way would be expected to depend on the method of extraction if the rate of isotopic equilibration is slow compared with the diffusion process (mainly in the soil solution) which transfers ions across the boundary, so that the system ceases to be in isotopic equilibrium once diffusion has started, GRAHAM-BRYCE [1]. It was in developing this argument that the sentence quoted was used.

Dr. Larsen's criticism of the statement depends on the interpretation of the term "isotopic exchange". This term was intended to include all processes in solution, surface and solid phases involved in the equilibration between ^{32}P and ^{31}P. This interpretation of the term, together with the use of "Exchangeable phosphate" ("E" value) to describe the amount of soil ^{31}P which equilibrates with added ^{32}P in a given time can be found frequently (e.g. MATTINGLY [2] RUSSELL, RICKSON and ADAMS [3]. It is generally agreed that the "E" value changes with time and that for most soils 80-90% of the equilibration would not be completed for considerably longer than 2-3 days (RUSSELL, RICKSON and ADAMS [3] TALIBUDEEN [4]). If the term "isotopic exchange" is used in this way, as it was in the publication referred to by Dr. Larsen, then the sentence quoted is valid. If exchange is taken to refer only to the so-called "surface exchange" - the initial relatively rapid phase of isotopic equilibration - then clearly the process cannot be regarded as taking place only to a small extent during the 2-3 d period of the experiment.

REFERENCES IN DISCUSSION

[1] GRAHAM-BRYCE, I.J., J. Soil Sci. 14 (1963) 195.
[2] MATTINGLY, G.E.G., Soils and Fertilizers 20 (1957) 59.
[3] RUSSELL, R.S., RICKSON, J.B. and ADAMS, S.N., J. Soil Sci. 5 (1954) 85.
[4] TALIBUDEEN, O., Rep. Rothamst. exp. Sta. for 1956 (1957) 55.

SELF-DIFFUSION OF CALCIUM-45 INTO CERTAIN CARBONATES AND CALCAREOUS SOILS

P. REINIGER AND N. LAHAV*
LABORATORY OF SOILS AND FERTILIZERS,
STATE AGRICULTURAL UNIVERSITY
WAGENINGEN, NETHERLANDS

INTRODUCTION

The investigations described in this paper were prompted by the lack of a reliable and accurate method for measuring exchangeable calcium in calcareous soils. A large group of arid-zone soils contains calcium carbonate and is under irrigation or planned to be irrigated in the future. For the purpose of predicting and measuring the influence of various types of irrigation water on these soils, especially the degree of alkalinization to be expected, an exact determination of exchangeable calcium is necessary.

In the various stripping procedures used for the determination of exchangeable cations, the amount of calcium found depends on the solubility of calcium carbonate in the stripping solution and thus on the solution-soil ratio employed. Therefore, the use of an isotopic dilution method of ^{45}Ca seemed most advantageous, also in view of the favourable characteristics of this isotope and its relatively low price. An accurate and easy counting technique employing an ordinary end-window G-M counter and dried-down samples had been developed, overcoming the disadvantage of the low-energy level of the beta-radiation of the isotope and placing its use within the reach even of small laboratories [2].

Before the use of ^{45}Ca to measure exchangeable calcium in calcareous soils could be considered, better insight into its interaction with the solid calcium carbonate present in those soils seemed imperative. This interaction could be foreseen to consist of surface exchange with calcium adsorbed on the surface of the carbonate crystals, and of diffusion into the crystal itself. As in the isotopic dilution method the amount 'adsorbed' is calculated by subtracting the amount in solution from the total; this 'adsorbed'

---

* At present at the Hebrew University, Rehovot, Israel

amount would, in the case of a considerable infusion of ^{45}Ca into the carbonate crystal, consist of calcium exchanged by surface exchange and that lost by infusion, and would be time-dependent. Knowledge, particularly of this infusion process, therefore, seemed most important. To obtain a basis of reference, well-defined systems of pure carbonates were first investigated.

EXPERIMENTAL TECHNIQUE

Full details of the experimental techniques have been given in other publications, in journals and in reports to the Agency [1, 4, 5]. Nevertheless, a few points may be stressed again here. In all the studies where suspensions of the pure or impure minerals or soil particles were used, three main conditions in preparing the systems were observed. The first two of these served to fulfil the boundary conditions necessary for solving the diffusion equation, the third one to attain sufficient accuracy in the measurements. These conditions were:

(a) To fulfil the boundary condition relevant to the mathematical solution chosen, the calcium concentration in the supernatant liquid had to be kept constant. This was attained by suspending the particles in a $CaCl_2$ solution at least 0.008 N, which is well above the solubility of calcium carbonate under the experimental conditions.

(b) Also, the specific activity of ^{45}Ca at the particle surface had to be the same as in the bulk solution. For this purpose the suspensions were agitated in a shaker during the experiment.

(c) To attain satisfactory accuracy of the measurements, the ratio of calcium in solution to calcium to be exchanged was kept below unity by adjusting the suspension concentration.

A short description of the experimental procedure reads as follows: The material under investigation was suspended in a $CaCl_2$ solution and brought to equilibrium with the solution by shaking. Amounts of 5-6 ml were transferred to 10-ml plastic bottles and at zero time a similar solution tagged with ^{45}Ca was added and agitation was started. At various time intervals bottles were taken out, centrifuged, and the specific activity of ^{45}Ca in the supernatant liquid determined. These determinations gave a picture of how the specific activity of ^{45}Ca in solution decreased with time, or, according to the law of conservation of matter, of its increase in the material investigated, i.e. the amount adsorbed or infused.

THEORETICAL

To compare the values of ^{45}Ca infusion found by the experimental technique described above with values to be expected from diffusion theory, the self-diffusion coefficient, D, of calcium in the various materials was calculated [4]. It appeared that the process could be described as one-dimensional diffusion of ^{45}Ca with a constant carrier concentration and a falling head, as the specific activity of ^{45}Ca in the solution decreased with time while the isotope entered the crystal. One-dimensional diffusion could be assumed, as maximum average penetration was about 40 Å compared with particle diameters smaller than 5 or even 50 μm.

One could, therefore, use Fick's Second Law, which was solved for the system by using the appropriate boundary conditions, stating:

(1) That the specific activity of ^{45}Ca in the crystal at zero time was zero; and

(2) That the crystal was semi-infinite for the time of the experiment.

The resulting differential equation was solved by applying the Laplace transformation. Allowing for various values of D, the decrease of ^{45}Ca activity in solution could be calculated as a function of time and a capacity factor, h. In the same way, the increase in specific activity in the crystal and the amount of isotopically-exchangeable calcium, i.e. that adsorbed and that lost by infusion into the crystal, could be calculated for various values of the diffusion constant, as a function of time.

EXPERIMENTAL

Following the theoretical equation, the amounts of Ca exchangeable in pure carbonates (calcite and dolomite) were plotted as a function of the capacity factor times the square root of time for different trial values of D. As is seen from Fig. 1, which gives the amount of isotopically-exchangeable Ca per cm^2 crystal for three size fractions of calcite plotted in the way described, the amount of isotopically exchangeable calcium increased with time. As the equilibration with adsorbed calcium is attained in a matter of minutes in the suspensions used, the increase in isotopically-exchangeable Ca is caused by the diffusion of ^{45}Ca into the calcite crystal with a diffusivity constant of about 10^{-19}cm^{2}s^{-1} (slope of the line plotted). A value of 10^{-20}cm^{2}s^{-1} was found for dolomite. Should natural carbonates in soils behave similarly, the amount of adsorbed calcium determined with the aid of ^{45}Ca would have to be corrected for the infusion according to the equilibration time and the diffusion constant of the carbonate salt.

The next step was, therefore, to take a natural impure calcium carbonate and measure its isotopically-exchangeable calcium as a function of time. EMKAL, a liming material containing some clay, was chosen for this purpose, and as may be seen in Fig. 2 it behaved entirely differently from the pure calcite. The amount of isotopically-exchangeable calcium did not increase with time, at least the increase was not detectable with the methods used, and thus the maximum possible value of the diffusion constant for Ca was a factor of 100-200 lower than that of calcite. The amount of isotopically-exchangeable calcium measured could be ascribed entirely to the surface adsorbed form of the cation.

Two further questions were therefore raised:

(1) What was the possible reason for the different behaviour of pure calcite and the impure EMKAL?

(2) Did soil carbonates interact in the same way with ^{45}Ca as the impure calcium carbonate EMKAL? If so, ^{45}Ca should lend itself very well to the determination of exchangeable calcium in calcareous soils, as all the isotopically-exchangeable calcium measured would be surface-adsorbed.

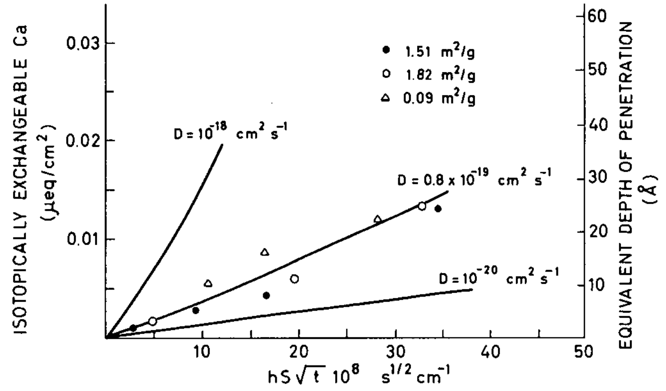


Fig. 1

Amount of calcium exchangeable against ^{45}Ca in three size fractions of calcite as a function of hS $\sqrt{t}$ (h = capacity factor, S = specific surface of crystal, t = time). The solid lines are the calculated theoretical curves.

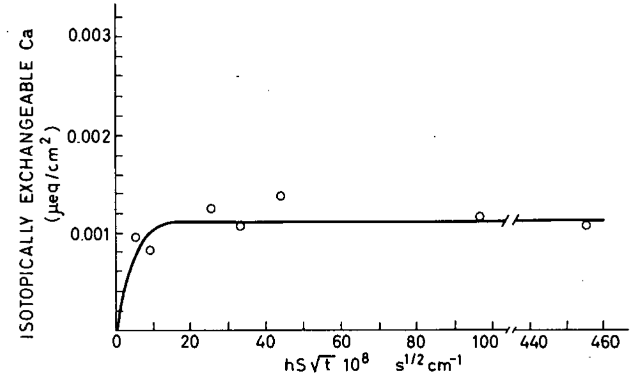


Fig. 2

Amount of calcium exchangeable against ^{45}Ca in EMKAL as a function of hS $\sqrt{t}$

Regarding 1., two answers suggested themselves:

(a) EMKAL was an entirely different form of calcite with a very low self-diffusion constant for calcium; this seemed improbable, as the D of dolomite was lower than that of calcite only by a factor of 10;

(b) A surface coating of some material was present on the calcium carbonate crystals, slowing down the infusion of ^{45}Ca. Along this line of thought a further experiment was carried out, comparing the amount of isotopically-exchangeable calcium as a function of time of pure $CaCO_3$ precipitate with that of the same precipitate plus Ca-bentonite [3]. Again, infusion was greatly inhibited in the presence of the clay, as compared to the infusion into the pure calcium carbonate. As the slowing down of infusion might be caused

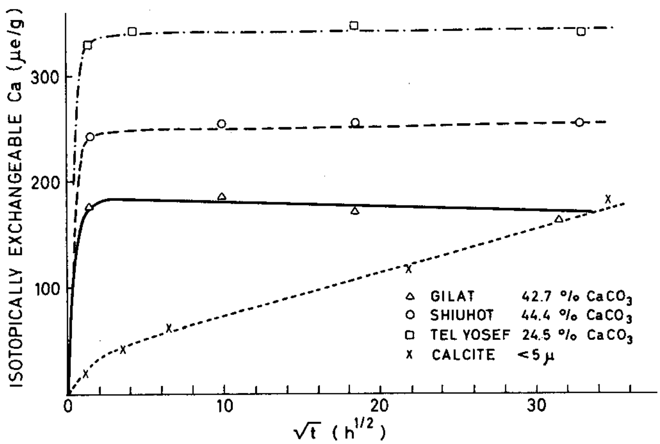


Fig. 3

Exchangeable calcium of four calcareous soils measured after various equilibration times with ^{45}Ca

either by a coating with clay particles, or by the adsorption of some dissolved material, such as silicate, the experiment was re-run, using a dialysate of calcium bentonite and Na-silicate, respectively, instead of the clay itself. Both the clay dialysate, which contained about 6 ppm SiO_2, as well as sodium silicate, inhibited the infusion process of ^{45}Ca. It should be noted here that the supernatant of the EMKAL suspensions contained about 4 ppm SiO_2. It was proposed, therefore, that silicate is adsorbed at the imperfections in the crystal structure where most of the diffusion takes place, these being the most active places, thus stopping the infusion of ^{45}Ca. In popular terms, one might think of silicate plastered like masking tape on the lines of imperfection, closing them for the diffusion of calcium.

Now for the second question, the behaviour of soil carbonates. There, the amount of isotopically-exchangeable calcium was measured as a function of time for three calcareous soils from Israel, containing between 24 to 44% $CaCO_3$. In Fig. 3 one can see clearly that no measureable infusion into the soil carbonates took place at equilibration times as long as 1000 h, the amount of exchangeable calcium staying constant with time. The comparative data for pure calcite given in the same figure show an increase in isotopically-exchangeable calcium with time, i.e. infusion took place and the amount exchangeable is composed of a constant surface exchange and an exchange by diffusion varying with time. In the case of the soil, all the isotopically-exchangeable calcium measured could be attributed to surface exchange with the clay and carbonate particles. Soil carbonates, therefore, behaved as the impure EMKAL and not like pure calcite. In the supernatant of the soil suspensions, as in that of EMKAL, a SiO_2 concentration of 6 - 9 ppm was measured, pointing to the same 'masking tape' effect of silicate.

In conclusion, the following picture may be drawn of the interaction of ^{45}Ca with carbonates:

(1) In the case of pure calcium carbonates, ^{45}Ca is exchanged on the surface of the carbonate crystal and by diffusion into the crystal.

This diffusion may be described with Fick's Second Law [4], worked out for the appropriate boundary conditions.

(2) In systems such as soil suspensions and impure calcites containing silicates in solution, ^{45}Ca is exchanged with surface-adsorbed calcium. Its infusion into the carbonate crystals is being suppressed by the 'masking tape' effect of adsorbed silicates [3, 4].

(3) In view of (2) the isotopic dilution of ^{45}Ca may be used to measure adsorbed calcium in calcareous soils. Successful measurements on a variety of calcareous soils from Holland, Israel and Turkey * were carried out at this laboratory [5].

REFERENCES

[1] BOLT, G.H. and De HAAN, F. A. M., Determination of ion exchange characteristics of soils and clays, Report, Research Contract No. 123/RB, IAEA, Vienna (1963).

[2] BOLT, G.H. and PIETERS, Beatrijs G. M., "Assessing the activity concentration of ß-emitters with the end-window G. M. -tube", Analyt. Chim. Acta 31 (1964), 64-70.

[3] LAHAV, N. and BOLT, G. H., "Interaction between calcium carbonates and betonite suspensions", Nature, 200, 4913 (1963) 1343-1344.

[4] LAHAV, N. and BOLT, G. H., "Self diffusion of Ca-45 into certain carbonates", Soil Sci. 97 (1964) 293-299.

[5] REINIGER P., LAHAV, N. and BOLT, G.H., "Determination of cation exchange characteristics of calcareous soils", Proc. VIIIth Int. Cong. of Soil Sci., Paper II/51 (1964) (in press)

TORTUOSITY EFFECTS IN CLAY GELS

H. LAUDELOUT AND A. CREMERS
INSTITUT AGRONOMIQUE, UNIVERSITÉ DE LOUVAIN
BELGIUM

The purpose of this paper is to show that the factor by which the mobility of ions is reduced in clay gels imbibed with an electrolyte solution can be predicted from the relationship which has been found to describe tortuosity effects in porous media formed by the random packing of particles less anisometric and coarser than clay plates. Estimating these tortuosity effects in a wide range of porosity by means of self-diffusion experiments would involve an almost prohibitive expense of labour. Electrical conductivity measurements provide an easy and rapid method for achieving the same result.

Since surface conductivity effects play an important role in determining the electrical conductivity of a clay gel, they must be eliminated in order to

---

* The work on Turkish soils was carried out at this laboratory by M. S. Yesilsoy, Toprak ve Gubre Aras. Enst., Ankara, Turkey, and will be published elsewhere.

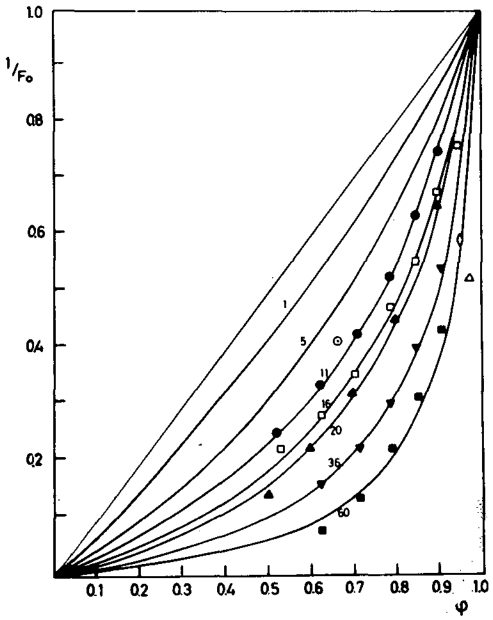


Fig. 1

Reciprocal of the formation factor,
i.e. ratio of electrical conductivity of a clay gel corrected
for surface conductance effects to conductivity
of imbibing electrolyte (NaCl) solution plotted versus porosity.
The curves represent Eq. (1) with shape factor k calculated for the axial ratios indicated.
The experimental points are as follows:

■ Wyoming Bentonite; ▼ Camp Berteau montmorillonite;
▲ Zettlitz kaolinite; ▭ illite; ● Boluvit kaolinite.
Other data from published information have been plotted:
⊙ self-diffusion of Na^+ in kaolinite;
△ self-diffusion of Na^+ in montmorillonite [4]
◇ Self-diffusion of Ca^{++} in montmorillonite [3]

estimate the factor by which the conductivity of a given electrolyte solution would have been reduced in the absence of surface conductance.

This is fairly easily achieved by techniques which have been fully described by CREMERS and LAUDELOUT [2]. When a set of experimental values of this factor at various porosities of the clay gel have been obtained it is possible to ascertain whether a formula such as that of BURGER [1], for instance, correctly describes the relationship between this factor and the porosity.

As is customary in petroleum exploration terminology the reciprocal of this factor is used and is called the formation factor; it is then defined by

$$1/F = K_g/K_1$$

where K_g is the electrical conductivity of the clay gel corrected for surface conductance effects and K_1 is the electrical conductivity of the electrolyte solution with which the porosity p of the gel is completely filled.

According to Burger F should be given by

$$F = 1 + k\frac{1-p}{p} \tag{1}$$

where k is a shape-dependent parameter which may be calculated when the axial ratio of the clay particles is known. Independent measurements, such as electron microscope observations, or viscosity measurements on clay suspensions, may provide an estimate of these axial ratios which can then be compared to those obtained from electrical conductivity measurements. Such a comparison has been presented by CREMERS and LAUDELOUT [2].

For practical purposes, however, it suffices to examine whether the formula correctly describes the change of F with p.

Figure 1 shows that this is actually the case for five clays of widely different properties: one illite, two montmorillonites and two kaolinites, for which one has chosen k parameters corresponding to axial ratios of 16 for the illite, 60 for the Wyoming bentonite, 36 for the Camp Berteau montmorillonite, 11 for the Boluvit kaolinite and 20 for the Zettlitz kaolinite. We have further drawn on this graph the curves corresponding to axial ratios of (spheres) and 5.

The agreement between the calculated value represented by the full lines and the experimental points may be deemed satisfactory. It may thus be concluded that even though clay particles exhibit a large anisometry and their packing in a gel may thus form a network of very fine pores, a simple formula may describe the tortuosity of the pore system.

REFERENCES

[1] BURGER, H.C., Phys. Zeit. 20 (1919) 73.
[2] CREMERS, A. and LAUDELOUT, H., to be published.
[3] FLETCHER, G.E. and SLABAUGH, N.K., J. Coll. Sci. 15 (1960) 485.
[4] BLOKSMA, A.H., J. Coll. Sci. 12 (1957) 40.

DISCUSSION

J.P. QUIRK: In discussing tortuosity Professor Laudelout has referred to electrical conductivity measurements and derived formation factors. In the equations presented he has used σ, the surface density of charge. It is not clear what meaning should be given to σ.

DESHPANDE and MARSHALL [1] have shown that cations in the diffuse part of the double layer have normal mobilities, whereas those in the Stern layer have zero mobility in D.C. conductance and normal mobility at high frequencies (10 000 cycles). A further feature, to which I will refer in greater detail in discussions on negative adsorption, is that ion bonding varies a great deal from one clay mineral to another, depending on the stoichiometric surface density of charge (exchange capacity divided by the nitrogen surface area for fixed lattice clays and total surface for expanding lattice clays). In these circumstances, it appears that the common procedure of using concentrated electrolyte solutions should be adhered to, as the variable conductivity due to double-layer ions may be safely neglected.

The tortuosity concept arises from the Kozeny-Carman equation (CARMAN [2]), which has been modified and further developed by oil industry research workers, WYLLIE and SPANGLER [3] for predicting permeabilities of oil-bearing rocks.

MILLINGTON and I [4] have used a different approach in which the probability of continuity replaces tortuosity. This is a statistical approach based on the pore size distribution and an interaction model similar to the one proposed earlier by CHILDS and COLLIS-GEORGE [5]. I will not discuss the detail of this work, which is already published, but will refer to a couple of aspects which are relevant to the subject of ion diffusion in soils.

An appropriate representation of phase continuity in partly-saturated porous materials may be obtained by arranging area interactions in rows and columns ("matrix" form). If there are m pore classes, each occupying the same fraction of the porosity, there is as a result of interaction m^2 terms. If only n of these pore classes remain full of liquid the following gives the pore continuity:

Air/Air $(m-n)^2$	Air/Water $n(m-n)$
Air/Water $n(m-n)$	Water/Water n^2

← m pore classes →

Where permeability is being considered, each of the m^2 terms is combined with value for r^2 for each pore class and a porosity function $\epsilon^{4/3}$. Diffusion of ions in the water-filled space is given by

$$\left(\frac{D}{D_0}\right)_n = \frac{n^2\epsilon_n^{4/3}}{m^2} = \left(\frac{1}{F}\right)_n,$$

where $(D/D_0)_n$ is the ratio of diffusion of the ion when n pore classes remain full of liquid to the diffusion of the ion aqueous solution. F represents the formation factor relating to the same conditions.

There has been some confusion in the literature because diffusion in partially-saturated materials is often regarded as being equivalent to diffusion in a saturated material with a lower porosity. That is, a unique curve obtained by measuring gas diffusion (D/D_0) in dry materials with different values of ϵ is referred to. In actual fact, the relationship as shown by the above equation leads to a series of curves.

REFERENCES

[1] DESHPANDE, K.B. and MARSHALL, C.E., J. Phys. Chem. 65 (1960) 33.
[2] CARMAN, P.C., Flow of Bases through Porous Media, Butterworths, London (1956).

[3] WYLLIE, M.R.J. and SPANGLER, M.B., Bull. Amer. Assoc. Petrol Geol. 36 (1952) 359.
[4] MILLINGTON, R.J. and QUIRK, J.P., Trans. Farad. Soc. 57 (1962) 1200; and Nature 202 (1964) 143.
[5] CHILDS, E.C. and COLLIS-GEORGE, N., Proc. Roy. Soc. A, 201 (1950) 392.

INTERACTIONS BETWEEN ANIONS AND SOIL CONSTITUENTS

G.H. BOLT AND F.A.M. de HAAN
LABORATORY OF SOILS AND FERTILIZERS,
STATE AGRICULTURAL UNIVERSITY, WAGENINGEN, NETHERLANDS

1. INTRODUCTION

Clay mineral crystals are characterized by a non-isotropic structure, in which a pattern is recognized (see schematic presentation in Fig. 1). It is known that the planar sides are negatively charged (as a result of the isomorphic replacement of Si^{4+} by Al^{3+} and/or Al^{3+} by Mg^{2+}). Under certain conditions the exposed alumina groups at the edges are charged positively.

Order of magnitude: Surface density of charge of the planar sides equals $1\text{-}3 \times 10^{-7}$ meq/cm^2 (or 1-3 electronic charges per 200 Å^2). The corresponding cation exchange capacity ranges from about 4 meq/100 g for well-crystallized kaolinites to 40 meq/100 g for illites and 100 meq/100 g for montmorillonites.

The number of exposed edge-alumina groups depends mainly on the crystal side (i.e. length and width of the clay plates). For a 2500-Å plate of the 2:1 type one finds about 2 mmol/100 g; for a 1000-Å plate about 5 mmol/100 g.

The different types of interaction between ions and clay crystals may be listed as follows:

(a) Cations: positive adsorption on planar side (electrostatic interaction modified by – non-electrostatic – specific factors); and possibly negative adsorption at positively charged edges (electrostatic effect).

(b) Anions: negative adsorption (exclusion) on planar side (electrostatic effect); and positive adsorption on the edges – in part electrostatic, if edge positively charged; furthermore chemisorption of certain anions, as e.g. PO_4, SiO_4.

Because the negative and positive adsorption occur simultaneously for both cations and anions, it is necessary to decide on the expected relative magnitude of counter-ion adsorption and co-ion exclusion. To this purpose the co-ion exclusion is expressed as a fraction of the total surface charge. Then one finds for the mono-monovalent symmetric system:

$$\frac{\gamma^-}{\gamma} \equiv \frac{\Gamma^-}{\Gamma} = \frac{2}{\bar{\Gamma}} - \frac{1}{2}\left(\sqrt{1+\frac{16}{\bar{\Gamma}^2}} - 1\right)$$

$$= \frac{2}{\bar{\Gamma}} - \frac{4}{\bar{\Gamma}^2} + \frac{16}{\bar{\Gamma}^4} - \frac{128}{\bar{\Gamma}^6} \qquad (1)$$

in which γ^- = co-ion exclusion, in meq/g, γ = counter-ion adsorption capacity, in meq/g, $\Gamma = \gamma/S$ = surface density of charge, in meq/cm^2, $\bar{\Gamma} = \Gamma\sqrt{\beta}/\sqrt{N_0}$, $\beta = 1.06 \times 10^{15}$ cm/meq, N_0 = total electrolyte concentration, in meq/cm^3.

Using the charge density values suggested above, one finds for $N_0 \leq 10^{-1}$, $\bar{\Gamma} = 10 - 300$. From Eq. (1) follows:

$$\frac{\gamma^-}{\gamma} \leq 0.16 \; (10^{-1} \; N_0)$$

and

$$\frac{\gamma^-}{\gamma} \leq 0.05 \; (10^{-2} \; N_0).$$

Thus, the general conclusion is that γ^-/γ varies between 1-15%. The suggested adsorption capacities for the edge and planar side yield the following situation for the 2 : 1-type clays (meq/100 g):

negative charge		Al groups at edge	
40-100		2-6	
positive adsorption	exclusion	positive adsorption	exclusion
cations	anions	anions	cations
30-99	1-15	2-6	0-1

Obviously the cation exclusion is always negligible in comparison with the cation adsorption. In contrast, the exclusion of anions at the planar side is comparable in magnitude to the anion adsorption at the edges. Thus a study of anion adsorption by clays must include the investigation of the anion exclusion at the planar side of the crystal.

Experimental data will, in principle, yield the overall adsorption: $\gamma_{tot} = \gamma^+_{an} - \gamma^-_{an}$. The separation of the two terms may be effected by (a) the use of an internal standard for γ^-_{an}, in combination with (b) calculation of the contribution of γ^-_{an} as a function of system variables. As an internal standard an anion is used which is a non-preferred species as regards anion adsorption (e.g. Cl). If a highly preferentially-adsorbed anion is also present (e.g. PO_4) the positive adsorption of the anion used as internal standard is effectively suppressed, thus yielding information on the contribution of the anion exclusion. Through calculation the corresponding exclusion of the pre-

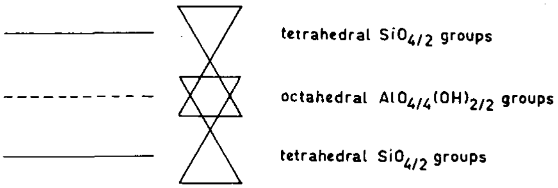


Fig. 1

Schematic representation of the crystal structure of 2:1-type clay minerals

ferred anion may be found which, upon addition to the overall adsorption, gives the correct value for the positive adsorption of the latter. The validity of the above combined approach may be verified by observations on extreme systems.

II. GENERALIZED CALCULATIONS

Introducing a system containing N_0 meq/cm³ of total electrolyte, divided over different cation and anion species of valence z_i, each at an equivalent concentration $f_i N_0$, the Poisson-Boltzmann equation of the diffuse double layer in the integrated form may be written as:

$$\frac{dy}{dx} = \sqrt{\beta N_0} \times \sqrt{\sum_i \left|\frac{f_i}{z_i}\right| (e^{z_i y} - e^{z_i y_c})}, \tag{2}$$

in which $y = -e\psi/kT$ = electric potential in units of 25 mV. The expression for the exclusion of anion j becomes:

$$\frac{\Gamma_j^-}{f_j N_0} = \int_{y_s}^{y_c} \frac{(1 - e^{z_j y})\,dy}{\left(\frac{dy}{dx}\right)}, \tag{3}$$

in which Γ^- is the anion exclusion in meq/cm² colloid surface, y_s is the value of y at the particle surface, y_c is the same at the end of the liquid layer in contact with this surface.

The combination of Eqs. (2) and (3) then gives:

$$\frac{\Gamma_j^-}{f_j N_0} = \frac{1}{\sqrt{\beta N_0}} \times \int_{y_s}^{y_c} \frac{(1 - e^{z_j y})\,dy}{\sqrt{\sum_i \left|\frac{f_i}{z_i}\right| (e^{z_i y} - e^{z_i y_c})}}. \tag{4}$$

Equation (4) may be solved for all mixtures of interest, although some of these solutions are cumbersome. In a recent publication by de HAAN [1] solutions are given for the following combinations (for all anions involved):

(a) $y_c = 0$, $z_i = +1, -1, -2, -3$
and $z_i = +2, +1, -1, -2, (-3)$

(b) $y_c \neq 0$, $z_i = +2, +1, -1$
and $z_i = +1, -1, -2, (-3)$.

The results of these computations may all be expressed as:

$$\frac{\Gamma_j^-}{f_j N_0} = \frac{1}{\sqrt{\beta N_0}} \left\{ \int_{\infty}^{y_c} (\dots\dots) - \int_{\infty}^{y_s} (\dots\dots) \right\}$$

$$= \frac{Q_j}{\sqrt{\beta N_0}} - \delta_j^- , \qquad (5)$$

in which Q_j is a number varying roughly between 1 and 3, and δ_j^- is a distance varying (for the charge densities mentioned) between 1 and 4 Å. The quantity Γ^-/fN_0 may be termed the distance of exclusion, d^-. Equation (5) may then be written:

$$d_j^- = D_j^- - \delta_j^- , \qquad (5a)$$

as illustrated in Fig. 2.

For the freely-expanded double layer the value of Q depends solely on the mixing ratio of the ions involved. In systems containing only a mono-monovalent salt, Q equals 2. In this case the value of δ^- is found as a series expansion of $\overline{\Gamma}$, according to:

$$\beta \Gamma \delta^- = 4 - \frac{16}{\overline{\Gamma}^2} + \frac{128}{\overline{\Gamma}^4} \dots\dots \qquad (6)$$

For $\overline{\Gamma} \geqq 10$ the first term suffices, which makes δ^- identical with δ, the extrapolated distance (behind the colloid surface) at which the anion concentration reaches the value zero. In systems containing a mixture of mono- and divalent cations, in addition to a monovalent anion one finds the value of the first term of δ^- as:

$$\delta^- \simeq \delta \simeq \frac{2}{\beta \Gamma} (1 + \sqrt{1 + K} - \sqrt{K}), \qquad (7)$$

with $K = f^{++}/[2(1 - f^{++})^2] \times \overline{\Gamma}^2$. Obviously K varies between zero and infinity; as a result δ^- varies between $4/\beta\Gamma$ for the monovalent cation, and $2/\beta\Gamma$ for the case of the divalent cation, when combined with a monovalent anion.

Finally it follows that the experimentally determined "volume of exclusion", $\gamma_j^-/f_j N_0$ (with γ^- = exclusion per gram of colloid = $S \times \Gamma^-$), when plotted against $Q_j/\sqrt{\beta N_0}$, should yield a straight line with a slope equal to the specific surface area of the colloid, S, as long as δ^- remains constant (i.e. at large values of $\overline{\Gamma}$). The above may be illustrated by the generalized plot

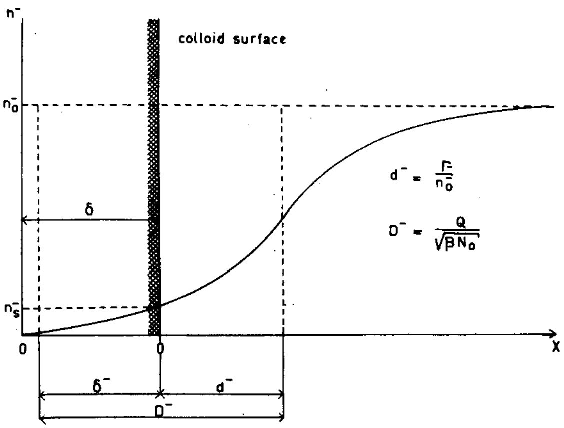


Fig. 2

Concentration distribution of anions

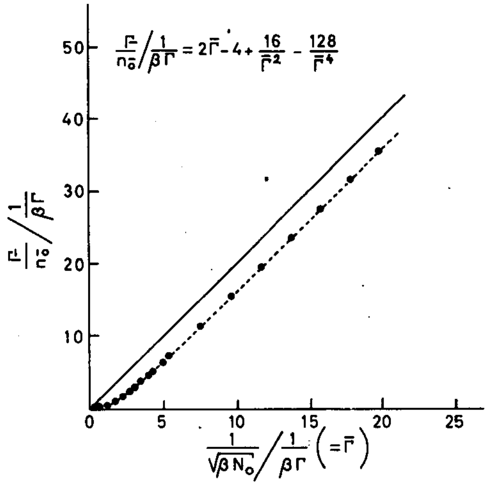


Fig. 3

$\frac{\Gamma^-}{n_0^-}\Big/\frac{1}{\beta\Gamma}$ as a function of $\frac{1}{\sqrt{\beta N_0}}\Big/\frac{1}{\beta\Gamma}$ for all systems containing mono-monovalent electrolytes

of $(\Gamma^-/n_0^-)/(1/\beta\Gamma)$ against $(1/\sqrt{\beta N_0})/(1/\beta\Gamma)$ valid for all systems containing mono-monovalent electrolytes (Fig. 3).

It should be noted that in this plot the quantity $1/\beta\Gamma$ in fact corresponds roughly to one-half of the Debye-Hückel parameter $1/K_s$, i.e. the value of $1/K$ pertaining to a solution concentration equal to that occurring at the colloid surface. Thus it is easily shown (from Eq. (2)) that C_s, the counter-ion concentration at the surface, equals about $\beta\Gamma^2/4$, so $1/K_s = 1/\sqrt{\beta C_s} = 2/\beta\Gamma$. For the particular case of montmorillonite ($\Gamma = 10^{-7}$ meq/cm^2) one finds that $1/\beta\Gamma$ equals roughly 1 Å. The above plot thus indicates the relationship between d^-, expressed in units of $(1/2)/K_s$, and $1/K$ (pertaining to the equilibrium solution), also expressed in units of $(1/2)/K_s$. The latter quantity then equals $\bar{\Gamma}$. It follows from Eqs. (5) and (6):

$$d^- / \frac{1}{\beta\Gamma} = 2\bar{\Gamma} - 4 + \frac{16}{\bar{\Gamma}^2} - \frac{128}{\bar{\Gamma}^4},$$

and thus for large values of $\bar{\Gamma}$ the above plot will yield a straight line with a slope of 2 at a vertical distance of 4 units of $1/\beta\Gamma$ from a line through the origin. For $\bar{\Gamma}$ approaching zero (i.e. at low values of Γ or high values of N_0) the line curves towards the origin.

III. DISCUSSION OF THE LIMITATIONS OF THE MODEL CALCULATIONS USED

(a) Tail-end interaction

Although the effect of double-layer interaction is already shown in Eq.(4), mention should be made of the anion exclusion in systems with interaction in terms of the maximum value that would be found in the absence of interaction. Introducing D^-_{int} and D^- for the corresponding (extrapolated) distances of exclusion it follows that

$$D^-_{int}/D^- = Q_{int}/Q.$$

The quantity Q_{int}/Q is now easily expressed as a function of D/D^-, in which D indicates the thickness of the liquid layers in contact with the colloid surface. As shown in Fig. 4, this relationship appears to be very similar for the different mixtures considered. The general conclusion is that, for $D/D^- \geq 2$ the reduction of D^-_{int} in comparison to D^- is negligible, whereas it is still small for $D/D^- \geq 1\frac{1}{2}$. For D values equal to or below D^- a considerable decrease in D^-_{int} is apparent, and for these cases the exact computation of the corresponding Q_{int} value may be necessary. Aside from the labour involved in these computations it appears that tail-end interaction offers no serious objection to the application of the above theory.

(b) Head-end disturbances

Under this heading one might classify all uncertainties incurred in applying the Gouy-Chapman theory. Obviously these uncertainties mainly concern the first few layers.

Giving attention first to the application of the simplified Boltzmann equation to the distribution of the anions themselves it is found that the uncertainties have little influence. As is evident from Eq. (3), the exclusion of the anion is computed by integrating the deficit, $(1 - e^{z_j y})$, over the entire layer. The Boltzmann factor $e^{z_j y}$ now takes into account only the electrostatic repulsion of the anion. Actually other factors will co-determine the

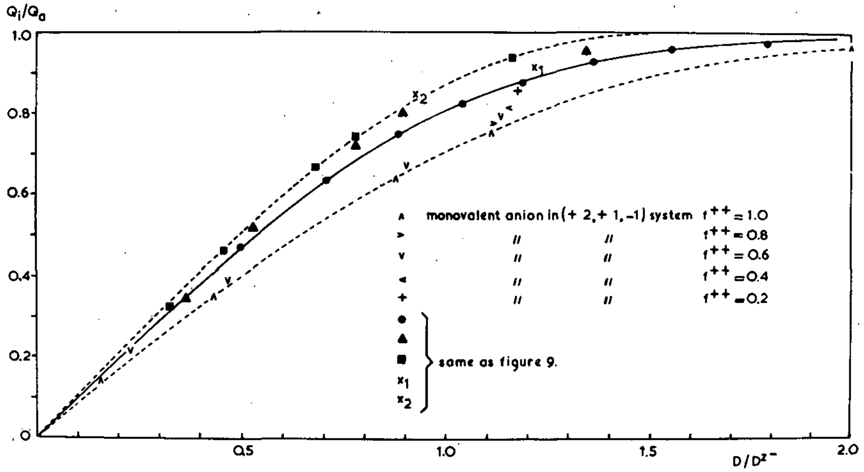


Fig. 4

The influence of double-layer interaction on anion exclusion

concentration of the anions in the first layers, as e.g. polarization energy, activity coefficients differing from unity, etc. Because in this region the "electrostatic" component of the Boltzmann factor amounts to a number as small as 10^{-2} or 10^{-3}, it is obvious that even the uncertainty of a factor of 2 or 3 will hardly change the magnitude of the deficit in these first layers.

Of greater importance is the uncertainty about the actual potential distribution, which follows from the application of the above simplified theory to the distribution of the cations. For the cations an under- or overestimate of the correct Boltzmann factor makes a considerable difference in the calculated concentration, and thus in the potential distribution. Upon closer consideration, however, it appears that here again the effect on the anion deficit will be of relatively small magnitude. In order to illustrate this, and for lack of a second (better) approximation for the actual cationic distribution, the effect of some fairly extreme deviations will be considered. Using NaCl-montmorillonite as an example one finds that for 10^{-3} $\underline{N}$ NaCl the distance of exclusion for "ideal" behaviour amounts to:

$$d^- = D^- - \delta^-$$

$$= 200 - 4 = 196 \text{ Å}.$$

This "ideal" distance is calculated, assuming that the counter-ions may closely approach the colloid surface which has a uniform charge density of 10^{-7} meq/cm^2. In actuality one may visualize any or all of the following conditions to be partly or fully applicable:

(a) A minimum distance of closest approach exists between cations and colloid surface of about 3 Å. The result is: $d^- = 196 + 3 = 199$ Å.

(b) Specific (short-range) attraction forces cause the formation of cation–colloid bonds to such an effect that 50% of the surface charge is already neutralized at the surface (counter-ions sunk into the surface). Thus

$$\delta^- = \frac{4 \times 10^8}{\beta \times \frac{1}{2} \times 10^{-7}} \text{ Å} = 8 \text{ Å}.$$

Therefore $d^- = 196 - 4 = 192$ Å.

(c) The combination of (a) and (b) (which appears as likely as (b) alone) would give

$$d^- = 195 \text{ Å}.$$

It may safely be assumed that all the above effects remain undetectable, if present, since the experimental error in γ^- will normally be at least 3%.

Obviously condition (b) will eventually ruin the applicability of the theory, if the short-range forces lead to reduction of the freely-diffusible countercharge to, e.g. less than 10%. However, disturbances in the cationic distribution must be rather gross disturbances before their effects will be felt on the anion exclusion. Particularly if such a reduction of free countercharge is coupled with a high electrolyte concentration (yielding small values of Γ) it should also be noted that the second and third terms of the series expansion of δ^- (Eq. (6)) may no longer be neglected. This indicates that in such a case a plot of the experimentally determined quantity γ^-/n_0^-, against $Q/\sqrt{\beta N_0}$, will no longer yield a straight line with a slope equal to the specific surface area (Fig. 5).

Apart from the above it is concluded that anion exclusion in clay systems may be described satisfactorily by the relations derived from the Gouy-Chapman theory.

IV. EXPERIMENTAL DATA

A short description of some experimental data on anion-clay interaction is presented below. For more data and detailed description of those given here see [1].

Figure 6 presents the results of Cl exclusion measurements in Na-Cl-montmorillonite systems (Osage, fraction < 2 μm). The exclusion was measured by means of titration and by means of isotopic dilution. The data indicate a specific surface area of about 700 m^2/g. At low concentration levels the titration data start to deviate as a result of inaccuracy of the measurements.

The results of Cl exclusion by this same clay at different cationic compositions (0, 50 and 100% Ca at the adsorption complex, respectively) are shown in Fig. 7. Within experimental error all points come to the 700 m^2/g line.

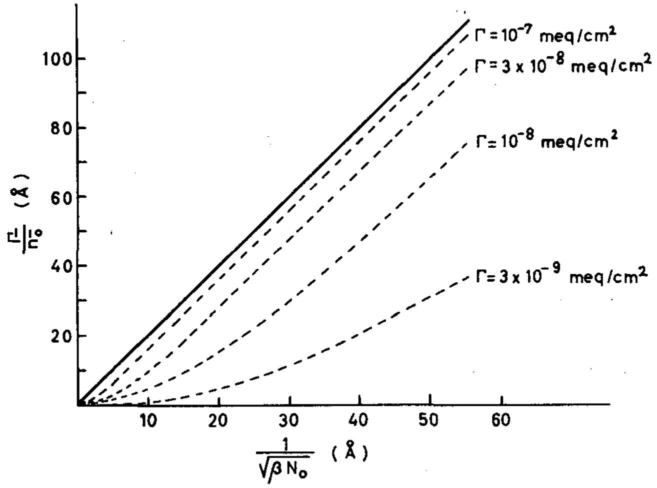


Fig. 5

The distance of exclusion as a function of $\frac{1}{\sqrt{\beta N_0}}$ for different values of the surface charge density

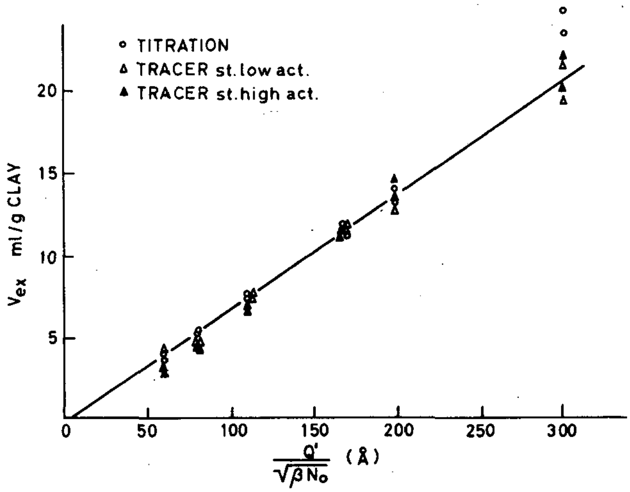


Fig. 6

The exclusion of Cl in Na-Cl-montmorillonite systems as measured according to different methods

Figure 8 presents results of the simultaneous determination of chloride and sulphate exclusion by Na-illite (Winsum, a fraction < 2 μm), indicating a specific surface area of 300 m²/g.

Chloride exclusion was also measured in soil systems. To this purpose the fraction < 50 μm of three Dutch clayey soils was used. The lines of Fig.9 indicate the values of the specific surface area as measured five-fold at a N_0 value of about 0.01 N. The points indicate exclusion values at different

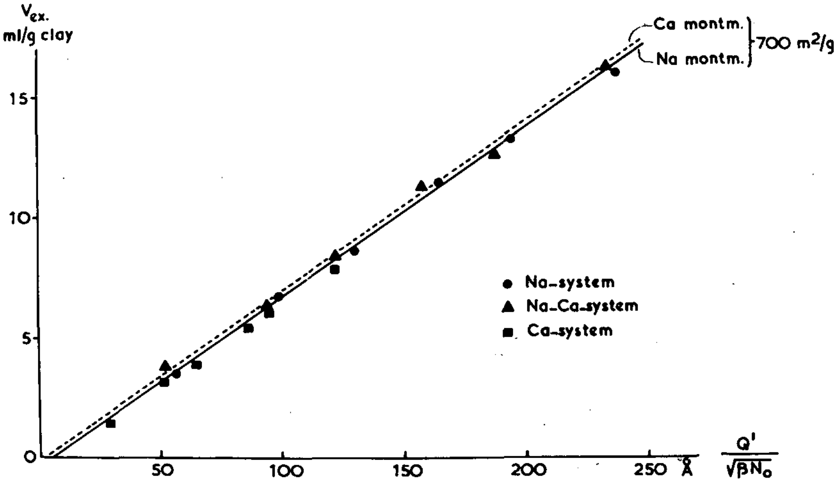


Fig. 7

The exclusion of Cl by montmorillonite at different cationic compositions

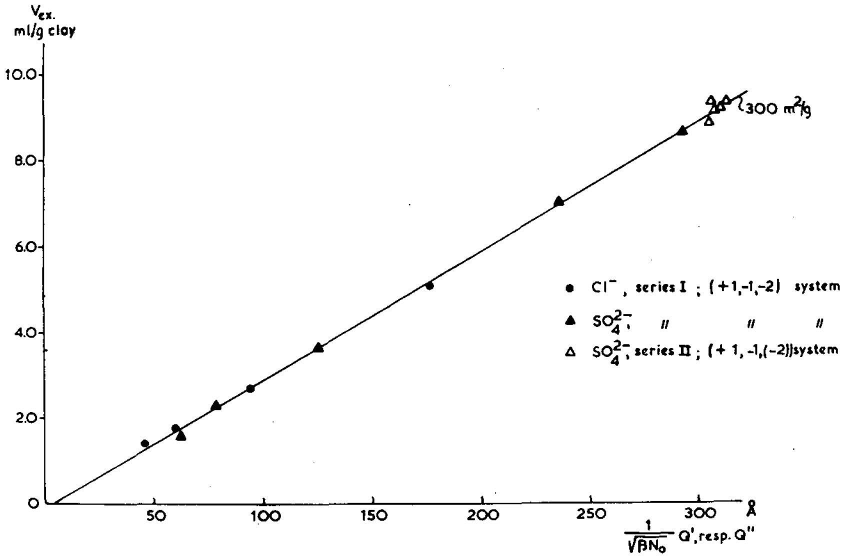


Fig. 8

Simultaneously measured exclusion of Cl and SO_4 by Na-illite

electrolyte concentrations. In this experiment phosphate was added to the soils to prevent a possible positive adsorption of chloride.

Chloride and sulphate exclusion data, measured simultaneously in montmorillonite, with a Ca composition of 0, 80 and 100% Ca, are shown in Fig.10. The deviations from the 700 m^2/g line are interpreted as the result of flocculation of the clay (especially occurring at high Ca saturation, combined with

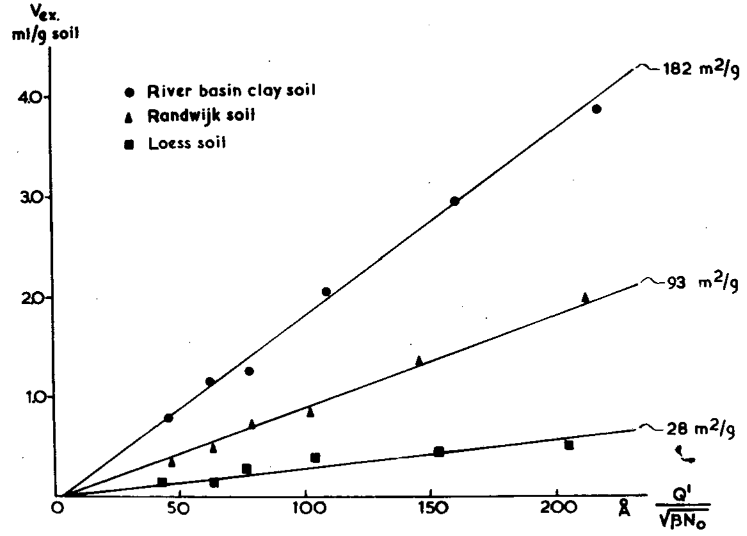


Fig. 9

The exclusion of Cl by three Dutch clayey soils

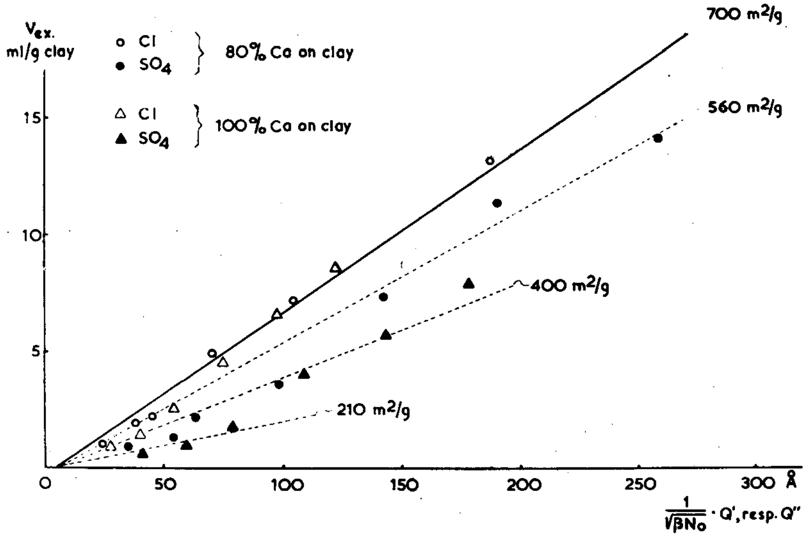


Fig.10

Simultaneously measured exclusion of Cl and SO_4 by montmorillonite at different cationic composition

high electrolyte levels). Since the exclusion distance of sulphate is larger than that of chloride, it could be expected that sulphate exclusion is more sensitive towards flocculation than chloride exclusion. It could be shown that the depression of sulphate relative to that of chloride was in accordance with theoretical expectations [1].

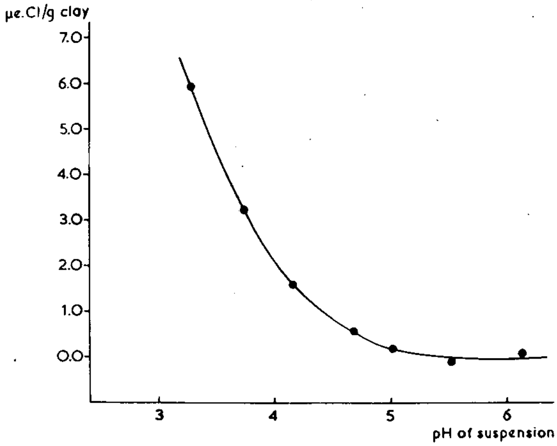


Fig. 11

The net positive adsorption of Cl on Na-kaolinite as a function of the pH

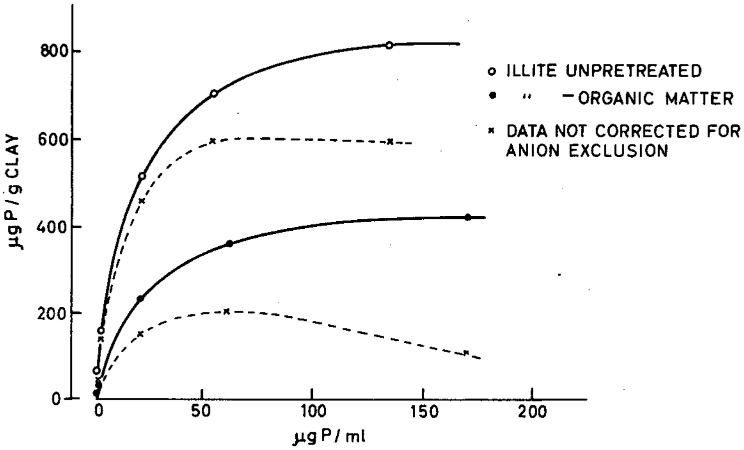


Fig. 12

Phosphate adsorption isotherm for illite

Figure 11 presents the relationship between pH and net adsorption of chloride by kaolinite (Drybranch, fraction < 2 μm). The net positive adsorption was found from the over-all adsorption measurements after correction for anion exclusion.

The necessity to correct anion adsorption measurements for anion exclusion is shown in Fig. 12, indicating phosphate adsorption isotherms for illite with and without organic matter. The increase of phosphate adsorption after removal of the organic matter indicates that organic substances may cover, at least in part, the reactive spots at the edges.

Figure 13 presents the phosphate adsorption on montmorillonite at a phosphate level of about 4×10^{-4} $\underline{N}$ as a function of the total electrolyte con-

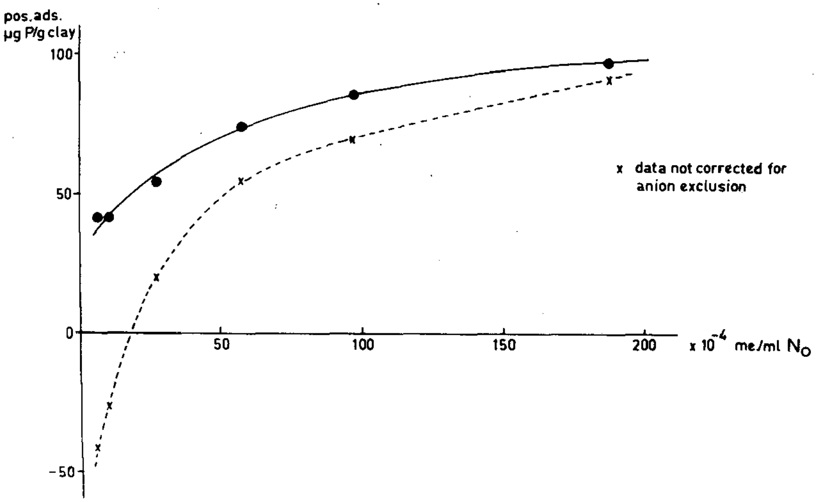


Fig. 13

The net positive adsorption of phosphate on Na-montmorillonite as a function of total electrolyte level

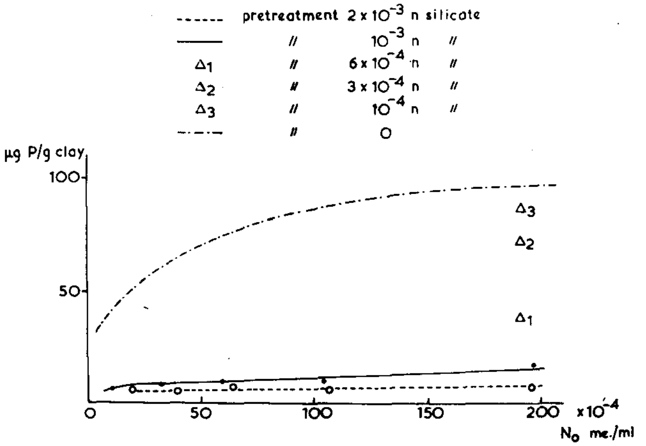


Fig. 14

The influence of silicate on the net positive adsorption of phosphate by Na-montmorillonite

centration. The dotted line, representing the uncorrected adsorption data, shows that the neglect of anion exclusion would indicate a negative phosphate adsorption, whereas actually a considerable positive adsorption prevails.

The influence of silicate on phosphate adsorption is presented in Fig. 14. It is evident that silicate serves as a good competitor for phosphate.

This competition has been used in an experiment in which the phosphate adsorption was completely suppressed by silicate addition. The exclusion of chloride, sulphate and phosphate was then measured simultaneously, applying the titration method with respect to chloride and the tracer method

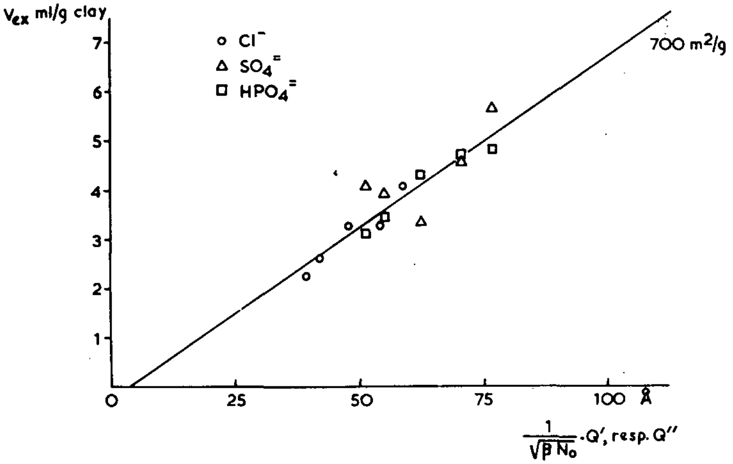


Fig. 15

Simultaneously measured exclusion of three different anions by Na-montmorillonite

with respect to both sulphate and phosphate (making use of the difference in half-life of S^{35} and P^{32} to distinguish between both isotopes). In Fig. 15 it is shown that all three anions behave, within experimental error, as would be expected from the theory of anion exclusion.

REFERENCES

[1] de HAAN, F. A. M., "The interaction of certain inorganic anions with clays and soils", Versl. Landbouwk. Onderz., Wageningen (1965).

[2] BOLT, G. H. and WARKENTIN, B. P., "The negative adsorption of anions by clay suspensions", Koll. Zeitschr. 156 Bd, 1 (1958) 41.

[3] BOLT, G. H., "The pressure filtrate of colloidal suspensions", Koll. Zeitschr. 175 Bd, 1 (1961) 33, 144.

[4] de HAAN, F. A. M. and BOLT, G. H., "Determination of anion adsorption by clays", Soil Sci. Soc. Am. Proc. 27 (1963) 636.

[5] de HAAN, F. A. M., "The negative adsorption of anions (anion exclusion) in systems with interacting double layers", J. Phys. Chem. 68 (1964) 2970.

DISCUSSION

J. P. QUIRK: The results presented by Professor Bolt on negative adsorption of mixed ion montmorillonite systems were extremely interesting and, in a general way, these results agree with results Edwards and I have published[1] and some more detailed results for montmorillonite that Dr. Edwards, Dr. A. M. Posner and I are preparing for publication. We have also made extensive investigations on monovalent and divalent homoionic illites. For the principal illite we used, the stoichiometric charge density was about 2.5 times that for montmorillonite. We have found for the alkali

---

[1] J. Coll. Sci. 17 (1962) 872.

metal cations a series of straight lines when the volume of exclusion is plotted against $q/\sqrt{\nu B C_0}$; the slope decreased from Li to Cs. For Cs-illite negative adsorption was not measurable. The most significant feature of our results is that the straight lines all project very close to the origin. If the decreasing slope were simply due to an increase in ion binding and the remaining dissociated or free ions (i.e. free to participate in double-layer formation) were regarded as smeared out, then a series of lines not passing through the origin should be obtained. These curves will be clearly different from a series of straight lines passing through the origin as they will show increasing intercepts on the x-axis as the surface density of charge decreases.

We have interpreted our results as evidence for discrete charged sites. An ion at each site may be free or bound. At a free site the ion forms double layers. The slope of the lines for the various cations is determined by the number of free sites and hence

$$\text{Slope} = A = N\left(\frac{2}{K}\right)^2 = N \times \frac{B}{C_0},$$

where N is the number of free sites, 1/K is the Debye-Hückel characteristic length, B is a constant and C_0 is the concentration in the external solution. Clearly, since the slope of the lines is constant, the number of sites must decrease with decreasing concentration. Because the charge density at the discrete sites is high, the straight lines project to the origin and the slope reflects the number of free sites.

The significance of these results for our immediate purpose is that the behaviour ions at a clay surface will obviously influence the movement of cations and anions in the system. The results also mean that negative adsorption measurements are not well suited for the measurement of surface areas. It should be remembered that kaolinite can vary widely in its surface charge density[2].

In speaking of phosphate adsorption measurements, Professor Bolt has rightly suggested that care should be taken to allow for negative adsorption. The particular case he has taken of an illite with a large surface area and relatively low phosphate adsorption emphasizes this point. In very dilute solutions this difficulty could be resolved by carrying out measurements in the presence of high concentrations of an indifferent electrolyte, such as potassium nitrate.

Muljadi, Posner and I have studied the uptake of phosphate by kaolinite, gibbsite and pseudoboehmite. We have found it possible to describe the adsorption in terms of three regions which can be clearly seen on the isotherms. Regions I and II are associated with $Al(OH)_2$; thus $\mathrm{Al}\!<\!\begin{matrix}\mathrm{OH}\ \ \mathrm{I.}\\ \mathrm{OH}\ \ \mathrm{II.}\end{matrix}$ at the edge face of the crystal or on an exchange site: Region I ≈ Region II. The amount of phosphate adsorbed in Region I corresponds to the amount of chloride adsorbed at low pH values. Region III is linear and corresponds to penetration into an amorphous region, probably at the crystal edges. The

---

[2] GREENLAND, D.J. and QUIRK, J.P., Trans. Internat. Cong. Soil Sci. Soc. New Zealand (1962) 79.

mechanism of adsorption is that a proton is adsorbed and H_2PO_4 is exchanged for OH^-. Calorimetric measurements and isotherms determined at a number of temperatures have shown that ΔH is very small and that the driving force is entropic, corresponding to the displacement of two water molecules. Some of these results will be published in the Transactions of the VIIIth International Congress of Soil Science.

G.H. BOLT: An example of such extreme reduction of the free countercharge appears to be present in certain systems studied by Professor Quirk (e.g. Cs-illite). Assuming that reduction of the surface area through plate-condensation did not occur in this case (as was indicated by Professor Quirk) it remains to be explained why the observed relationship between the exclusion volume and $1/\sqrt{\beta N_0}$ appeared to be linear with a deficient slope. One explanation seems to be that the observed range falls entirely at the beginning part of the curve of Fig. 3. A slight curvature might remain unnoticed if only very small values of Γ (corresponding to a small fraction of free countercharge) occurred in the systems studied. In Fig. 5 the expected behaviour for small values of the free countercharge is indicated. Obviously the expected line for a free countercharge amounting to 0.3×10^{-8} meq/cm^2 might be regarded as close to linear in the range from 0-40 Å for $1/\sqrt{\beta N_0}$. At the same time the above will never explain an observation of a straight line with a slope of, say 0.7 times the true surface area. Such a line appears to indicate, as was pointed out by Professor Quirk, a "free" countercharge which is continually decreasing with increasing values of $1/\sqrt{\beta N_0}$.

Using the first-term approximation for δ^- (Eq. (6)) it can easily be shown that, for a reduction of the observed slope with a factor p, the Gouy-Chapman calculations above then require that

$$\frac{\Gamma_{\text{free}}}{\Gamma} = \frac{2}{1-p} \Big/ \bar{\Gamma} = \frac{2}{1-p} \Big/ \frac{\Gamma\sqrt{\beta}}{\sqrt{N_0}} .$$

Using the value of 3×10^{-7} meq/cm^2 for the charge density of illite produces results shown in Table I. Whether the above assumptions are tenable, i.e. a decreasing amount of free countercharge with decreasing electrolyte concentration, remains to be seen.

TABLE I

RELATION BETWEEN ELECTROLYTE CONCENTRATION, N_0, AND DISTANCES BETWEEN FREE CHARGES, FOR $\Gamma\sqrt{\beta}$ = 10 and p = 0.5

N_0 (meq/cm^3)	1	0.25	0.04	0.01	0.0025	0.0004
2/K (Å)	6	12	32	62	126	314
$\Gamma_{\text{free}}/\Gamma$	0.40	0.20	0.08	0.04	0.02	0.01
Distance between free charges (Å)	10	15	25	35	50	70

The explanation forwarded by Professor Quirk, that is, the formation of isolated exclusion spheres around localized "free" charges, according to the present authors, leads to the same conclusions as the one above. That is to say, that again a decrease in free countercharge upon a decreased electrolyte concentration must be made acceptable. In addition, Professor Quirk's hypothesis requires the fractional free charge to be proportional to the first power of the electrolyte concentration, indicating that the decrease would be much steeper than the one required in the above treatment. In conclusion, the present authors feel that the data presented do not warrant a decision as to the necessity of introducing the localized charge treatment, without further calculations. In fact the case shown in Table I indicates that only at concentrations above 0.1 N would such a treatment appear to be necessary.

DETERMINATION OF SOME MACROCOMPONENTS OF SOIL SOLUTIONS BY NEUTRON ACTIVATION ANALYSIS

W. ŻMIJEWSKA AND J. MINCZEWSKI
INSTITUTE OF NUCLEAR RESEARCH, ANALYTICAL DEPARTMENT,
WARSAW, POLAND

This paper reports on part of the investigation on the possibility of applying the neutron activation method to the analysis of soil solutions. The problem is being worked on in the authors' laboratory under an IAEA research contract.

The first part of the work was devoted to the study of some analytical parameters, i.e. detectability and precision of the determination of individual elements. The mutual influences of the elements to be determined were studied and a suitable analytical procedure was worked out. The experiments were performed on synthetic mixtures prepared in the laboratory. The composition of the mixtures was established on the basis of literature data. It has been accepted that the concentration of individual macrocomponents of the soil solutions varies approximately in the ranges shown in Table I.

Experiments were restricted to the use of radioisotopes of relatively long half-lives, since the nuclear reactor EWA used for irradiation is located in Swierk, a distance of about 30 km from the laboratory in Warsaw. This requires time for transportation of the irradiated samples and short-lived radioisotopes cannot be used. For example, it was impossible to determine magnesium, since magnesium radioisotope Mg^{27} ($T_{\frac{1}{2}}$ = 9.45 min) can only be used for the determination of this element if the cooling period is of the order of several minutes. Nuclear characteristics of the radioisotopes used in the experiments are given in Table II. According to this data the macrocomponents of the soil solutions can be divided into two groups: elements which, on neutron irradiation yield radioisotopes emitting beta

TABLE I

CONCENTRATION OF INDIVIDUAL MACROCOMPONENTS OF THE SOIL SOLUTION

Component	Concentration range (μg/ml) - (mg/ml)
Na^+	100 - 10
K^+	10 - 1
Mg^{2+}	10 - 5
Ca^{2+}	100 - 5
$Fe^{2+, 3+}$	- -
PO_4^{3-}	100 - 1
SO_4^{2-}	100 - 10
Cl^-	100 - 10

and gamma radiation; and elements which, on neutron irradiation yield pure beta emitters. The elements of the first group were determined by gamma-spectrometry; those of the second required radiochemical separation.

GAMMA SPECTROMETRIC DETERMINATION OF Cl, Na, K, and Fe

All gamma-emitters presented in Table II can be divided into three groups:

(a) Short-lived radioisotopes, Cl^{38};
(b) Medium-lived radioisotopes, Na^{24}, K^{42}; and
(c) Long-lived radioisotopes, Fe^{59}.

Determination of individual gamma emitters was carried out according to these groups.

To determine chlorine, samples were irradiated in the thermal column of the nuclear reactor at a neutron flux of 1×10^{12} n/cm$^2 \cdot$ s for 30 min. The cooling period was approximately 2 h. Determination of sodium and potassium was carried out after irradiation in the thermal column of the reactor for 24 h, and cooling for 4 h. To determine iron the samples were irradiated in the reactor core at a neutron flux of 1×10^{13} n/cm$^2 \cdot$ s for two weeks and cooled for one week.

The gamma-ray spectra were taken by means of a 256-channel gamma spectrometer (Finska Kabelfabriken), with a 2" × 2" NaI(Tl) crystal, except for preliminary experiments, which were carried out with the aid of a single channel spectrometer.

TABLE II

NUCLEAR DATA OF SOME MACROCOMPONENTS OF THE SOIL SOLUTION

Element	Target nuclide	Natural abundance (%)	Cross section (b)	Radio-isotope formed	Half-life	Energy of radiation (MeV) Beta	Gamma
Na	Na^{23}	100.0	0.51	Na^{24}	15.0 h	1.39	1.37 2.75
Mg	Mg^{26}	11.3	0.026	Mg^{27}	9.45 min	1.8	0.84 1.02
P	P^{31}	100.0	0.19	P^{32}	14.6 d	1.71	-
S	S^{34}	4.21	0.26	S^{35}	87.1 d	0.165	-
Cl	Cl^{37}	37.3	0.56	Cl^{38}	37.3 min	4.81	1.60 2.15
K	K^{41}	6.91	1.0	K^{42}	12.5 h	3.58	1.53
Ca	Ca^{44}	2.06	0.63	Ca^{45}	152.0 d	0.25	-
Fe	Fe^{58}	0.31	0.9	Fe^{59}	45.0 d	0.46	1.10 1.28

The analytical data obtained in experiments performed on pure solutions of individual elements are given in Table III. They characterize generally the detectability and precision of the method. To work out the analytical procedure it was necessary to study the mutual influence of all elements determined. The following results were obtained:

Determination of Cl

Experiments have shown that Ca^{2+}, Mg^{2+}, SO_4^{2-} and PO_4^{3-} do not interfere with the determination of chlorine, even if present in amounts higher by two orders of magnitude. Calcium, sulphur and phosphorus form pure beta-emitters on neutron irradiation but during the short period of irradiation they are scarcely activated at all. The activity of the short-lived magnesium radioisotope, Mg^{27}, decays during the cooling period (about 2.5 h) to a low level. Both Mg^{27} photopeaks occur on the left side of the Cl^{38} photopeaks, and thus do not interfere with the determination of chlorine.

If potassium is present in a concentration ten times higher than that of chlorine, the determination of chlorine should be based on the 2.15-MeV photopeak.

Serious interferences occur if sodium is present. Determination of chlorine is possible if the concentration ratio Na : Cl is less than 1. Determination should be based on the 1.62-MeV photopeak; determination on the basis of the 2.15-MeV photopeak leads to error because of the coincidence of the Cl^{38}-2.15-MeV photopeak and the 2.24 MeV Na^{24} escape peak.

If sodium is present in higher concentration, separation of chlorine from sodium is necessary. This, of course, would extend the cooling period and result in lower Cl^{38} activity. In the authors' laboratory, separation was impossible due to the time which had already elapsed in the course of transportation of the irradiated samples.

Determination of sodium

Ca^{2+}, Mg^{2+}, K^{+}, PO_4^{3-} in concentrations up to 100 times higher than that of sodium do not interfere with the determination of sodium.

Determination of potassium

Mg^{2+}, Ca^{2+}, Cl^{-}, SO_4^{2-} and PO_4^{3-} in concentrations up to 100 times higher than that of potassium do not interfere with the determination of potassium.

The most serious interference is caused by sodium. Non-destructive determination of potassium in the presence of sodium is possible if the concentration ratio $K/Na > 100$. The results presented in Table III were obtained from samples containing sodium. If the ratio $K/Na < 100$, a non-destructive determination cannot be carried out and separation from sodium is necessary. Ion-exchange chromatography was the most convenient technique for this purpose.

The results obtained using amberlite IR-120 (diam. 0.1 mm), flow-rate about 0.7 ml/min, temperature 24°C and 1 $\underline{N}$ HCl solution are given in Table IV.

The anions Cl^{-}, SO_4^{2-} and PO_4^{3-} are not absorbed on the cation exchanger and appear in the effluent in the first fractions up to 8 ml. Magnesium and calcium ions are absorbed on the exchanger and must be eluted from the column.

As has been stated above, magnesium and calcium do not interfere with the determination of potassium; nevertheless their presence must be considered, because they lower the exchange capacity of the column and must be taken into account during the regeneration process of the resin in the column.

Determination of iron

During the cooling period all short- and medium-lived radioisotopes of the elements investigated decay to a negligible level. Calcium, phosphorus and sulphur produce the long-lived isotopes Ca^{45}, P^{32} and S^{35} on irradiation in the reactor. All of them are pure beta-emitters; S^{35} and Ca^{45} emit soft beta radiation which does not interfere with the determination of iron. Concentrations higher by two orders of magnitude than that of iron do not influence the gamma-ray spectrum of the latter. However P^{32} emits hard

TABLE III

ANALYTICAL DATA FOR PURE SOLUTIONS OF INDIVIDUAL GAMMA EMITTERS (Cl, Na, K, Fe) OBTAINED BY THE GAMMA SPECTROMETRIC METHOD

Neutron flux (n/cm² · s)	Radio-nuclide	Photo-peak energy of the gamma spectrum (MeV)	Irradiation time	Cooling time	Added (μg)	Found (the range of the results) (μg)	Number of experiments	Mean ± standard deviation [μg (%)]	Spectrum storage time (min)
10^{12}	Cl^{38}	1.60	30 min	2-3 h	10.0	8.8 - 13.0	9	11.2 ± 0.42 (3.7)	2
						9.0 - 12.0		10.2 ± 0.36 (3.5)	
10^{12}	Na^{24}	1.37	24 h	4 h	0.10	0.096 - 0.11	6	0.10 ± 0.0075 (7.5)	
		2.75				0.086 - 0.11	5	0.098 ± 0.0038 (3.9)	
		1.37			0.01	0.010 - 0.013	5	0.011 ± 0.0006 (5.5)	10
10^{12}	K^{42}	1.53	24 h	4 h	10.0	9.6 - 12.0	12	10.4 ± 0.39 (3.7)	
					1.0	1.0 - 1.4	6	1.1 ± 0.1 (9.0)	10
10^{13}	Fe^{59}	1.10	2 weeks	1 week	11.4	10.4 - 11.5	6	11.2 ± 0.17 (1.5)	30
		1.28				7.8 - 12.2	6	10.2 ± 0.51 (5.0)	
		1.10			3.4	3.4 - 4.3	4	3.8 ± 0.20 (5.2)	
		1.28				2.7 - 3.3	4	3.1 ± 0.17 (5.4)	

TABLE IV

DETERMINATION OF POTASSIUM AFTER SEPARATION FROM SODIUM BY ION-EXCHANGE

Experiment (No.)	Potassium (μg)		
	Added	Determined (a)	Determined (b)
1	10.0	9.8	11.2
2	10.0	10.6	10.4
3	10.0	11.0	12.4
4	10.0	9.2	11.4
5	2.0	1.7	1.9
6	2.0	1.7	1.8
7	2.0	2.0	2.1
8	2.0	2.1	-

beta radiation which gives rise to a continuous spectrum of bremsstrahlung. If the concentration ratio P/Fe > 100, the bremsstrahlung of P^{32} interferes with the determination of iron.

Determination of calcium, phosphorus and sulphur

Determination of calcium, phosphorus and sulphur was carried out after irradiation in the reactor core at the neutron flux 1×10^{13} n/cm$^2 \cdot$ s for two weeks and cooling for one week.

Phosphorus-32, Ca^{45}, and S^{35} are long-lived radioisotopes, while other macrocomponents of the soil solutions (expect iron) yield short- or medium-lived radioisotopes on irradiation with thermal neutrons. This is of great advantage since only iron must be considered as a radioactive contaminant, when elaborating a method for the determination of calcium, phosphorus and sulphur. The radioisotopes of the other macrocomponents are allowed to decay to a negligible activity level by choosing a suitable cooling period.

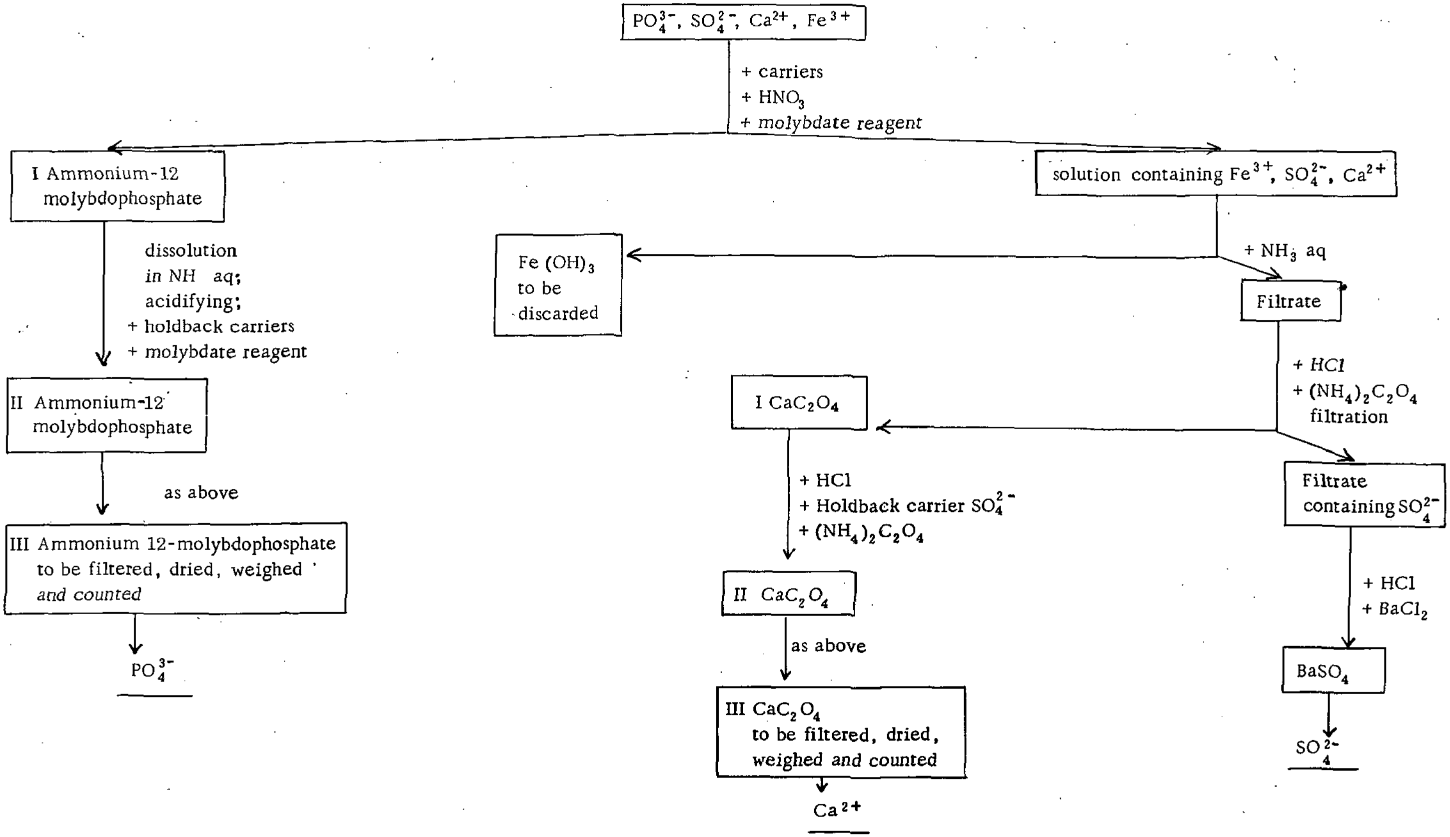
Though, on irradiation with thermal neutrons chlorine forms a short-lived radioisotope Cl^{38}, it must be considered as a radioactive contaminant, because of the interfering nuclear reaction $Cl^{35}(n,\alpha)P^{32}$ and $Cl^{35}(n,p)S^{35}$. These reactions are discussed below.

The scheme of separation elaborated for this system is shown in Table V.

An end-window G-M counter was used for counting P^{32}. An aluminium filter (60 mg/cm^2) was used to check the radiochemical purity of the isolated precipitate of ammonium-12 molybdophosphate. The ratio of the activity counted without a filter to the activity counted through the filter was 1.44 for

TABLE V

THE SEPARATION SCHEME OF PO_4^{3-}, SO_4^{2-}, Ca^{2+}, Fe^{3+}



pure phosphate standard. The same ratios were obtained for the precipitates isolated from synthetic mixtures, indicating the precipitates to be radiochemically pure.

The β-rays of Ca^{45} were counted in the same way. The radiochemical purity of the precipitate of calcium oxalate was checked by means of the same aluminium filter. If the precipitate was not contaminated by any γ-emitters or β-emitters of energy higher than that of calcium, its activity counted through the filter was equal to the background activity.

Since the β-rays of Ca^{45} are soft, the self-absorption effect is considerable and must be taken into account. The self-absorption corrections were taken from a graph which had been constructed experimentally. There are some nuclear reactions which interfere with the determination of calcium and phosphorus by this method and must be therefore taken into account. Two of them lead to the formation of Ca^{45}:

$$Sc^{45}(n, p)Ca^{45}$$

$$Ti^{48}(n, \alpha)Ca^{45}.$$

Both reactions occur with fast neutrons. Since the irradiation of calcium is carried out in the reactor core where the fast neutron flux is significant, these reactions may lead to erroneous results for calcium.

We have studied the effect of these reactions and found that 1 μg of Ti and Sc gives rise to Ca^{45} activity, equivalent roughly to 0.005 μg or 0.2 μg of Ca, respectively.

Titanium may be present in the soil solution; its concentration however is not likely to be higher than that of calcium, hence the effect of the second above-mentioned reaction can be regarded as negligible.

The effect of the $Sc^{45}(n, p)Ca^{45}$ reaction is more significant. Fortunately, Sc occurs in trace amounts in soils, i.e. the concentration of Sc is by several orders of magnitude lower than that of calcium. Hence, no interferences from this reaction should be expected in the determination of calcium in the soil solution.

Serious interferences arise in the determination of phosphorus in the presence of chlorine and sulphur owing to the following nuclear reactions with fast neutrons:

$$S^{32}(n, p)P^{32} \text{ and}$$

$$Cl^{35}(n, \alpha)P^{32}.$$

The authors' experiments pointed out that 1 μg of sulphates or chlorides gives rise to P^{32} activity roughly equivalent to 0.05 μg PO_4^{3-} when the irradiation was carried out in the reactor core. The same amount (1 μg) of sulphates or chlorides irradiated in the thermal column of the reactor gives rise to P^{32} activity equivalent to 0.0005 μg of P^{32}.

As both sulphates and chlorides may be present in the soil solution in concentration exceeding that of phosphorus, the irradiation should be carried out in the thermal column of the nuclear reactor instead of irradiating the sample in the reactor core. However, the sensitivity of the determination in this case will be approximately 100 times lower, owing to the lower thermal neutron flux in the thermal column (10^{11} n/cm^2 · s as compared with 10^{13} n/cm^2 · s in the reactor core).

If the concentration of PO_4^{3-} ions in the sample is so low that it requires irradiation in the reactor core, corrections for the content of chlorine and sulphur are necessary. These corrections require preliminary determination of chlorine and sulphur in the analysed sample.

Some results of calcium and phosphorus determinations are shown in Tables VI and VII.

The results shown in Table VI indicate that calcium can be determined in the presence of phosphates, sulphates, chlorides and iron with reasonably good accuracy. The ratio of other ions to calcium does not influence the accuracy of the determination of calcium in the range 1-10 for PO_4^{3-} and 10-100 for other ions (compare Experiments 1 and 2, Table IV).

The accuracy of the determination of calcium decreases when the concentration of calcium approaches the sensitivity limit (0.2 μg Ca). This is undoubtedly due to the error involved in counting low-level activity. Net activity equal to the background activity of the counter was regarded as the sensitivity limit.

Analysis of the results of the determination of phosphorus presented in Table VII indicates that the ratio of sulphur and chlorine to phosphorus does not influence the accuracy of the determination of phosphorus within the range 1-10 if the correction for S and P contents is applied. The accuracy of the determination in series 6 and 7 is roughly the same, though the ratio of Cl and S to phosphorus is different.

The results of series 6 and 7 show a negative bias. This is probably due to the error involved in estimating the value of the correction for the contents of P and S.

The concentration level within the range investigated influences the accuracy of the determination. The sensitivity of the determination of phosphorus is 0.003 μg PO_4^{3-}, when the net activity of the sample equals the background activity of the counting unit.

The determination of sulphur presents a rather difficult problem due to interfering nuclear reactions.

Determination of sulphur by the neutron activation method can be based upon two nuclear reactions:

$$S^{34}(n,\gamma)S^{35} \quad (1)$$

$$S^{32}(n,p)P^{32} \quad (2)$$

Reaction (2), takes place with fast neutrons; reaction (1) occurs with thermal neutrons. Sulphur-35 is a pure beta emitter with a half-life of 87.1 d. The relatively long half-life and the low natural abundance of the target isotope S^{34} (4.2%) result in a very low sensitivity of about 20 μg. Separation of sulphur-35 in a radiochemically pure state is inconvenient, owing to the insolubility of barium sulphate which makes reprecipitation difficult. The measurement of S^{35} activity presents difficulties owing to the strong self-

TABLE VI

RESULTS OF Ca DETERMINATIONS

Series (No.)	$\frac{PO_4^{3-}}{Ca^{2+}}$	$\frac{SO_4^{2-}}{Ca^{2+}}$	$\frac{Cl^-}{Ca^{2+}}$	$\frac{Fe^{3+}}{Ca^{2+}}$	Calcium added (μg)	Calcium found (mean) (μg)	Standard deviation of the mean
1	1	10	10	10	1.00	0.97	0.0141
2	10	100	100	100	1.00	0.99	0.0138
3	10	100	100	100	0.20	0.22	0.0122

TABLE VII

RESULTS OF PHOSPHORUS DETERMINATIONS

Series (No.)	$\frac{Cl^-}{PO_4^{3-}}$	$\frac{SO_4^{2-}}{PO_4^{3-}}$	$\frac{Ca^{2+}}{PO_4^{3-}}$	$\frac{Fe^{3+}}{PO_4^{3-}}$	PO_4^{3-}		Standard deviation of the mean
					Added (μg)	Found (mean)	
5	10	10	10	10	1.0	0.95	0.0478
6	1	1	1	1	0.1	0.090	0.00265
7	10	10	10	10	0.1	0.090	0.00239
8	10	10	10	10	0.02	0.020	0.00077

absorption effect of the soft beta rays (E_β = 0.16 MeV). Chlorine interferes with the determination of sulphur, due to the reaction with fast neutrons:

$$Cl^{35}(n, p)S^{35}.$$

The interferences from this reaction are very serious. Our experiments have shown that 1 μg of chlorine gives rise to S^{35} activity, equivalent to 500 μg of sulphur, when the irradiation is carried out in the reactor core at a neutron flux of 10^{13} n/cm^2 ·s. Hence, the determination of sulphur cannot be carried out in the presence of chlorine. Since so many disadvantages were encountered, the method based upon reaction (1) has been abandoned.

The following nuclear reactions must be considered when the determination of sulphur is based on reaction (2):

$$S^{32}(n, p)P^{32} \tag{2}$$

$$Cl^{35}(n, \alpha)P^{32} \tag{3}$$

$$P^{31}(n, \gamma)P^{32} \tag{4}$$

The nuclear data concerning these reactions are shown in Table VIII.

TABLE VIII

INTERFERING NUCLEAR REACTIONS

(No.)	Nuclear reaction	Neutron energy	Cross-section (mb)	Natural abundance of the target isotope (%)
1	$S^{32}(n,p)P^{32}$	fast, 0.9 MeV	60	95.0
2	$Cl^{35}(n,\alpha)P^{32}$	fast	140	75.53
3	$P^{31}(n,\gamma)P^{32}$	thermal	190	100.0

Chlorine and phosphorus are likely to be present in the soil solution, hence reactions (3) and (4) interfere with the determination of sulphur.

Since reaction (2) occurs with fast neutrons and reaction (4) with thermal neutrons, it is possible to determine sulphur and phosphorus in the presence of each other by the application of the double-irradiation technique.

The double-irradiation technique consists in the irradiation of sample and standards at two different positions in the nuclear reactor. These positions should differ with regard to the ratio of fast/thermal neutrons. The contents of sulphur and phosphorus in the sample can be then calculated. Unfortunately, reaction (3), i.e. $Cl^{35}(n, \alpha)P^{32}$, interferes with the determination of sulphur by this technique.

Some results of sulphur and phosphorus determinations performed by this method are shown in Tables IX and X.

It follows from Tables IX and X that sulphur can be determined in the presence of phosphorus, if the ratio SO_4^{2-}/PO_4^{3-} is greater than unity. Phosphorus can be determined with reasonable accuracy when the ratio PO_4^{3-}/SO_4^{2-} is greater than 0.1. If this ratio approximates to 0.01 a positive bias (about 40%) is observed.

The sensitivity of the determination of sulphur by this technique is about 0.1 μg S.

The interferences caused by the reaction $Cl^{35}(n,\alpha)P^{32}$ have been mentioned already. It has been found that 1 μg of Cl gives rise to P^{32} activity, equivalent to 1 μg of S.

TABLE IX

RESULTS OF SULPHUR DETERMINATIONS

Experiments (No.)	SO_4^{2-}/PO_4^{3-} ratio	SO_4^{2-}		Standard deviation of the mean
		Added (µg)	Found (mean) (µg)	
1- 4	10	100	101.8	4.57
5- 9	100	100	94.5	2.3
10-14	1	10	9.96	0.81

TABLE X

RESULTS OF PHOSPHORUS DETERMINATIONS

Experiments	SO_4^{2-}/PO_4^{3-}	PO_4^{3-}		Standard deviation of the mean
		Added (µg)	Found (mean) (µg)	
1- 4	10	10	10.37	0.485
5- 9	100	1	1.34	0.051
10-14	1	10	9.54	0.345

The determination of sulphur can then be carried out in the presence of chlorine only when the ratio SO_4^{2-}/Cl exceeds 100. In this case, the error caused by the presence of chlorine does not exceed several per cent.

CONCLUSIONS

Neutron activation analysis can be used for the determination of some macrocomponents of soil solution, i.e. chlorine, sodium, potassium, phosphorus and calcium. Determination of sulphur by this technique is strongly restricted by the content of chlorine and phosphorus in the sample solution.

If the application of the neutron activation method to the determination of some macrocomponents of the soil solutions is confined to the use of medium-lived or long-lived radioisotopes, as in the case of the present investigation, it does not show any advantages over other analytical methods, e.g. flame photometry, spectrophotometry, and should be used in general only as a comparative method.

Since the neutron activation technique offers great sensitivity, it can be of great value when the sample of the soil solution to be analysed is very small, or when the content of the element to be determined is very low. It should be stressed, however, that a nuclear reactor equipped with pneumatic facilities would allow making use of the short-lived radioisotopes, e.g. Mg^{27}, Ca^{49}, and would increase the sensitivity of the determination based on relatively short-lived radioisotopes, i.e. chlorine. It would also shorten the time of analysis for most macrocomponents yielding medium-lived radioisotopes, e.g. Na. In this case activation analysis could successfully compete with other analytical techniques. Finally, neutron activation analysis will be of great value for the determination of microcomponents of the soil solution. This problem will be the objective of the next part of our investigation.

ACTIVATION ANALYSIS IN SOIL/PLANT RELATION STUDIES IN SOUTH-EAST ASIA

S. NISHIGAKI
DEPARTMENT OF CHEMISTRY
NATIONAL INSTITUTE OF AGRICULTURAL SCIENCES
NISHIGAHARA, KITAKU, TOKYO, JAPAN

1. ATOMIC REACTORS AND THEIR USE

Seven countries, Ceylon, Indonesia, Japan, Korea, Philippines, Thailand and Viet Nam were visited during 1963-1964. Six of these seven countries possess atomic reactors, and reactors are ready for activation analysis in five countries. However, active use of atomic reactors for agricultural activation analysis was observed in two countries only; how activation analysis can be used more widely for agricultural research is the point of this discussion.

Ceylon has been devoting its efforts exclusively to the use of isotopes. This country intends to develop the full use of isotopes first, and then activation analysis will be considered as the next step. This plan is one of the wise ways of establishing steady development of atomic energy while conserving national funds.

Installation of the Triga Mark II experimental atomic reactor in Indonesia is progressing. Activation analysis in this country will be started in late 1965.

The Philippines Research Reactor I reached criticality in the middle of August 1964. A training course of four weeks on activation analysis was held in September 1964 to promote the use of activation analysis in the Philippines, so research on methods of activation analysis for agricultural studies will be started in the near future.

The condition of the Viet Nam Triga Mark II atomic reactor is such that it can be used for activation analysis, but this reactor has not yet been used for such purposes, as the country is more interested in the production of isotopes than activation analysis. However, following my visit, Viet-Nam has started to show interest in activation analysis.

Since 1962 the condition of the Korean Triga Mark II atomic reactor has been such that it could be used for activation analysis, and it has been put to limited use for agricultural analysis.

The Thai Research Reactor I has been in good condition for activation analysis since it reached criticality in October 1962. Trials in the use of it for activation analysis were carried out in 1962 and 1963. In December 1963 a large-scale project was started for its use in activation analysis in research for practical improvements in agriculture. As a first step methods for agricultural activation analysis were studied and, starting in July 1964, non-destructive methods of the activation of Al, Mn, Na and Zn in agricultural samples were tentatively employed. Since that time, routine analysis of Al, Mn and Na in soils was carried out by activation analysis instead of by the convential chemical method. In September 1964 a preliminary soil/plant relations study of physiological diseases of rice was started to improve practical rice culture in the country. Sets of samples, consisting of soil, soil solution and rice plants were collected from farmers' fields in many districts where physiological diseases were common. The samples are now being subjected to activation analysis for Al, Na and Mn.

In Japan, studies on methods of activation analysis for agricultural samples were begun in 1959, and non-destructive methods for Mn, Cu, Na, Zn and Sb were employed, starting in the same year. Also a method of chromatographic activation analysis for the separation and determination of seven rare earth elements was also established. These methods were utilized for fundamental studies on soil/plant relations and such methods were also employed in practical studies to solve farmers' problems.

2. WHY USE ACTIVATION ANALYSIS IN AGRICULTURE?

Activation analysis is the only tool to analyse certain elements in samples required by agricultural researchers.

It is well known that activation analysis provides the highest sensitivity among many methods of analysis. Yet, agricultural research in South East Asia does not always require the very high sensitivity of activation analysis. The writer nevertheless strongly advocates promoting the use of activation analysis because of its applicability in routine analysis in agricultural research and because of its high sensitivity in some special kinds of agricultural research.

(a) How activation analysis can enter into routine agricultural analysis

In the fundamental and practical agricultural studies now going on in South East Asia, the content in samples of various elements is too high in many cases to require the very high sensitivity of activation analysis. Essential elements mostly have a higher concentration than certain threshold level in media or plants. In many cases, this threshold concentration is not too low for conventional chemical methods. Therefore, the high sensitivity of activation analysis need not be used.

However, if a method of activation analysis of an element is more time-saving or labour-saving than the conventional chemical method of analysis agricultural researchers will use activation analysis, so simple specific methods of activation analysis for specific groups of samples in agricultural research should be studied. The non-destructive method of activation analyses of Al, Mn, Cu and Zn, etc. employed in Japan and Thailand are good examples.

(b) How the high sensitivity of activation analysis can be efficiently utilized in agricultural research

For example, plant nutrients in soil can be discussed. Recent advances in soil chemistry have indicated the importance of available nutrients in the solid phase of the soil, but they have also shown the importance of the concentration of nutrients in the liquid phase of the soil. The former is important for the capacity factor of the nutrients in soil and the latter is important for the intensity factor of nutrients in rice soils. If it is intended to study nutrients in soil solution, the high sensitivity of activation analysis will be very helpful. The concentration of phosphorus in soil solutions of rice soil which has been heavily fertilized annually, as in Japan, can be determined by colorimetric methods. However, the concentration of phosphorus in the soil solution of rice soils, which have received little or no fertilizer, as in South East Asia, can be determined by activation analysis, although it is difficult to determine by colorimetric methods.

Concentration of nutrients in soil solution is also important for practical problems in South East Asia. In this region the rainfall is very heavy in the rice season, and almost all rice fields depend on rainfall or river water which overflows uncontrolled into the rice field during floods.

Therefore, the rice is subjected to substantial excesses of water, and loss of nutrients from the soil will occur when nutrient concentration in the liquid phase of the soil exceeds the same limits.

Also, some rice fields in this region have failed to give good yields even under adequate fertilization and good plant protection, and these problems are referred to as the "physiological diseases" of rice*. Some of the physiological diseases are probably due to deficiency, or excess, or balance of some elements in the soil. Activation analysis of the soil-liquid phase should be effective in research to uncover the causes of these physiological diseases.

---

* The Food and Agriculture Organisation of the United Nations International Rice Commission meeting held in November 1964 discussed this problem.

DETERMINATION OF MICRO-QUANTITIES OF SEVERAL ELEMENTS IN SOIL SOLUTION BY ISOTOPE DILUTION AND ACTIVATION ANALYSES

C. M. CHO AND H. AXMANN
AGRICULTURE SECTION, SEIBERSDORF LABORATORY,
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, AUSTRIA

INTRODUCTION

Determination of small quantities of plant nutrients in the soil solution of flooded rice soils is a difficult problem. The concentrations of Mn, Fe and P, for example, in some soil solutions are so small that no chemical method gives any accurate result.

Neutron activation analysis was reported to give a much lower limit of detectability [1,2, 3, 5] for several elements, while for elements with low-induced activity after neutron irradiation, substoichiometric isotopic dilution analysis was applied [4, 7].

One of the advantages of neutron activation analysis lies in the fact that simultaneous activation of every inducible element in a sample takes place. This gives an opportunity to determine many elements by one sample preparation and irradiation. This, however, is not a simple task since identification of the activated products and their quantitative estimation becomes very difficult. Certain operations of separation must be carried out before activity measurements.

Ion-exchange resin columns [6] and chemical separation following the addition of carriers [1, 2] were successfully used for the determination of many elements after neutron irradiation. These procedures, however, cannot be directly applied to the determination of the elements of agronomic interest.

A procedure was developed to determine several elements of agronomic interest. Times of irradiation and cooling, quick separation by ion-exchange columns, together with chemical precipitation for β-emitters of relatively long half-lives, were all combined to get the maximum benefit from neutron activation analysis.

For Fe, for which no satisfactory neutron activation analysis has yet been developed, a modified substoichiometric double isotope dilution procedure is applied.

THEORETICAL CONSIDERATION

Of the elements of agronomic interest the following were tentatively chosen for determination: Na, K, Mn, Fe, P, S and Cl. The isotopic abundance, reaction products, cross-section for (n,γ) reaction and the properties of the reaction products of the elements are shown in Table I.

TABLE I

NUCLEAR PROPERTIES OF THE ELEMENTS FOR (n, γ) REACTION

Elements	Abundance (%)	Cross-section (b)	Half-life	Decay
^{23}Na	100	0.5	14.97 ln	β γ
^{41}K	6.9	1.1	12.52 ln	β γ
^{55}Mn	100	13.0	2.57 ln	β γ
^{58}Fe	0.31	1.0	45.1 d	β γ
^{31}P	100	0 .19	14.2 d	β
^{34}S	4.2	0.2	87 d	β
^{37}Cl	25.0	0.5	37.3 min	β γ

With the short irradiation time of 1~2 h at a flux of 10^{13} n cm^{-2} s^{-1}, for an amount of 1 ppm in 1 ml, the elements which will give appreciable activity are: Na, K, Mn and Cl. If, however, the irradiation time is prolonged for several days, phosphorus will give appreciable activity, while no detectable activity from ^{59}Fe and ^{35}S is to be expected. Because of the low abundance of ^{58}Fe (0.3%) and ^{34}S (4.2%), one ppm each of natural Fe and S corresponds to 0.003 and 0.04 ppm of ^{58}Fe and ^{34}S respectively. Activation analysis by (n, γ) reaction does not seem to be suited to the determination of these elements. Because of the high abundance of ^{32}S (95%) and relatively high flux of fast neutron in a reactor, ^{32}S (n, P)^{32}P reaction is chosen for the determination of S by reactor activation analysis, while for Fe, substoichiometric isotopic analysis is chosen.

In the determination of P by ^{31}P (n, γ)^{32}P reaction there is always interference from ^{32}S (n, P)^{32}P and ^{35}Cl (n, α)^{32}P if the sample contains ^{31}P, ^{32}S and ^{35}Cl together. The presence of P and Cl also interferes in the determination of S by ^{32}S (n, P)^{32}P. The double irradiation technique [2] enables the simultaneous determination of P and S in a given sample. If, however, a sample contains an appreciable amount of Cl, ^{32}P formed from ^{35}Cl (n,α)^{32}P becomes significant and direct application of the double irradiation technique cannot be carried out. Phosphorus-32 activity originating from ^{35}Cl (n, α)^{32}P should be subtracted from measured ^{32}P activity of the sample.

The following simultaneous equations are used for P and S determination:

$$Cu_1 - Ccl_1 \times \frac{Acl_1}{\overset{*}{A}cl_1} = \frac{Cp_1}{Wp} x_p + \frac{Cs_1}{Ws} x_s \qquad (1)$$

$$Cu_2 - Ccl_2 \times \frac{Acl_2}{\overset{*}{A}cl_2} = \frac{Cp_2}{Wp} x_p + \frac{Cs_2}{Ws} x_s \qquad (2)$$

where Cu_1 and Cu_2 are the measured ^{32}P activities of the same amount of unknown sample irradiated at reactor positions 1 and 2;
Ccl_1 and Ccl_2 are the measured ^{32}P activities of the same amount of standard Cl samples irradiated at positions 1 and 2;
Acl_1 and Acl_2 are the measured ^{38}Cl activities of the unknown samples at positions 1 and 2;
A^*cl_1 and A^*cl_2 are the measured ^{38}Cl activities of the standard samples at 1 and 2;
Cp_1 and Cp_2 are the measured ^{32}P activities of the standard P samples at 1 and 2;
Cs_1 and Cs_2 are the measured ^{32}P activities of the standard S samples at 1 and 2;
W stands for the weight of the respective standards of phosphorus and sulphur;
x_p and x_s are the unknown weights of P and S in the sample.

It is, therefore, necessary to irradiate at least four samples consisting of 1 unknown, 1 Cl standard, 1 P standard and 1 S standard at a particular position (position 1) of a reactor, where the ratio of fast neutrons to thermal neutrons is different from the other irradiation position (position 2). Phosphorus-32 activities from all the samples, and the ^{38}Cl activities from the unknown and Cl standards must be determined in order to solve the simultaneous equations.

The substoichiometric isotope dilution analysis as originally proposed [7] was slightly modified to include the double isotope dilution analysis proposed by LANDGREBE et al. [4].
The equation used is

$$x = \frac{a_1b_1 - a_2b_2}{a_2 - a_1} - y, \tag{3}$$

where b_1 and b_2 are the amounts of carrier added to the same amount of sample 1, and 2; a_1 and a_2 are the activities of equal amounts of substoichiometrically-separated samples, after labelling the samples with ^{59}Fe with a carrier level of y; x is the quantity of Fe in the sample. In cases where the carrier level of the ^{59}Fe is not specified, the value of y is determined by the above equation on the basis of $x = 0$, i.e. with blank dilution analysis.

PROCEDURE

Na, K, Mn, and Cl determination

Approximately 2 ml of standard solution consisting of 5 ppm Na, 5 ppm K and 1 ppm Mn prepared from either chloride or chloride and nitrate salts are placed in a plastic vial and sealed tight; 2 ml of sample is also prepared in the same way.

The two vials are irradiated in a reactor for 30 min at 10^{13} n cm^{-2} s^{-1}, or an integrated flux of approximately 10^{16} n cm^{-2}. After cooling for 20 min, the vial is opened and 1 ml each of the standard and sample is separately added to the top of Dowex 2 × 10 Cl^- columns. The column has an inside diameter of 2 cm, filled with 10 ml of wet resin. The resin is washed with 15 ml of water at the rate of 2 ml/min and the effluent is directly passed onto a Dowex 2 × 10 Cl OH column. The OH column has a diameter of 2 cm and a wet resin volume of 10 ml.

The Dowex 2 × 10 Cl^- resin is transferred to a plastic counting vial of 4 cm diam., and the 1.6 MeV photopeak area of ^{38}Cl is determined by a γ-spectrometer.

The Dowex 2 × 10 OH^- resin is washed with 20 ml of H_2O at the rate of 2 ml/min, the effluent being collected in a 50-ml beaker. The resin in the column is then transferred into the counting tray and the 0.85-MeV photopeak area of ^{56}Mn is determined by a γ-spectrometer.

To the effluent in the beaker, 3 mg of K-carrier and 3 ml of 3% Na-dipicrylate solution are added and warmed. To minimize the co-precipitation of Na with K, the precipitation is carried out by cooling the solution very slowly from approximately 50° C to about 2°C. The K-dipicrylate formed is filtered with a demountable filter stick, washed with saturated K-dipicrylate solution and the activity of the precipitate on the filter paper is counted for ^{42}K activity by an end-window G-M counter.

The filtrate is directly passed through a Dowex 50 × 12 H^{+-} column, and after transferring the resin into a counting vial the 1.37-MeV photopeak area of ^{24}Na is determined by a γ-spectrometer. The amount of the element in the sample is calculated from the equation:

$$W_i = \frac{C_i}{C_s} W , \tag{4}$$

where C stands for count-rate, W for the weight, and subscripts i and s are the element i in the sample and in the standard.

P, S AND Cl DETERMINATION

Quartz vials of P standard (2 ml, 1 ppm P), S standard (2 ml, 5 ppm S), Cl standard (2 ml, 10 ppm Cl), and sample (2 ml soil solution) are prepared in duplicate. The quartz vials should be carefully checked for complete sealing.

A set consisting of four vials, one each of P, S, Cl standards and sample is irradiated at the centre of the core of the reactor while the other set is irradiated at the edge of the reactor. The irradiation time generally chosen is 3 d at 10^{13}n cm^{-2} s^{-1}, or an integrated flux of over 2.5 × 10^{18}n cm^{-2}.

After irradiation and cooling for approximately 20 min, phosphorus is separated from all the samples as follows. An aliquot of 1 ml is taken from a sample and is placed on top of a Dowex 2 × 10 NO_3^- column of 1 cm inside diam. and a resin height of 7.5 cm; 25 ml of water is used to elute cations from the resin, at a rate of 3 ml/min. The eluate is discarded.

Phosphate is eluted from the resin with 20 ml of 0.1 $\underline{N}$ HNO_3 at a rate of 2 ml/min and the effluent is received in a 50-ml beaker.

Chlorine-38 activities in the resins from both soil samples and Cl^- standards are determined γ-spectrometrically, after transferring the resin to counting trays.

The ^{32}P activity in every sample is counted directly by liquid G-M counter after making the volume of the effluent in every sample equal. Alternatively, it may be counted by end-window G-M counter after precipitating the P as ammonium phosphomolybdate with 5 mg carrier and collecting on filter paper.

If the presence of ^{76}As is detected in the samples by γ-spectrometry, the samples should be left until ^{76}As ($t_{\frac{1}{2}}$ = 26 HV) activity decays to a negligible quantity.

The measured activity of ^{32}P from every sample, and the photopeak area measurements of 1.6-MeV γ of ^{38}Cl from the two Cl standards and the soil solutions, are substituted in Eqs. (1) and (2), and the amounts of phosphorus and sulphur in the sample are calculated.

Fe DETERMINATION

To each of five 50-ml Erlenmeyer flasks, 5 ml of soil solution and 1 ml of ^{59}Fe solution are added. To the first flask is added 1-γ Fe carrier and 1 ml of 10^{-5} M EDTA, to the second 0.1-γ Fe and 10^{-6} meq EDTA, to the third 0.01-γ Fe and 10^{-6} meq EDTA, to the fourth, 0.001-γ Fe and 10^{-7} meq EDTA and to the fifth 0.0001-γ Fe and 10^{-7} meq EDTA. Before the EDTA solutions are added, the solution is mixed well. Each solution is adjusted to $pH \simeq 3$ by adding 1 ml of 0.01 M HCl, and then heated to about 50° C on a sand bath for 30 min. After cooling the solution 1 g of Dowex 50 × 12 - H^+ is added to every flask, shaken constantly for 20 min and then allowed to stand for the resin particles to settle.

Two millilitres of each supernatant is pipetted into an Al-planchet, dried under an infrared lamp and the β-activity measured by end-window G-M counter or γ-activity measured by scintillation counter. Before calculating the amount of Fe present in the soil solution, using Eq. (3), the activities of 2-ml aliquots should be adjusted to either the 10^{-5} meq EDTA or the 10^{-6} meq EDTA addition.

In cases where the value of Y, the carrier level of ^{59}Fe solution is not known, the same procedure as above is followed, except that 5 ml of water is run instead of 5 ml of soil solution.

By observing the decreasing activities of 2-ml aliquots adjusted by carrier addition, the best pair is chosen for calculation of the Fe in the soil solution and the carrier content of ^{59}Fe solution, using Eq. (3)

SUMMARY

A routine method of determining Na, K, Mn, Cl, P and S in soil solution by activation analysis has been developed. The method employs quick separation of γ-emitters by ion exchange resin, and chemical precipitation of the principal β-emitters.

The technique of double irradiation was applied for P and S determinations. If the sample contains much chlorine, the correction for ^{32}P formed by (n, α) reaction from ^{35}Cl is applied.

For Fe determination in a sample, double substoichiometric isotope dilution analysis was applied.

It has been confirmed that the present method gives accurate measurement of the elements listed.

REFERENCES

[1] BLANCHARD, R.L., LEDDICOTTE, G.W. and MOELLER, D.W. "Neutron activation analysis of drinking water", Proc. 2nd UN Int.Conf. P.UA.E. 28 (1959) 511.

[2] BOWEN, H.J.M. and GIBBONS, D., Radioactivation Analysis, Clarendon Press, Oxford (1963) p.106.

[3] KOCH, R.C. and ROESMER, J., "Application of activation analysis to the determination of trace elements in meats", Modern trends in Activation Analysis, Proc., 1961, Texas A & M Univ., USA.

[4] LANDGREBE, A.R., McCLENDON, L.T. and DeVOE, J.R., "Substoichiometric radiometric analysis: determination of trace amount of cobalt", Radiochem. Methods of Analysis, Proc. IAEA Symp., Salzburg, (Oct. 1964), IAEA, Vienna II (1965) 321.

[5] MEINKE, W.W., "Trace element sensitivity: comparison of activation analysis with other methods", Science 121 (1955) 177.

[6] SAMSAHL, K., "A chemical eight group separation method for routine use in gamma spectrometric analysis. I. Ion exchange experiment", Aktiebolaget Atomenergi A.E. 54, Stockholm, Sweden (1961).

[7] STARÝ, J and RŮŽIČKA, J., Isotopic dilution analysis by ion exchange. I. Determination of traces of iron", Talanta 8 (1961) 775.

PHOSPHORUS DIFFUSION TO PLANT ROOTS

S.R. OLSEN
NORTHERN PLAINS BRANCH,
SOIL AND WATER CONSERVATION RESEARCH DIVISION,
AGRICULTURAL RESEARCH SERVICE,
UNITED STATES DEPARTMENT OF AGRICULTURE
AND
COLORADO AGRICULTURAL EXPERIMENT STATION,
FORT COLLINS, COLORADO, UNITED STATES OF AMERICA

A knowledge of ionic diffusion rates is important in solving many soil and plant nutrition problems. Most phosphate uptake mechanisms by plant roots involve a transport phase by diffusion and mass flow, but very few quantitative measurements of diffusion rates have been reported [1, 6, 7, 9, 12, 14, 17].

This paper describes two methods based on transient and steady-state systems for measuring the diffusion coefficient of P in soils. The paper shows also how to apply the diffusion coefficients to explain and predict soil P - plant behaviour as related to soil differences. Details of the methods have been reported elsewhere [14]. In this paper are discussed mainly the theoretical aspects and the significance explained of introducing the capacity factor for P diffusion measurement and for transfer of P to plant roots. From previous studies the author concluded that diffusion of P appears to account for the observed rate of P uptake by corn roots. Mass flow of water and P contributes to the supply of P at the root surface, but this process is not essential in the soil-plant system for uptake of P.

THEORY AND ASSUMPTIONS

Movement of P can be detected by using ^{32}P tracer in a system of constant chemical composition. Diffusion of ^{32}P ions occurs as a direct consequence of thermal motion and a concentration gradient. The process is an interchange of labelled and unlabelled ions such that no net transfer of charged ions occurs. The self-diffusion coefficient of P is measured, but this value should be nearly the same as the mutual diffusion coefficient of a phosphate salt in the soil [14].

In this paper diffusion of P ions is assumed to take place in the soil solution. Surface diffusion along soil particles is assumed to be small or negligible. The rate of transfer between P in the labile part of the solid phase and the soil solution is assumed to be fast and non-limiting compared to the rate of diffusion and rate of uptake by roots [5].

THE CAPACITY FACTOR

An important idea in understanding P diffusion in soil involves the role of the capacity factor. Often, we associate this term with an amount of available P but in this paper the capacity factor is the slope of the line relating labile P to concentration of P in the soil solution for soils where the relationship is linear as indicated in Fig. 1. Thus, the amount of labile P in a soil could vary for different samples or treatments, but the capacity factor would be a constant. Labile P is defined as the amount of P in the soil that readily exchanges with the ^{32}P isotope. This amount is not an absolute quantity because the exchange reaction does not come to a definite equilibrium, but the amount exchanging in a 24-h reaction period includes most of this form.

The soil P system is somewhat more complex than simple Cl^- or NO_3^- diffusion where all the ions exist in the solution phase. Most of the P potentially available for diffusion exists in the solid phase and this P contributes to the total amount of P diffusing by renewing the solution concentration. Therefore, a relationship must be determined between the solid phase and the solution, which we have termed a capacity factor [12, 14]. This capacity factor enters into the diffusion equation for transient state systems, but it does not appear in the equations for steady-state systems. To calculate the quantity of P arriving at a cylindrical surface, such as a root in soil, or a spherical surface, values must be known for the diffusion coefficient and the capacity factor. Apparent diffusion coefficients, such as a diffusion coefficient divided by a capacity factor, cannot be used correctly in such cases.

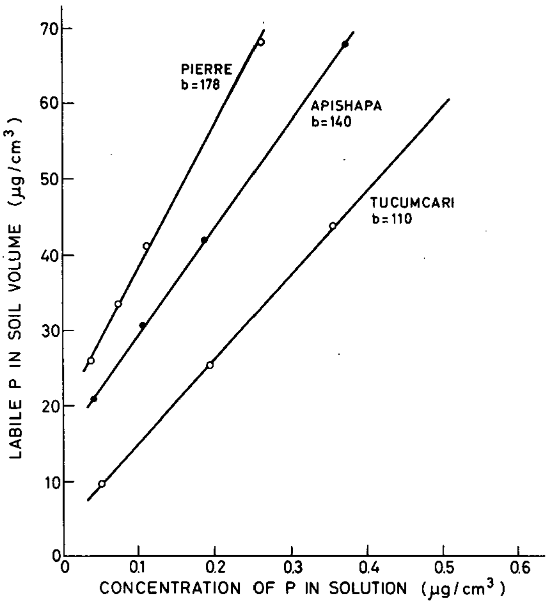


Fig. 1

Relation between labile P and concentration of P in solution on three soils

A better conception of the capacity factor can be obtained by considering how it enters into the diffusion equation. Equation (1) based on Fick's law is modified to apply to a porous system [14],

$$\frac{\Delta Q}{\Delta t} = DA\,\alpha\gamma(L/L_e)^2\,\theta\,\frac{\Delta c}{\Delta x}\,. \tag{1}$$

By substituting,

$$D_p = D\alpha\gamma(L/L_e)^2\,\theta, \tag{2}$$

equation (1) is simplified as follows,

$$\frac{\Delta Q}{\Delta t} = D_p A\,\frac{\Delta c}{\Delta x}\,, \tag{3}$$

where

D_p is a porous system diffusion coefficient,
D is for P in bulk solution ($cm^2\,s^{-1}$),
Q is the amount diffusing,
t is the time (seconds),
A is the cross-sectional area (cm^2),
c is the concentration in the solution (g/cm^{-3}),
x is the thickness of soil (cm),

α is a factor for viscosity of water,
γ is a factor for negative adsorption related to non-uniformity of pore size,
$(L/L_e)^2$ is a tortuosity factor, and
θ is the volumetric moisture content.

When Δt and Δx approach zero and Q/A equals q, equation (3) becomes,

$$\frac{\partial q}{\partial t} = D_P \frac{\partial c}{\partial x} . \tag{4}$$

The diffusive flow of P in a linear system may be evaluated as follows for the rectangular co-ordinate case with flow in one direction. The rate of accumulation in a volume element, $V = 1 \times 1 \times dx$, contained between the planes x and x+dx, is expressed as Eq. (5) for flow left to right,

$$\frac{dq'}{dt} = \frac{dq}{dt}\text{in} - \frac{dq}{dt}\text{out} = D_P \left\{ \frac{\partial c}{\partial x}\Big]_{x+dx} - \frac{\partial c}{\partial x}\Big]_x \right\} . \tag{5}$$

Equation (5) results from combining the equation of continuity and Fick's first law of Eq. (4).

To proceed, it is necessary to express q' in terms of c, the concentration in solution. When P may be adsorbed or released by the solid phase, q' does not equal $C\theta V$, but q' equals some function of the concentration, i. e. $q' = f(c)$. Then,

$$\frac{\partial q'}{\partial t} = \frac{\partial q'}{\partial c} \frac{\partial c}{\partial t} \tag{6}$$

and

$$\frac{\partial q'}{\partial t} = \frac{\partial f(c)}{\partial c} \frac{\partial c}{\partial t} . \tag{7}$$

By substituting Eq. (7) into Eq. (5) we find,

$$\frac{\partial c}{\partial t} = \frac{D_P}{\partial f(c)/\partial c} \left\{ \frac{\partial c}{\partial x}\Big]_{x+dx} - \frac{\partial c}{\partial x}\Big]_s \right\} . \tag{8}$$

Now refer to the relationship shown in Fig. 1. If $q' = CV(\theta + b) + k$, where $V = 1 \times 1 \times dx$, and b is the amount of labile P in the solid phase per cm^3 of soil volume per unit of solution concentration increase, then

$$f(c) = CV(\theta + b) + k \tag{9}$$

and

$$\frac{\partial f(c)}{\partial c} = (\theta + b)dx . \tag{10}$$

By substituting Eq. (10) into Eq. (8), then Eq. (11) follows by definition of the second derivative,

$$\frac{\partial c}{\partial t} = \frac{D_p}{\theta + b} \frac{\partial^2 c}{\partial x^2}, \tag{11}$$

when $(\theta + b)$ is a constant, independent of c, t, and x. In Fig. 1, $\theta + b$ is the slope, or the capacity factor. This development is essentially the same as the equation shown in earlier work except that θ was dropped previously because it was less than 1% of b.

Equation (11) is identical to the heat-flow equation where D_p corresponds to K, $D_p/(\theta + b)$ is equivalent to small kappa and c corresponds to the temperature. Solutions for many boundary values are published for Eq. (11) in CARSLAW and JAEGER [3].

COMPARISON OF D_p BY TWO INDEPENDENT METHODS

By using Eq. (3) the diffusion coefficient for P was measured for a steady-state system. A capacity factor does not enter into Eq. (3) because there will be no net exchange of ions between the liquid and solid phase when $\Delta c/\Delta t = 0$, a steady-state condition reached experimentally.

The transient system is described by Eq. (11) and Eq. (12) presents an integrated form applicable for measuring D_p,

$$\frac{D_p}{\theta + b} = \frac{\pi}{t} \left(\frac{q}{q_0}\right)^2 l^2, \tag{12}$$

where q is the total quantity diffused per unit of soil, q_0 is the initial quantity of diffusible ion per unit of soil, l is the thickness of the soil into which net diffusion occurs, $b + \theta$ is the capacity factor, and the other terms have been described.

The self-diffusion coefficients calculated from Eq. (12) and (13) for P in two soils are shown in Fig. 2 as a function of θ. Although a direct comparison between D_p by these two methods is not possible at the same value of θ, data obtained by either method fit on a curve of a type expected between D_p and θ, as indicated in Eqs. (1) and (2). The value of $\alpha\gamma(L/L_e)^2$ increases linearly as θ increases [15]. From Eq. (1), if $\Delta c/\Delta x$ remains constant as θ changes, the rate of diffusive movement of ions will be a hyperbolic function of the moisture content, i. e. as in Fig. (2). The relationship between θ and concentration of P is not exactly known, but existing data have indicated only small changes in concentration of P would be expected as θ changes over the range shown in Fig. 2 [10]. Thus, values of D_p found by each method can be considered in agreement.

The standard errors of the mean values as θ decreased, shown in Fig. 2, were 0.08, 0.46, 0.26, 0.20, and 0.11, respectively, for the Tucumcari soil, and the standard errors were 0.09, 0.14, 0.45, 0.06, 0.12 and 0.20, respectively, for the Apishapa soil. The bulk density was 1.32 and 1.56 g/cm^3 for each method for the Apishapa and Tucumcari soils, respectively. The capacity factor for Eq. (13) was 163 and 123 for the Apishapa and Tucumcari soils, respectively.

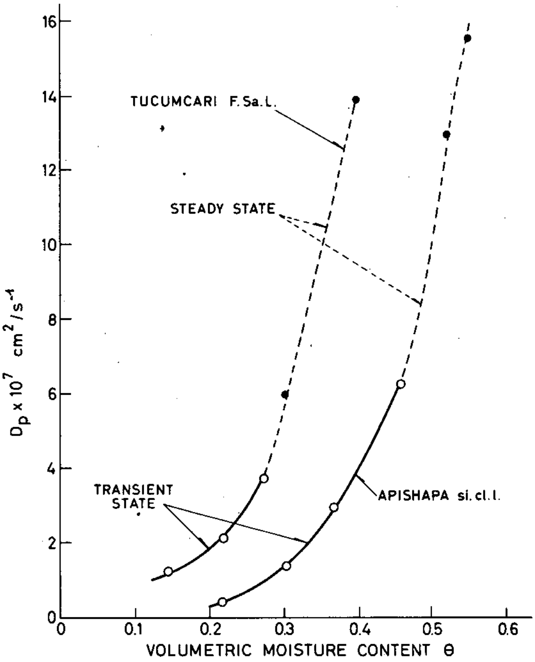


Fig. 2

Porous system self-diffusion coefficients of P in soil as related to volumetric moisture content

In Fig. 2, as θ increased the corresponding values for soil moisture suction were 1, 0.33, 0.1, 0.1, and 0.05 bar on the Tucumcari soil and 6, 1, 0.33, 0.1 and < 0.1 bar on the Apishapa soil. These data clearly illustrate the marked dependence of D_p on θ, the volumetric moisture content.

The important significance of the agreement in D_p by these two methods stems from the necessity of measuring a capacity factor when D_p is to be determined by a transient state method. In addition, the necessity of knowing D_p and D_p/b has been demonstrated for uptake equations describing the flow of phosphate to plant roots [12].

Diffusion coefficients in porous systems can be measured with less effort and simpler equipment with the transient state method than by steady-state experiments, especially for moisture suctions > 0.2 bar. The validity of the transient state method must be established, however, by comparing the results with an independent method that does not rely on evaluating the capacity factor. This statement applies particularly to systems where the relationship between the potentially diffusible ion in the solid phase and the same ion in solution is not well known or established. The linear relationship used in this work is not expected to hold for all soils. Non-linear cases can be approached by numerical integration procedures [4, 12].

EVALUATION OF D FROM POROUS SYSTEM D_p

In a porous soil system, D_p is related to D in bulk solution by Eq. (2). In the steady-state experiment, D_p was measured for P in Apishapa soil from which values of $\alpha\gamma(L/L_e)^2$ had been measured by Cl^- diffusion [15]. The linear relationship between $\alpha\gamma(L/L_e)^2$ and θ was assumed to extend to higher values of θ [15], such as observed in the steady-state experiment (Fig. 2). By using D_p from the steady-state experiment and a value of $\alpha\gamma(L/L_e)^2$ from previous data [15], with Eq. (2), D was found to be 5.1×10^{-6} cm^2/s, which compares favourably with the value of $D = 5.0 \times 10^{-6}$ cm^2/s, reported by MORENO [18], and SALVINIEN et al. [16] for P concentrations and pH values commonly found in soils. This agreement serves as evidence that the factors in Eq. (2) adequately accounted for the differences between a porous system and bulk solutions at low moisture suctions.

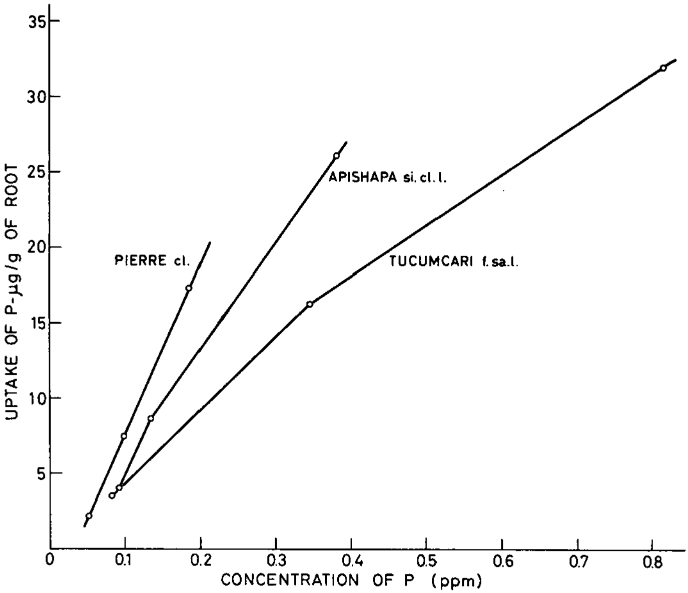


Fig. 3

Absorption of P by corn seedlings as a function of concentration of P in solution on three soils varying in clay content (uptake period is 24 h)

PREDICTION OF PLANT UPTAKE OF P FROM DIFFUSION

Some earlier work [11, 13] had produced the data shown in Fig. 3, but without a satisfactory explanation. The interesting feature of these data stems from the unequal rate of uptake from the same concentration of P in the soil solution, i. e. compared at 0.15 and 0.20 ppm. When values for D_p and $b + \theta$, the capacity factor, were obtained on these soils, as shown in Table I, a probable explanation appeared. The clay soil had a higher diffusion coefficient and capacity factor than the sandy soil.

TABLE I

RELATIONSHIP BETWEEN D_p AND CLAY CONTENT, AND RELATED SOIL PROPERTIES

Soil type	Clay content (%)	Moisture suction (bars)	θ	$\alpha\gamma(L/L_e)^2$	$b+\theta$	$D_p \times 10^7$ (cm^2/s)
Pierre cl.	51.1	0.33	0.54	0.428	178	5.40
Apishapa si. cl. l.	36.6	0.33	0.35	0.308	140	3.23
Tucumcari f. sa. l.	17.0	0.33	0.22	0.236	110	2.11

TABLE II

COMPARISON OF UPTAKE OF P BY CORN ROOTS, CALCULATED AND OBSERVED, ON THREE SOILS DURING 24 h

Soil type	P in solution (ppm)	Q calculated (μg/g)	Q observed (μg/g)
Pierre cl.	0.20	21.4	18.7
Apishapa si. cl. l.	0.20	14.5	13.1
Tucumcari f. sa. l.	0.20	10.3	9.0

An integrated form of Eq. (11) is shown in Eq. (13), defined for the boundary condition assuming a constant concentration at the root surface,

$$Q = a(b+\theta)(c_0 - c_r)\left[\frac{2}{\sqrt{\pi}} T^{1/2} + \frac{1}{2}T - \frac{1}{6\sqrt{\pi}} T^{3/2} \ldots\right] \qquad (13)$$

where Q is the amount of P adsorbed by the root per unit surface area in time, t, a is the root radius, $(b+\theta)$ the capacity factor, c_0 the initial concentration, c_r the concentration at the root surface, and $T = D_p t/(b+\theta)a^2$. Equation (13) is valid when $T \leq 1$.

The uptake, Q from Eq. (13), was calculated and these values are compared with the observed uptake of P in Table II. The calculated values depend on the assumed boundary condition for Eq. (13) and also by assuming that one-half of the final root surface area was effective during the 24-h uptake period. An average value, $c_r = 0.65\ c_0$, was obtained from calculating

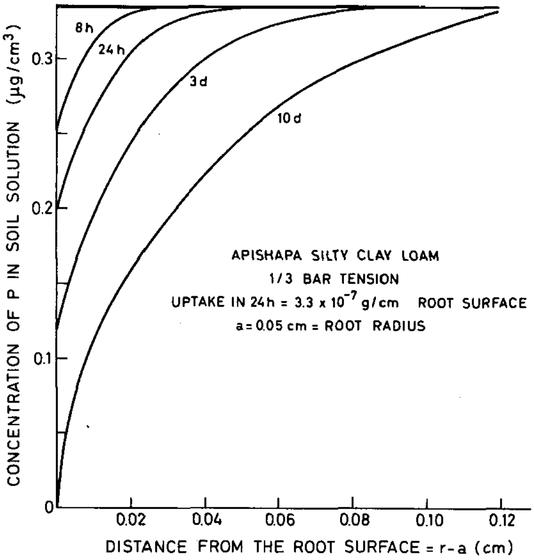


Fig. 4

Calculated P concentration in the soil solution near a root surface (assuming constant uptake rate)

c_r from three boundary conditions, i.e. two from OLSEN *et al.* [12] and one from BOULDIN [2].

The significant feature of the data in Table II is that the differences in rates of P uptake at a constant P concentration are explained by the variations in D_p and the capacity factor. The relationship of these observations to the fertilizer P needs of soils varying in texture has been discussed [13].

CONCENTRATION OF P NEAR A ROOT SURFACE

The concentration of P in the soil solution is shown in Fig.4 as a function of distance from the root surface. These data were obtained from Eq. (14),

$$c_0 - c_r = \frac{2aq}{D_p}\left(\frac{a}{q}\right)^{1/2} T^{1/2}\left[\mathrm{ierfc}\frac{r-a}{2aT^{1/2}} - \frac{3r+a}{4r}T^{1/2}\, i^2\mathrm{erfc}\frac{r-a}{2aT^2}\right], \quad (14)$$

where r - a equals the distance in centimetres from the root surface and the other terms have been defined [13]. The boundary condition was assumed for a constant rate of uptake per unit of root surface area.

The curves in Fig. 4 indicate that phosphate ions can diffuse to root surfaces at rates fast enough to account for the observed uptake. In 24 h the concentration at the root surface dropped to 0.6 of the initial value. Other calculations show that root hairs, if present, could increase the uptake rate fourfold per centimetre of main root cylinder. The observed uptake rate of these roots is similar to the rates calculated from field experiments.

SUMMARY

Self-diffusion coefficients for phosphorus in soils have been measured by two independent methods. The results agree and thereby confirm the necessity of determining a capacity factor in transient systems. The diffusion equations necessary to calculate the transfer of P to plants or to calculate the flux at the root surface require a knowledge of the diffusion coefficient and the capacity factor.

The nature of the capacity factor was emphasized. It should not be identified with an amount or quantity of labile P.

Differences in the diffusion coefficients of P and capacity factor between clay and sandy soils were applied successfully to explain the observed variations in rates of P uptake by corn seedlings.

Phosphate ions can diffuse to root surfaces at rates fast enough to account for the observed uptake.

REFERENCES

[1] BARBER, S.A., "*A diffusion and mass flow concept of soil nutrient availability*", *Soil Sci.* 93 (1962) 39-49.

[2] BOULDIN, D.R., "Mathematical description of diffusion processes in the soil-plant system", Soil Sci. Soc. Amer. Proc. 25 (1961) 476-79.

[3] CARSLAW, H.S. and JAEGER, J.C., Conduction of Heat in Solids, Oxford Univ. Press, Oxford, Ed. 2, (1959) 335-41.

[4] CRANK, J., The Mathematics of Diffusion, Oxford Univ. Press, Oxford (1956) 186-218.

[5] FRIED, M., HAGEN, C.E., SAIZ del RIO, J.F. and LEGGETT, J.E., "Kinetics of phosphate uptake in the soil-plant system", Soil Sci. 84 (1957) 427-37.

[6] GRAHAM-BRYCE, I.J., "Self-diffusion of ions in soil. I. Cations", Jour. Soil Sci. 14 (1963) 188-94.

[7] GRAHAM-BRYCE, I.J., "Self-diffusion of ions in soil. II. Anions", Jour. Soil Sci. 14 (1963) 195-200.

[8] KEMPER, W.D., MAASLAND, D.E.L. and PORTER, L.K., "Mobility of water adjacent to bentonite surfaces", Soil Sci. Soc. Amer. Proc. 28 (1964) 164-67.

[9] LEWIS, D.G. and QUIRK, J.P., "Diffusion of phosphate in soil", International Soil Conf., Comm. IV and V, Int. Soc. Soil Sci., New Zealand (1962) pp. 2-8.

[10] OLSEN, S.R., WATANABE, F.S. and COLE, C.V., "Soil properties affecting the solubility of calcium phosphates", Soil Sci. 90 (1960) 44-50.

[11] OLSEN, S.R., WATANABE, F.S. and DANIELSON, R.E., "Phosphorus absorption by corn roots as affected by moisture and phosphorus concentration", Soil Sci. Soc. Amer. Proc. 25 (1961) 289-94.

[12] OLSEN, S.R., KEMPER, W.D. and JACKSON, R.D., "Phosphate diffusion to plant roots", Soil Sci. Soc. Amer. Proc. 26 (1962) 222-27.

[13] OLSEN, S.R. and WATANABE, F.S., "Diffusion of phosphorus as related to soil texture and plant uptake", Soil Sci. Soc. Amer. Proc. 27 (1963) 648-53.

[14] OLSEN, S.R., KEMPER, W.D. and van SCHAIK, J.C., "Self-diffusion coefficients of phosphorus in soil measured by transient and steady state methods", Soil Sci. Soc. Amer. Proc. 29 (1965).

[15] PORTER, L.K., KEMPER, W.D., JACKSON, R.D. and STEWART, B.A., "Chloride diffusion in soils as influenced by moisture content", Soil Sci. Soc. Amer. Proc. 24 (1960) 460-63.

[16] SALVINIEN, J., MARIGNAN, R. and CORDIER, S., "The diffusion of tagged Na_2HPO_4 in a chemically homogeneous medium", C.R. Acad. Sci. Paris 238 (1954) 888-90.

[17] SCHOFIELD, R.K. and GRAHAM-BRYCE, I.J., "Diffusion of ions in soil", Nature, London 188 (1960) 1048-49.

[18] MORENO, E., Diffusion Rates of Soil Phosphorus from Solid to Liquid Phase, Ph.D. Thesis, University of California, Berkeley (1957).

DISCUSSION

H.C. THOMAS: I suggest that it might be misleading to assume that the self-diffusion coefficient is necessarily near in numerical value to a salt diffusion coefficient. In general there is no simple necessary relation between the self-diffusion coefficient of an isotopic species and that of the chemical species in which it happens to be found. Particularly in complex systems, such as those involved in soil phosphate, care should be taken to ensure that no gross error is incurred by such an assumption.

B. ULRICH: The model underlying this theoretical and experimental treatment makes the basic assumptions that during plant growth neither the soil nor the plant change their relevant properties. Regarding the soil, one has to consider the influence of root respiration acting as a hydrogen ion generator, which may change the soil properties near the root surface quite drastically. Besides this one can think of other ways in which plant growth influences soil properties. A better knowledge of these facts seems desirable too.

I.J. GRAHAM-BRYCE: To calculate the theoretical quantity of ions supplied to a plant by diffusion, using flux equations of the kind presented by Dr. Olsen, it is necessary to assume a value for c_r (the concentration at the root surface) or to estimate its value indirectly. In Dr. Olsen's treatment c_r was calculated from experimentally determined values for Q (the quantity of ions taken up by the plant in a given time) and it is shown that the value of c_r is similar whatever boundary conditions are inserted into the flux equations used for the calculations. However, these estimations must involve a number of assumptions, such as that D (the diffusion coefficient) remains constant and that diffusion is the only significant nutrient transport mechanism. On the basis of the estimated c_r the agreement between experimentally determined values of Q, and those calculated from flux equations, was tested for various time periods. It is perhaps not surprising that the agreement was good since the value of c_r used for the calculation of Q was itself obtained by calculations from experimentally determined Q values in previous experiments. Any error in this value of c_r would therefore possibly be such as to compensate for lack of agreement between experimental and theoretical values of Q. This sort of uncertainty seems to be a fundamental difficulty in testing the applicability of the theoretical equations to measured nutrient uptake.

The agreement between the observed and calculated quantities of phosphate supplied to the plant depends also on the use of the correct value for b, the capacity factor - this requires a correct assessment of the "labile pool". Dr. Olsen has used the quantity of P which undergoes isotopic exchange with ^{32}P in the 24 h for the labile pool, but other measurements could be proposed which would give different values for b. For the situation which Dr. Olsen is considering the labile pool should be that portion of the soil P whose equilibration with solution P is not rate-limiting in comparison with the transport to the roots. Agreement between the experimentally-determined and calculated uptake quantities suggests that the 24 h exchangeable P coincides with this fraction of the soil P.

J. P. QUIRK: There are similarities between the work Dr. Olsen has described and that which Dr. Lewis and I have given in our paper. There are, however, two notable points of difference.

(1) Dr. Olsen's work has been based on what is, in effect, a linear isotherm between adsorbed phosphate and solution phosphate. In our experiments we have used a relationship between added phosphate and diffusion coefficient and there is a curvilinear relationship between added phosphate and solution concentration.

Crank[1] has discussed the case of simultaneous diffusion and chemical reaction by reference to a general isotherm equation:

$$S = RC^n,$$

where S is the amount adsorbed and C is the solution concentration, R and n are constants. For a linear isotherm n is 1 and diffusion is governed by a diffusion coefficient $D/(R+1)$ where D is the diffusion coefficient of the ion in aqueous solution. The solutions of diffusion problems for given initial boundary conditions are the same as the corresponding problem in simple diffusion.

When the isotherm is not linear the effective diffusion coefficient, given by

$$(D/n)(1/R)^{1/n}S^{(1-n)/n} \quad ,$$

increases as the concentration S increases, and the situation is obviously more complex.

(2) Dr. Olsen has referred to the fact that some of our solution concentrations are high. The very high ones, 20 μgρ/ml and greater, refer to those cases where large additions of phosphate have been made. However, the concentration of solution at which phosphate sufficiency was achieved was about 0.2 to 1.5 μgρ/ml. These solutions were obtained by a displacement technique and might thus be expected to be somewhat larger than those reported by OLSEN and WATANABE [1]: 0.1 to 0.4 μg/ml obtained by using solution : soil ratio of 10 : 1. For the Seddon soil we used, differences as much as four-fold were obtained between the displacement and 10 : 1 solution : soil ratio.

In addition to these comments, there are a few relatively minor points. The agreement between the phosphate diffusion coefficient derived from experiments with phosphate and chloride in soils and that in aqueous solution is remarkable, but I feel it should be viewed with some caution. For a calcareous soil $HPO_4^=$ would be the diffusing species and in the soil solution Ca^{++} would be the dominant cation, and hence the good agreement with measured diffusion coefficients for NaH_2PO_4 is to a certain extent fortuitous. One interesting feature is that as H_2PO_4 is regarded as the ion absorbed by plants rather than $HPO_4^=$, hence a transformation to the monovalent ion presumably takes place at the root surface.

---

[1] "Mathematics of Diffusion", Clarendon Press, Oxford.

When Dr. Olsen was presenting the theoretical background to the diffusion measurements he referred to the work of PORTER et al. [2] and used in one of his equations a factor γ which is supposed to take into account ionic interaction and increased viscosity of water in the porous system. I would prefer to see this and similar factors lumped into a single factor because the use of specific symbols implies that we know very much more about the factor concerned than we actually do.

It is interesting that the root hair density for corn plants observed by BOULDIN [3] is very similar to that Dr. Lewis and I have measured for wheat roots.

REFERENCES TO DISCUSSION

[1] OLSEN, S.R. and WATANABE, F.S., Proc. Soil Sci. Soc. Amer. 27 (1963) 648.

[2] PORTER, L.K., KEMPER, W.D., JACKSON, R.D. and STEWART, B.A., Proc. Soil Sci. Soc. Amer. 24 (1960) 460.

[3] BOULDIN, D.R., Proc. Soil Sci. Soc. Amer. 25 (1961) 476.

TENTATIVE INTEGRATION OF NEW TRENDS AND METHODS IN THE STUDY OF SOIL/PLANT RELATIONSHIPS

C. G. LAMM
TECHNICAL UNIVERSITY OF DENMARK,
COPENHAGEN, DENMARK

SUMMARY

The planning meeting held at the IAEA in Vienna in 1964 under the co-ordinated research programme of "Plant Nutrient Supply and Movement in Soil Systems" gave the impulse for a joint Scandinavian research programme to co-ordinate research efforts and apply modern techniques in questions relevant to soil/plant relationships. The countries involved work through specialized committees of the N.J.F. (Nordiske Jordbrugsforskeres Forening).* These committees consist of three to five scientists from each country and they represent scientific institutions or laboratories*.

Basically the joint efforts would be those of applying modern ideas and techniques to a limited number of representative Scandinavian soils to gain more information on the availability of soil nutrients than that obtained through conventional soil testing or fertilization experiments. In this context, and with regard to phosphorus, the assessment of P-potentials, E-values,

---

* The author represents these committees at this Panel.

P-adsorption isotherms or diffusion patterns could be mentioned. Thermodynamic as well as kinetic approaches would be investigated in the over-all study of the mechanism by which soil-P is transported from the solid phases and through the soil solution to the root surfaces.' Thus isotopic exchange might tell us the rate at which various solid soil-P fractions are dissolved, and the diffusion experiments would elucidate the rates at which dissolved phosphorus migrates through the soil solution as, e.g. a function of the water content.

Parallel to this work, fertilization experiments might complete the picture. Yield curves should be established under standardized conditions, and by using labelled fertilizers we would obtain additional information on soil-P availability or capacity parameters. Soil-solution concentrations should be evaluated through activation analysis.

Although at a preparatory stage, this work could be started possibly early next year.

Here is a situation where a number of people in these countries are prepared to apply new methods in practice and to unite their efforts in a co-ordinated programme because no one could possibly undertake it alone. My question to the Panel is: Are we today in a position to take practical advantage of these new methods?

DISCUSSION

During the discussion which followed the foregoing paper, the author asked the Panel a question concerning the significance of activity coefficients for the exchanger phase of a soil. The following is a summary of the discussion in which remarks were made by G. H. Bolt, H. Laudelout, S. R. Olsen and H. C. Thomas

Given an experimental definition of a surface region it is often possible to demonstrate experimentally that there exists a well-defined exchange reaction for which a standard free energy may be deduced from sufficiently complete experiments. Only in highly exceptional real cases, or in purely theoretical cases is a chemical potential in a condensed phase expressible in terms of a known function of composition. A practical approach is to assume some simple function of solid phase composition, such as will refer to some idealized case, and then on the basis of experiment to deduce numerically the excess chemical potential which summarizes the deviations of the real from the ideal system. For example, if solid phase (or surface region) compositions are expressed in terms of equivalent fractions N, the excess chemical potential may be expressed in terms of an activity coefficient f given by

$$RT \ln f = \mu_{obsd} - (\mu^o + RT \ln N).$$

The numerical value but not the significant behaviour of f is determined by the arbitrary choice of the level μ^o from which μ is measured. A change in this level merely changes f by a constant factor.

Nothing in the foregoing implies that the exchanger phase need be a pure substance. An arbitrary uniform mixture of several exchangers would exhibit qualitatively the same behaviour as a single substance and neither would necessarily be expected to show simple behaviour.

SUMMARY AND RECOMMENDATIONS

SUMMARY

Analysis of the processes by which a nutrient ion, potassium for instance, is removed from its position in the lattice of a potassium-bearing mineral, moves through the soil and becomes incorporated in the plant, shows that a very complicated set of rate processes is being dealt with. Any of these may be rate-limiting for the overall process of ion uptake by the plant. As was shown by the papers presented at this Panel, and by perusal of recent literature, various phases of these rate processes are now being actively studied, notwithstanding the complexity of the problems involved. It is realized that to rationalize the empirical practice of improving plant nutrition by methods at the disposal of the agriculturist, such as rate and time of fertilizer application, irrigation, choice of variety, spacings and so on, it is necessary to know where the rate-limiting process is located.

Two types of approach are possible, as shown by the papers presented here, which comprise a representative sample of present trends in research in this subject.

Examination of the very complicated system represented by a plant growing in natural soil necessitates numerous and sweeping assumptions to make it amenable to study, whereas simplified systems can be studied with few or no assumptions. The latter may consist of the investigation of only one of the rate processes involved in the overall process of ion uptake, for example the diffusion of ions in soils and clays, the rate of uptake by intact plants in solution, the rate of solubilization of primary or secondary soil minerals, the rate of mineralization of soil organic matter, and so on.

For instance, in self-diffusion studies, even though the process is one of the simplest that can be isolated, the answer is by no means easy. Fortunately, it seems that electrical conductivity measurements, which are very cheap and rapid, provide the information needed to estimate the effect of such factors as the tortuosity of the pores of the system on the self-diffusion coefficients. Even when results on the mobility of ions in soil systems are obtained, there still remains the very serious problem of obtaining the actual interdiffusion constant of the ion - essential for maintaining the electrical neutrality of the system - when considered against a counterflow of other ions originating from the root system.

An entirely different type of simplification of the system is represented by equilibrium studies. The interest in a problem where rate processes only are involved lies in the fact that, at a given point in the chain of processes, the rate may be so slow that it does not disturb the equilibrium concentrations of preceding reactions. It could be said that there is an obvious advantage in knowing the ease with which hydrogen ions introduced in the system by root respiration will replace other cations adsorbed on the soil surface.

Description of the experimental results concerning the equilibrium concentrations of ions in solution, and on the surface of soil colloids, may be made either by correlating them with the consequences derived from physical models, such as the diffuse double-layer theory, or by the classical thermodynamic methods. It is not useful to attempt to prove that empirical ion-exchange formulae are of value just because it can be proved that the most commonly-used formulae, those of Gapon and Vanselow, can be correlated with thermodynamic formulae. It is preferable to use the thermodynamic formulae directly.

The approach that consists of studying the system in its whole complexity by a variety of simplifying assumptions is subject to criticism. However, until enough is known of the individual processes involved there is no substitute for looking at the process as a whole. The fair agreement observed between the rate of accumulation of phosphate by plants growing in soil and the calculated fluxes of phosphate through the soil system may be due to a fortuitous compensation of the errors in the several assumptions made. This would not be a fair judgement on the usefulness of this method since, if it can provide us with a means of correlating several important parameters of the soil-plant system with total uptake, it has amply fulfilled its purpose. That such is the case has been actually demonstrated and it may be hoped that a more "integrated" approach to the problem of evaluating response to phosphate fertilizer can be found, even though its fundamental basis is not very certain. On the other hand, it may not be said that such a treatment, because it is to some extent successful, demonstrates that diffusion processes are, or are even likely to be rate-determining in nutrient uptake by plants.

The same could be said of course about the knowledge which may be gained from the study of simple rate processes in the soil system.. Oversimplification of the processes implies that the significance in the whole picture of any rate process which is studied separately may become seriously diminished. This is apparent from some of the remarks which were made after the papers presented at this Panel.

The classical thermodynamic approach is restricted to equilibrium situations and, even when a state of quasi-equilibrium has been reached, translating the results obtained by this method in terms of quantities of immediate interest for plant nutrition may not always be easy, or even feasible.

There may be speculation why programmes such as those sponsored by the Agency to assist developing countries, often at the level of subsistence agriculture, should have as their basis the most recent trends in soil-plant relationship studies. There is a natural tendency to believe that at a low level of intensification of agriculture simple techniques and simple concepts are preferable. In other words that, since the technical knowledge of agricultural practice cannot be simply transposed from the temperate regions of the world to the dry or humid tropical regions, development of agriculture in the latter should occur in the same empirical way that has characterized the intensification of agriculture during the last 150 years. This neglects, however, a very important difference; the intensification of agriculture in the temperate zone occurred parallel to the development of medical science. Therefore, increase in life expectancy achieved by medical progress did not strain the supply of foodstuffs, which continuously increased, particularly since, at the same time, the enormous agricultural potentials of North America were developed. The situation is entirely different in the tropical countries where agricultural development cannot keep pace with the increasing population pressure brought about by progress in medicine, the techniques of which, contrary to those in agriculture, can be transferred immediately, regardless of the country of origin.

Time is thus essential to solve the practical problems of agricultural development, and this precludes the empirical approach alone. If the aim is to solve a given problem empirically, the number of experimental possibilities is always enormous. Any conceptual guide, whether the most recent trend or not, any method, whatever its apparent sophistication, that limits the choice to a few alternatives to be decided upon by local experimentation, should be welcomed. This also applies when practical results, obtained in a specific region, have to be generalized to other soil types, climates or plants. Then the most of what modern soil science has to offer will be needed to generalize in the safest possible way.

RECOMMENDATIONS

The Panel emphasized the necessity of bridging the gap between new information on the nature of the rate processes which determine nutrient uptake by plants and the research programmes on the efficient use of phosphate and nitrogen fertilizers which are sponsored by the Agency for the benefit of developing countries in South East Asia and South America.

The following steps might be the key to implement this:

1. In their individual capacity, or as a group, the members of the Panel are ready to provide the Agency with the information it will need for the interpretation or the planning of its co-ordinated programmes.
2. To make the information available to a wide circle of persons interested in the new trends in studying plant nutrient supply and movement in the soil, it is recommended that a technical report embodying the papers given at the Panel meeting and the essence of the discussions should be published by the Agency.
3. Meetings such as the present Panel held on the initiative of the Agency fulfil a very useful purpose and it is recommended that they be organized whenever it is deemed suitable.
4. Research is needed on the subject matter; this could be promoted by the Agency by the grant of research contracts which may, in certain cases,. be on a cost-free basis.
5. Close contact should be maintained between the various members of the Panel interested in this rapidly changing field. It is therefore recommended that individual members should circulate to other Panel members summaries of their papers which are accepted for publication.

Finally, the Panel was of the opinion that the solution of problems of wide concern will be advanced by the co-ordination of research effort. In this respect the Panel acknowledges with interest the suggestions on such co-ordination in Scandinavian countries, as outlined by Dr. C.G. Lamm.

RÉSUMÉ ET RECOMMANDATIONS

RÉSUMÉ

L'analyse des processus, sous l'effet desquels un ion d'élément nutritif comme le potassium est enlevé à la position qu'il occupe dans le réseau d'un minéral porteur de potassium, se déplace dans le sol et s'incorpore à la plante, montre que l'on se trouve en présence d'un ensemble très complexe de phénomènes qui tous peuvent limiter la vitesse du processus général de fixation des ions par la plante. Comme on a pu le constater en consultant les mémoires présentés au Groupe d'étude et en parcourant les ouvrages récemment publiés sur la question, les problèmes qui se posent sont complexes, mais les différentes phases de ces processus font l'objet d'une étude attentive. On se rend compte que pour rationaliser les procédés empiriques qu'utilise l'agriculteur pour améliorer la nutrition des végétaux, tels que l'application d'engrais en certaines quantités et à des époques déterminées, l'irrigation, le choix de la variété, l'espacement des plants, etc., il faut pouvoir localiser le processus qui limite la vitesse de fixation des ions.

Il est possible d'aborder le problème de deux manières différentes, ainsi qu'il ressort des mémoires présentés au Groupe d'étude, qui expriment bien les tendances actuelles de la recherche dans ce domaine.

Pour étudier le système très complexe que représente une plante croissant sur un sol naturel, il est nécessaire d'établir des hypothèses nombreuses et audacieuses afin de pouvoir poser le problème, alors que la simplification des systèmes permet de les étudier à partir de quelques hypothèses ou même en l'absence d'hypothèses. Dans ce cas, il peut suffire de faire des recherches sur l'un des processus qui interviennent dans la fixation des ions, par exemple la diffusion des ions dans les sols et les argiles, la fixation des éléments nutritifs par des plantes intactes en solution, la solubilisation des minéraux primaires ou secondaires, la minéralisation des matières organiques des sols, etc. Si l'on veut par exemple étudier l'autodiffusion, qui est pourtant l'un des processus les plus simples pouvant être isolés, il n'est pas facile d'arriver à des résultats. Heureusement, il semble que des mesures de la conductivité électrique, qui sont très rapides et très peu coûteuses, fournissent les renseignements nécessaires pour évaluer l'effet de facteurs tels que la tortuosité des pores du système sur les coefficients d'autodiffusion. Même si l'on obtient des données sur la mobilité des ions dans les différents sols, il faut encore résoudre le problème difficile consistant à mesurer la constante d'interdiffusion des ions essentielle au maintien de la neutralité électrique du système - en présence d'un mouvement contraire d'autres ions provenant du système radiculaire.

Un type de simplification entièrement différent consiste à étudier le système dans des conditions d'équilibre. L'intérêt d'un problème qui ne met en jeu que des processus continus tient à ce que, en un point donné de la chaîne des processus, l'évolution peut être assez lente pour ne pas déranger les concentrations à l'équilibre lors des réactions précédentes. On pourrait dire qu'il est manifestement utile de savoir avec quelle facilité les ions hydrogène introduits dans le système par la respiration au niveau des racines remplaceront d'autres cations absorbés à la surface du sol.

Pour décrire les résultats expérimentaux concernant les concentrations d'ions à l'équilibre soit en solution soit à la surface des colloïdes du sol, on peut rapporter ces résultats aux déductions établies à partir de modèles physiques, telles que la théorie de diffusion à double couche, ou utiliser les méthodes thermodynamiques classiques. Il est inutile de vouloir trouver que des formules empiriques d'échange ionique sont intéressantes simplement parce qu'il est possible d'établir une corrélation entre les formules les plus courantes, celles de Gapon et Vanselow, et les formules thermodynamiques. Il est préférable d'utiliser directement les formules thermodynamiques.

On peut critiquer la méthode qui consiste à étudier le système dans toute sa complexité en établissant des hypothèses très diverses pour en simplifier les données. Cependant, tant que l'on ne connaîtra pas suffisamment les différents processus en cause, il n'y a pas d'autre solution que de considérer le phénomène dans son ensemble. La bonne concordance que l'on observe entre le taux de fixation du phosphate par les plantes croissant dans un sol et les mesures du flux de phosphate à travers ce sol peut être due à une compensation fortuite des erreurs inhérentes aux différentes hypothèses que l'on a établies. Toutefois, il ne serait pas juste de juger par là de l'intérêt de la méthode; en effet, si celle-ci peut nous fournir un moyen d'établir une corrélation entre plusieurs paramètres importants du système sol-plante et la fixation des éléments nutritifs, son utilité sera largement démontrées. Il a été prouvé que tel est bien le cas, et on peut espérer qu'il sera possible de trouver une méthode plus synthétique pour évaluer la réponse des plantes aux applications d'engrais phosphatés, encore que les bases de cette méthode ne soient pas absolument sûres. D'autre part, le succès relatif de cette méthode ne permet pas d'affirmer que les processus de diffusion influent sur la vitesse de fixation des éléments nutritifs par les plantes, ni même que cela soit probable.

Cette observation pourrait naturellement s'appliquer également aux données que l'on peut obtenir en étudiant les processus continus simples intervenant dans le sol. En simplifiant les processus à l'excès, on risque d'amoindrir sérieusement l'importance relative des processus considérés séparément. Certains des membres du groupe qui ont formulé des observations à la suite de la présentation des mémoires ont fait ressortir ce danger.

La méthode fondée sur la thermodynamique classique ne s'applique qu'aux conditions à l'équilibre, et même lorsqu'un état proche de l'équilibre est atteint, il n'est pas toujours facile ni même possible d'exprimer les résultats obtenus au moyen de cette méthode en quantités présentant un intérêt immédiat pour la nutrition des plantes.

On peut se demander pourquoi des programmes comme ceux que l'Agence organise pour aider les pays en voie de développement, souvent au niveau d'une agriculture de subsistance, devraient s'appuyer sur les résultats les plus récents des études de phytopédologie. On a naturellement tendance à penser que dans les pays où l'agriculture est peu intensive, il est préférable d'utiliser des techniques simples reposant sur des notions simples. Autrement dit, étant donné qu'il est impossible d'appliquer directement dans les régions tropicales sèches ou humides les techniques agricoles des régions tempérées, le développement agricole de ces régions devrait avoir le même caractère empirique que celui des régions tempérées, au cours des 150 dernières années. Cependant, en raisonnant ainsi, on néglige une différence très importante; dans la zone tempérée, le développement de l'agriculture est allé de pair avec le progrès des sciences médicales. L'augmentation de l'espérance de vie résultant des progrès de la médecine n'a pas pesé sur les ressources en denrées alimentaires, qui n'ont cessé d'augmenter étant donné, surtout, qu'à la même époque l'énorme potentiel agricole de l'Amérique du Nord se développait. La situation est entièrement différente dans les pays tropicaux où le dévoloppement de l'agriculture ne peut faire face à la pression démographique croissante résultant des progrès de la médecine, domaine dans lequel, à la différence de l'agriculture, les techniques nouvelles peuvent être immédiatement appliquées, quel que soit leur pays d'origine.

Le temps est donc un facteur essentiel pour la solution des problèmes pratiques du développement de l'agriculture, et c'est pourquoi il est impossible de se limiter aux méthodes empiriques. Si l'on cherche à résoudre de manière empirique un problème donné, le nombre des possibilités expérimentales est toujours énorme. Il faut donc accueillir favorablement tous principes directeurs, qu'ils se fondent ou non sur les données les plus récentes, et toute méthode, quelle que soit sa complexité apparente, qui limite le nombre des possibilités entre lesquelles un choix sera fait en fonction de l'expérience locale. Ceci s'applique également au cas où il y a lieu d'étendre les résultats pratiques obtenus dans une région déterminée à d'autres types de sols, d'autres climats, ou d'autres plantes. Pour généraliser dans les meilleures conditions, il faudra donc faire appel à toutes les connaissances de la pédologie moderne.

RECOMMANDATIONS

Le Groupe d'étude a souligné la nécessité d'intégrer les données récentes sur la nature des processus qui déterminent la fixation des éléments nutritifs par les plantes aux programmes de recherches sur l'utilisation des engrais phosphatés et azotés que l'Agence organise à l'intention des pays en voie de développement de l'Asie du Sud-Est et de l'Amérique du Sud. A cette fin, le Groupe a présenté les recommandations suivantes:

1. Les membres du Groupe, à titre individuel ou collectivement, devraient fournir à l'Agence les renseignements qui lui seront nécessaires pour interpréter ou établir des programmes de recherches coordonnées.
2. Afin de mettre ces renseignements à la disposition de tous ceux qui s'intéressent à l'étude de la présence et du mouvement des éléments nutritifs des plantes dans le sol, l'Agence devrait publier un rapport technique contenant le texte des mémoires présentés lors de la réunion et un compte rendu analytique des discussions.
3. L'Agence devrait organiser chaque fois qu'il y a lieu des réunions comme celles du Groupe d'étude, dont l'utilité est démontrée.
4. Comme la question doit être étudiée plus à fond, l'Agence pourrait encourager les recherches nécessaires sur la question en accordant des contrats de recherche, dans certains cas sans frais pour elle.
5. Les différents membres du Groupe d'étude s'intéressant à ce domaine qui évolue rapidement devraient demeurer étroitement en rapport les

uns avec les autres. Chacun d'eux devrait donc communiquer aux autres membres du Groupe des résumés des mémoires rédigés par lui dont la publication aura été acceptée.

Enfin, le Groupe a estimé qu'il serait plus facile de résoudre les problèmes d'intérêt commun en coordonnant les efforts de recherche. A ce propos, il a reconnu l'intérêt d'un système de coordination analogue à celui qui existe dans les pays scandinaves, et dont Dr C.G. Lamm a exposé les grandes lignes.

ВЫВОДЫ И РЕКОМЕНДАЦИИ

ВЫВОДЫ

Анализ процессов, в результате которых питательные ионы, например ионы калия, удаляются со своих мест в кристаллической решетке минералов, содержащих калий, перемещаются в почве и поглощаются растениями, показывает, что с этим связан очень сложный комплекс процессов, определяющих скорость поглощения питательных веществ. Любой из этих процессов может ограничивать скорость общего процесса поглощения ионов растением. Как показали работы, представленные на данное совещание экспертов, и изучение вышедшей в последнее время литературы, в настоящее время активно исследуются различные фазы этих, определяющих скорость поглощения, процессов, несмотря на сложность этой проблемы. Очевидно, для того, чтобы рационализировать сложившуюся практику улучшения питания растений с помощью имеющихся в распоряжении агрономов методов, таких как выбор количества и времени внесения удобрений, ирригация, выбор сортов, частоты посадок и т. д., необходимо знать, в каком месте цепи находится процесс, ограничивающий скорость поглощения.

Как показали представленные на совещание экспертов доклады, существуют два возможных пути решения проблемы, которые представляют существующие тенденции в исследовании этого вопроса.

Для исследования очень сложной системы, каковой является растение, выращиваемое на естественной почве, требуются многочисленные и радикальные предположения, тогда как упрощенные системы могут быть изучены с очень небольшим числом предположений или без таковых. Исследование упрощенных систем может включать только один из определяющих скорость поглощения факторов, связанных с общим процессом поглощения ионов, например процесс диффузии ионов в почвах и глинах, скорость поглощения питательных веществ из раствора целыми растениями, скорость растворения первичных и вторичных минералов почвы, скорость минерализации органических веществ почвы и т.д.

Например, при исследовании самодиффузии, являющейся одним из самых простых процессов, которые могут быть выделены, найти ответ совсем не просто. К счастью, измерения электропроводимости, которые проводятся очень быстро и не требуют больших затрат, позволяют, кажется, получить данные, необходимые для оценки влияния таких факторов, как кривизна пор системы, на коэффициенты самодиффузии. Даже после получения данных о мобильности ионов в почвенных системах, все еще остается очень серьезная проблема определения константы фактической взаимной диффузии для иона (имеющей важное значение для поддержания электрической нейтральности системы) в зависимости от встречного потока других ионов, образующихся в корневой системе.

Совершенно другой тип упрощения системы представляют собой исследования равновесного состояния. Интерес к проблеме, связанной только с процессами, определяющими скорость поглощения, объясняется тем фактом, что в данной цепи процессов скорость может быть настолько небольшой, что она не нарушает равновесных концентраций предшествующих реакций. Можно сказать, что имеется очевидный прогресс в познании того, насколько легко ионы водорода, попавшие в систему в результате дыхания корней, заменят другие катионы, поглощенные с поверхности почвы.

Описание экспериментальных результатов, касающихся равновесных концентраций ионов в растворе и на поверхности коллоидов почвы, может быть произведено или путем установления их связи с результатами, полученными на основании физических моделей, таких как двухслойная теория диффузии, или с помощью классических термодинамических методов. Не имеет смысла пытаться доказать, что эмпирические ионообменные формулы представляют ценность, хотя бы потому, что наиболее распространенные формулы (формулы Гапона и Ванзелоу) могут быть увязаны с термодинамическими формулами. Лучше непосредственно использовать термодинамические формулы.

Путь решения проблемы, состоящий в изучении системы во всей ее сложности с использованием различных упрощающих предположений, подвергается критике. Однако до тех пор пока не будет достаточно известно об отдельных процессах, не существует другой возможности рассмотрения процесса в целом. Хорошее согласие, наблюдаемое между скоростью поглощения фосфата растениями, растущими на почве, и расчетными потоками фосфата через данную почвенную систему, может быть объяснено случайной компенсацией ошибок в нескольких принятых предположениях. Это было бы несправедливой оценкой полезности этого метода, так как, если он может стать для нас средством корреляции между несколькими важными параметрами системы почва-растение и общим поглощением, он полностью выполнит задачу. То, что это так, было по существу уже продемонстрировано, и можно надеяться, что будет найден более "полный" путь решения проблемы оценки реакции на фосфатные удобрения, хотя и не совсем ясны теоретические основы этого явления. С другой стороны, нельзя сказать, что такой путь решения, поскольку он является до некоторой степени удачным, показывает, что диффузионные процессы являются или, вероятно, должны быть процессами, определяющими скорость поглощения питательных веществ растениями.

То же самое можно, конечно, сказать о сведениях, которые могут быть получены в результате изучения простых процессов, определяющих скорость поглощения в почвенной системе. Чрезмерное упрощение процессов может привести к тому, что значение всей картины любого определяющего скорость поглощения процесса, изучаемого отдельно, может быть значительно уменьшено. Это явствует из некоторых замечаний, сделанных после представления докладов на данном совещании экспертов.

Возможность применения классической термодинамики для решения проблемы ограничена равновесными состояниями, и, даже в том случае, когда достигнуто квазиравновесное состояние, перевод результатов, полученных с помощью этого метода, в величины, представляющие непосредственный интерес для понимания питания растений, не всегда является простым или даже возможным.

Можно поразмыслить о том, почему программы, осуществляемые, например Агентством, с целью оказания помощи развивающимся странам, должны основываться на самых последних тенденциях, существующих в области изучения связи растений с почвой. Существует естественная тенденция считать, что при низком уровне интенсификации сельского хозяйства предпочтительными являются простые методы и простые концепции. Другими словами, поскольку опыт сельскохозяйственной практики нельзя просто перенести из районов с умеренным климатом в сухие или влажные тропические районы, развитие сельского хозяйства в этих последних должно происходить тем же эмпирическим путем, который был характерен для интенсификации сельского хозяйства в течение последних 150 лет. При этом, однако, не учитывается очень важная разница; интенсификация сельского хозяйства в районах с умеренным климатом происходила параллельно с развитием медицинской науки. Поэтому увеличение вероятной продолжительности жизни, достигнутое благодаря успехам медицины, не создавало трудностей со снабжением продуктами питания, производство которых непрерывно увеличивалось благодаря, главным образом, использованию огромных потенциальных возможностей Северной Америки в отношении сельского хозяйства. Совершенно иначе дело обстоит в тропических странах, в которых развитие сельского хозяйства отстает от увеличения населения вследствие развития медицины, методы которой, в отличие от методов сельского хозяйства, могут быть немедленно перенесены в эти страны из других стран независимо от того, в какой стране они возникли.

Таким образом, время имеет основное значение для решения практических проблем развития сельского хозяйства, и это делает невозможным исключительно эмпирический подход к решению этой проблемы. Если цель состоит в том, чтобы решить данную проблему эмпирическим путем, экспериментальных возможностей для этого всегда имеется огромное количество. Любая концепция, соответствует она самым последним тенденциям или нет, любой метод, каким бы он ни казался сложным, ограничивающие выбор несколькими альтернативами, которые должны быть определены путем проведения экспериментов на месте, должны всячески приветствоваться. Это также относится и к тем случаям, когда практические результаты, полученные в конкретном районе, должны быть распространены на другие виды почв, другой климат или другие культуры. Тогда большая часть того, чем располагает современное почвоведение, потребуется для наиболее правильного распространения таких результатов.

РЕКОМЕНДАЦИИ

Совещание экспертов подчеркивает необходимость ликвидации разрыва между новыми данными о характере процессов, которые определяют поглощение питательных веществ растениями, и исследовательскими программами по эффективному использованию фосфатных и азотных удобрений, организуемыми Агентством в качестве помощи развивающимся странам Юго-Восточной Азии и Южной Америки.

Решающее значение для этого может иметь следующее:

1. Члены совещания экспертов, выступая в качестве частных лиц или в виде группы, готовы предоставить Агентству информацию, необходимую ему для интерпретации или планирования своих согласованных программ.
2. Для обеспечения информацией широкого круга лиц, интересующихся новыми тенденциями в изучении снабжения растений питательными веществами и их перемещения в почве, рекомендуется, чтобы Агентство опубликовало технический доклад, включающий работы, представленные на данное совещание экспертов, и краткое изложение дискуссий.
3. Совещания, подобные настоящему совещанию экспертов, которые проводятся по инициативе Агентства, очень полезны. Поэтому рекомендуется проводить такие совещания всякий раз, когда это будет признано необходимым.
4. Необходимо проводить исследования по данному вопросу; Агентство может способствовать этому путем предоставления исследовательских контрактов, которые в определенных случаях могут выполняться бесплатно.
5. Между членами настоящего совещания экспертов, интересующимися этой быстро развивающейся областью, должны поддерживаться тесные контакты. Поэтому рекомендуется, отдельным членам настоящего совещания экспертов передать другим участникам краткое изложение своих докладов, принятых для опубликования.

И, наконец, совещание экспертов считает, что в решении проблем, имеющих большое значение, будут достигнуты успехи благодаря координации исследовательских работ. В этой связи совещание экспертов с интересом отмечает предложения о такой координации в скандинавских странах, о чем сообщил д-р С.Г.Ламм.

RESUMEN Y RECOMENDACIONES

RESUMEN

El estudio de los procesos en virtud de los cuales un ion de una sustancia nutritiva -el ion potasio, por ejemplo-se ve separado del lugar que ocupa en la red de un mineral de potasio, se mueve a través del suelo y termina incorporándose a una planta, pone claramente de manifiesto que el investigador se enfrenta con un conjunto sumamente complejo de procesos cinéticos. Cualquiera de esos procesos puede constituir la fase limitadora de la velocidad con que se desarrolla el proceso total de la absorción de los iones por la planta. Conforme se desprende de las memorias presentadas en la reunión de este Grupo de expertos y de la lectura de las publicaciones aparecidas recientemente sobre la materia, en la actualidad se están investigando activamente diversas fases de esos procesos cinéticos, a pesar de la complejidad de los problemas que tal labor entraña. En efecto, se ha llegado a la conclusión de que para poder aplicar con un criterio racional los métodos meramente empíricos que el agricultor tiene a su alcance para mejorar la nutrición de las plantas (frecuencia y momento de la aplicación del fertilizante, riego, selección, espaciado de las plantas, etc.), es necesario conocer el lugar que ocupa la fase limitadora del proceso total.

Las memorias presentadas en esta reunión, representativas de las actuales tendencias de la investigación sobre esta materia, ponen de manifiesto que existen dos formas principales de abordar el problema.

El estudio de un sistema muy complejo, como el representado por una planta que crece en un suelo natural, exige el planteamiento previo de gran número de supuestos de carácter muy general; por el contrario, el estudio de sistemas simplificados puede realizarse partiendo de muy pocos supuestos e incluso de ninguo. Este último tipo de estudio puede consistir en la investigación de uno solo de los procesos cinéticos que intervienen en el proceso total de la absorción de los iones, entre los que cabe mencionar la difusión de los iones en los suelos y arcillas, la velocidad de absorción por plantas intactas cultivadas en solución, la velocidad de solubilización de los minerales primarios y secundarios de los suelos, la velocidad de mineralización de la materia orgánica del suelo, etc.

Por ejemplo, en los estudios sobre la autodifusión, si bien el proceso investigado es uno de los más sencillos que resulta posible aislar, su explicación no es en modo alguno fácil. Afortunadamente, parece ser que las mediciones de la conductividad eléctrica -cuya realización es muy económica y rápida- proporcionan la información necesaria para evaluar la influencia que sobre los coeficientes de autodifusión ejercen factores tales como la tortuosidad de los poros del sistema. Incluso cuando se obtienen resultados sobre la movilidad de los iones en al suelo, sigue sin resolver el difícil problema de obtener el valor real de la constante de interdifusión del ion -fundamental si se quiere mantener la neutralidad eléctrica del sistema- cuando se la considera en relación con una circulación en contracorriente de otros iones provenientes del sistema radicular.

Un tipo completamente distinto de simplificación del sistema es el representado por los estudios sobre el equilibrio. El interés que ofrece un problema en el que solamente intervienen procesos cinéticos estriba en el hecho de que, en un determinado eslabón de la cadena de procesos, la velocidad puede ser tan lenta que no perturbe el equilibrio de las concentraciones resultante de reacciones anteriores. Cabría decir que constituye una ventaja evidente conocer la facilidad con que los iones hidrógeno introducidos en el sistema por la respiración radicular, sustituirán a otros cationes adsorbidos en la superficie del suelo.

Los resultados experimentales relativos a las concentraciones en equilibrio de iones en solución y a los coloides de la superficie del suelo pueden exponerse correlacionándolos con las conclusiones derivadas de modelos físicos (como el empleado en la teoría de la doble capa de difusión) o recurriendo a los métodos termodinámicos clásicos. No tiene utilidad alguna tratar de demostrar que la validez de las fórmulas empíricas del intercambio iónico se debe únicamente a que puede probarse que la mayoría de las fórmulas de empleo más corriente -las de Gapon y Vanselow- pueden correlacionarse con fórmulas termodinámicas. En efecto, es preferible emplear directamente estas últimas.

La forma de abordar el problema que consiste en estudiar el sistema en toda su complejidad partiendo de una serie de supuestos para simplificarlo, ha sido y sigue siendo objeto de críticas. Ahora bien, hasta que no se haya profundizado lo suficiente en el conocimiento de los diversos procesos que integran el proceso total, no es posible prescindir del estudio de este último. Es cierto que la notable concordancia observada entre la velocidad de acumulación de fosfatos por plantas cultivadas en el suelo y los flujos calculados de fosfatos a travês del suelo, puede deberse a una compensación fortuita de errores debidos a los diversos supuestos utilizados. Sin embargo, esta posibilidad no puede servir de criterio para juzgar sobre la utilidad de ese método que cumple sobradamente su finalidad si facilita un medio para correlacionar varios parámetros importantes del sistema suelo-planta con los valores de la absorción total. Que éste es efectivamente el caso es algo que ha quedado ya perfectamente demostrado, y es de esperar que sea posible encontrar una forma más "completa" de abordar el problema de evaluar la respuesta a los fertilizantes fosfatados, aun cuando la base de dicho problema adolezca de cierta imprecisión. En cambio, no cabría afirmar, por ejemplo, que tal método, simplemente por haber resultado hasta cierto punto satisfactorio, baste para demostrar que los procesos de difusión son (ni siquiera que es probable que sean) los que determinan la velocidad del proceso total de absorción de sustancias nutritivas por las plantas.

Lo mismo podría decirse, como es natural, de los conocimientos que pueden adquirirse del estudio de procesos cinéticos simples que tienen lugar en el suelo. La simplificación excesiva de esos procesos entraña el riesgo de que quede muy reducida la importancia que realmente tiene en el conjunto cualquiera de los procesos que se estudie por separado. Esta posibilidad se desprende de manera inequívoca de algunas de las observaciones formuladas sobre las memorias presentadas en la reunión del Grupo de expertos.

La posibilidad de recurrir al empleo de los métodos termodinámicos clásicos queda circunscrita a las situaciones de equilibrio, e incluso cuando se ha alcanzado un estado de cuasiequilibrio la conversión de los resultados obtenidos por este método en valores numéricos de interés inmediato en la esfera de la nutrición de las plantas no siempre resulta fácil y, en ocasiones, ni siquiera es posible.

Puede que haya quienes se pregunten por qué razones los programas que el Organismo patrocina a fin de prestar asistencia a los países en desarrollo, (asistencia limitada con frecuencia al nivel de la explotación agrícola imprescindible para la subsistencia de sus habitantes), deben basarse en las corrientes que se manifiestan en los estudios más modernos sobre las relaciones suelo-planta. Existe una tendencia natural a creer que, cuando se trata de fomentar la agricultura en un nivel modesto, es preferible emplear métodos y conceptos sencillos. En otras palabras, que como el conocimiento técnico de las prácticas agrícolas propias de las regiones templadas de nuestro planeta no puede transferirse sencillamente a las regiones tropicales, tanto áridas como húmedas, el desarrollo de la agricultura en estas últimas regiones debe tener la misma forma empírica que ha tenido durante los 150 últimos años. Este razonamiento no tiene en cuenta una diferencia muy importante: la intensificación de la agricultura en la zona templada tuvo lugar paralelamente al progreso de las ciencias médicas; por tanto, el aumento de la vida probable debido a ese progreso no se tradujo en una disminución de la oferta de productos alimenticios, que fue aumentando continuamente, en particular debido a que, al mismo tiempo, se explotaron las enormes posibilidades agrícolas de América del Norte. Ahora bien, la situación es totalmente distinta en los países tropicales, en los que el desarrollo de la agricultura no puede mantener el mismo ritmo que el aumento de la demanda de alimentos por parte de una población que aumenta continuamente debido a los progresos de la medicina, cuyas técnicas, a diferencia de las empleadas en agricultura, pueden llevarse immediatamente hasta esos países, cualquiera que sea aquel en que se idearon.

Se tiene, de esta forma, que el factor tiempo es fundamental para resolver los problemas prácticos que plantea el fomento de la agricultura, con lo que queda descartada la posibilidad de recurrir exclusivamente a métodos empíricos. Si la meta perseguida es resolver empíricamente un problema dado, el número de posibilidades experimentales de lograrlo es siempre enorme. Toda orientación conceptual -trátese o no de la tendencia más reciente- y todo método -por complicado que pueda parecer- que limiten las posibilidades de elección a un número reducido de alternativas sobre las que se decidirá según lo aconsejen los resultados de una experimentación local, deben ser bien acogidos. Esta afirmación se aplica también al caso en que hayan de generalizarse, haciéndolos extensivos a otros tipos de suelos, de climas o de plantas, los resultados prácticos obtenidos en una determinada región. En este caso, para proceder a esa generalización con el menor riesgo posible de error, se necesitará casi la totalidad de cuanto puede ofrecer la moderna ciencia del suelo.

RECOMENDACIONES

El Grupo de expertos subraya la necesidad de colmar la laguna existente entre la nueva información sobre la naturaleza de los procesos cinéticos que determinan la absorción de sustancias nutritivas por las plantas y los programas de investigaciones sobre el empleo eficaz de los abonos nitrigenados y fosfatados que el Organismo patrocina en beneficio de los países en desarrollo del Sudeste de Asia y de América del Sur.

Para conseguir esa finalidad, podría tener importancia fundamental la adopción de las siguientes medidas:

1. Los miembros del Grupo están dispuestos a facilitar al Organismo, a título individual o colectivamente, la información que éste necesite para la interpretación o la preparación de sus programas coordinados de investigación.

2. A fin de poner la información aportada a la reunión del Grupo de expertos al alcance de un amplio círculo de personas que se interesen por las nuevas tendencias imperantes en los estudios de la disponibilidad y movimiento de las sustancias fitonutritivas en el suelo, se recomienda que el Organismo publique un informe técnico que incluya las memorias presentadas en la reunión del Grupo de expertos así como la esencia de sus deliberaciones.
3. Reuniones como la que este Grupo de expertos ha celebrado por iniciativa del Organismo cumplen una finalidad sumamente útil, por lo que se recomienda que se convoquen otras siempre que se estime oportuno.
4. Es preciso intensificar las investigaciones sobre la materia examinada en la reunión; el Organismo puede contribuir a ello adjudicando contratos de investigación que, en ciertos casos, podrían tener carácter gratuito.
5. Los diversos miembros del Grupo de expertos que se interesan por estas cuestiones en constante y rápida evolución deben mantener un estrecho contacto. Por ello se recomienda que cada miembro facilite a los demás resúmenes de las memorias que le sean aceptadas para su publicación.

Por último, el Grupo de expertos opina que la resolución de diversos problemas de amplio alcance se verá facilitada si se coordinan los trabajos de investigación. A este respecto, el Grupo de expertos acoge con interés las sugerencias que el Dr. C. G. Lamm ha formulado en relación con la forma en que se procede a esa coordinación en los países escandinavos.

LIST OF PARTICIPANTS

Name	Institution	Nominating State or Organization
Bolt, G.H.	State Agricultural University, Laboratory of Soils and Fertilizers, 3, De Dreyen, Wageningen, Netherlands	Netherlands
Broeshart, H.	Division of Research and Laboratories, International Atomic Energy Agency, Vienna	International Atomic Energy Agency
Chaussidon, J.	Institut national de la recherche agronomique, Station central d'agronomie, Route de Saint Cyr, Versailles (S. et O.), France	France
Cho, C.M.	Division of Research and Laboratories, International Atomic Energy Agency, Vienna	International Atomic Energy Agency
Dakshinamurti, C.	Division of Agricultural Physics, Indian Agricultural Research Institute, New Delhi, India	India
Darab, K.	Istotope Laboratory, National Institute for Agricultural Quality Testing, Budapest, Hungary	Hungary
Graham-Bryce, I.J.	Rothamsted Experimental Station, Harpenden, Herts., United Kingdom	United Kingdom
Lamm, C.G.	Kemisk Laboratorium A. Danmarks Tekniske Højskole, Sølvgade 83, Copenhagen K, Denmark	Denmark
Larsen, S.	Levington Research Station, Department of Soil Science, Levington, Ipswich, Suffolk, United Kingdom	United Kingdom
Laudelout, H.	Institute of Agronomy, Catholic University of Louvain, Parc d'Arenberg, Heverlee, Louvain, Belgium	Belgium
Minczewski, J.	Analytical Chemistry Department, Institute of Nuclear Research, Dorodna 16, Warsaw 9, Poland	Poland
Nishigaki, S.	Department of Chemistry, National Institute of Agricultural Sciences, Nishigahara, Kitaku, Tokyo, Japan	Japan

Name	Institution	Nominating State or Organization
Olsen, S.R.	United States Department of Agriculture, Agricultural Research Service, Colorado State University, Fort Collins, Colorado, United States of America	United States of America
Quirk, J.P.	University of Western Australia, Department of Soil Science and Plant Nutrition, Nedlands, Western Australia	Australia
Reiniger, P.	State Agricultural University, Laboratory of Soils and Fertilizers, 3, De Dreyen, Wageningen, Netherlands	Netherlands
Szabolcs, I.	Research Institute of Soil Science and Agricultural Chemistry, Hungarian Academy of Sciences, Herman O. u. 15, Budapest II, Hungary	Hungary
Thomas, H.C.	Department of Chemistry, University of North Carolina, Chapel Hill, N.C., United States of America	United States of America
Ulrich, B.	Institut für Bodenkunde der forstlichen Fakultät, Universität Göttingen, Hannoversch Münden, Federal Republic of Germany	Federal Republic of Germany
Yesilsoy, M.S.	State Agricultural University, Laboratory of Soils and Fertilizers, 3, De Dreyen, Wageningen, Netherlands	Netherlands

Scientific Secretaries:

M. Fried	Joint FAO/IAEA Division, International Atomic Energy Agency, Vienna
P.B. Vose	Joint FAO/IAEA Division, International Atomic Energy Agency, Vienna

OTHER IAEA PUBLICATIONS IN THE FIELD

RADIATION IN AGRICULTURAL RESEARCH AND PRACTICE
(Review Series No. 10)

by Karl Kaindl and Hans Linser (Austrian Nitrogen Company, Linz, Austria). An essay in English.

(48 pp. 14.8×21 cm, paper-bound, 16 figures, 12 tables)
(1961) US $1.00; 6/- stg.

RADIOISOTOPES IN SOIL-PLANT NUTRITION STUDIES
(Proceedings Series)

The 32 papers (with discussions) presented at a symposium jointly organized by the IAEA and the Food and Agriculture Organization and held in Bombay, February - March 1962.

Contents: Soil chemistry and physics (12 papers); Ion uptake and translocation (8 papers); Biological measurement of soil characteristics (8 papers); Fertilizer usage (4 papers).

Papers are in their original languages with abstracts in English, French, Russian and Spanish.

(461 pp., 16×24 cm, cloth bound, 99 figures, tables)
(1962) US $9.00; £2.14.0 stg.

LABORATORY TRAINING MANUAL ON THE USE OF ISOTOPES AND RADIATION IN SOIL-PLANT RELATIONS RESEARCH
(Technical Reports Series, No. 29)

This laboratory manual represents a joint undertaking by IAEA and FAO. The present manual consists of two parts: a basic part which contains lectures and laboratory exercises on the properties and use of radioisotopes and radiation and a second part containing a series of detailed lectures and laboratory exercises on the application of radioisotopes and radiation in the field of soil-plant relationships.

In English.

(166 pp., 16×24 cm, paper-bound, 37 figures, 10 tables)
(1964) US $3.50; £1.1.0 stg.

IAEA SALES AGENTS

Orders for Agency publications can be placed with your bookseller or any of our sales agents listed below:

ARGENTINA
Comisión Nacional de
Energía Atómica
Avenida del Libertador
General San Martin 8250
Buenos Aires - Suc. 29

AUSTRALIA
Hunter Publications,
23 McKillop Street
Melbourne, C.1

AUSTRIA
Georg Fromme & Co.
Spengergasse 39
Vienna V

BELGIUM
Office international de librairie
30, avenue Marnix
Brussels 5

BRAZIL
Livraria Kosmos Editora
Rua do Rosario, 135-137
Rio de Janeiro

Agencia Expoente Oscar M. Silva
Rua Xavier de Toledo, 140-1° Andar
(Caixa Postal No. 5.614)
São Paulo

BYELORUSSIAN SOVIET SOCIALIST REPUBLIC
See under USSR

CANADA
The Queen's Printer
Ottawa, Ontario

CHINA (Taiwan)
Books and Scientific Supplies
Service, Ltd.,
P.O. Box 83
Taipei

CZECHOSLOVAK SOCIALIST REPUBLIC
S.N.T.L.
Spolena 51
Nové Město
Prague 1

DENMARK
Ejnar Munksgaard Ltd.
6 Nörregade
Copenhagen K

FINLAND
Akateeminen Kirjakauppa
Keskuskatu 2
Helsinki

FRANCE
Office international de
documentation et librairie
48, rue Gay-Lussac
Paris 5^{e}

GERMANY, Federal Republic of
R. Oldenbourg
Rosenheimer Strasse 145
8 Munich 8

HUNGARY
Kultura
Hungarian Trading Co. for Books
and Newspapers
P.O.B. 149
Budapest 62

ISRAEL
Heiliger and Co.
3 Nathan Strauss Street
Jerusalem

ITALY
Agenzia Editoriale Internazionale
Organizzazioni Universali (A.E.I.O.U.)
Via Meravigli 16
Milan

JAPAN
Maruzen Company Ltd.
6, Tori Nichome
Nihonbashi
(P.O. Box 605)
Tokyo Central

MEXICO
Libraría Internacional
Av. Sonora 206
Mexico 11, D.F.

NETHERLANDS
N.V. Martinus Nijhoff
Lange Voorhout 9
The Hague

NEW ZEALAND
Whitcombe & Tombs, Ltd.
G.P.O. Box 1894
Wellington, C.1

NORWAY
Johan Grundt Tanum
Karl Johans gate 43
Oslo

PAKISTAN
Karachi Education Society
Haroon Chambers
South Napier Road
(P.O. Box No. 4866)
Karachi 2

POLAND
Ośrodek Rozpowszechniana
Wydawnictw Naukowych
Polska Akademia Nauk
Pałac Kultury i Nauki
Warsaw

ROMANIA
Cartimex
Rue A. Briand 14-18
Bucarest

SOUTH AFRICA
Van Schaik's Bookstore (Pty) Ltd.
Libri Building
Church Street
(P.O. Box 724)
Pretoria

SPAIN
Libraría Bosch
Ronda de la Universidad 11
Barcelona

SWEDEN
C.E. Fritzes Kungl. Hovbokhandel
Fredsgatan 2
Stockholm 16

SWITZERLAND
Librairie Payot
Rue Grenus 6
1211 Geneva 11

TURKEY
Librairie Hachette
469, Istiklâl Caddesi
Beyoğlu, Istanbul

UKRAINIAN SOVIET SOCIALIST REPUBLIC
See under USSR

UNION OF SOVIET SOCIALIST REPUBLICS
Mezhdunarodnaya Kniga
Smolenskaya-Sennaya 32-34
Moscow G-200

UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
Her Majesty's Stationery Office
P.O. Box 569
London, S.E.1

UNITED STATES OF AMERICA
National Agency for
International Publications, Inc.
317 East 34th Street
New York, N.Y. 10016

VENEZUELA
Sr. Braulio Gabriel Chacares
Gobernador a Candilito 37
Santa Rosalía
(Apartado Postal 8092)
Caracas D.F.

YUGOSLAVIA
Jugoslovenska Knjiga
Terazije 27
Belgrade

IAEA publications can also be purchased retail at the United Nations Bookshop at United Nations Headquarters, New York, at the news-stand at the Agency's Headquarters, Vienna, and at most conferences, symposia and seminars organized by the Agency.

In order to facilitate the distribution of its publications, the Agency is prepared to accept payment in UNESCO coupons or in local currencies.

Orders and inquiries from countries where sales agents have not yet been appointed may be sent to:

Distribution and Sales Group, International Atomic Energy Agency,
Kärntner Ring 11, Vienna I, Austria

INTERNATIONAL
ATOMIC ENERGY AGENCY
VIENNA, 1965
PRICE: USA and Canada: US $3.50
Austria and elsewhere: S 73,50
(£1.1.0; F.Fr.14,-; DM 12,25)