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(Soil Fertility and Plant Nutrition)

DUBLIN, JULY, 1952

TRANSACTIONS

VOLUME I

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Section A

SESSIONS 1 TO 6

SESSION 1

CARBON AND NITROGEN IN SOILS

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Soil organic matter is of edaphic importance in at least three ways. By its slow breakdown it provides mineral nitrogen for nutrition of the plant, it acts as a base exchange material, and it helps to cement the small soil particles into crumbs, thereby conferring "structure" and water holding capacity on the soil. Tests carried out in the laboratory to assess the carbon and nitrogen status of a soil in relation to fertility are therefore fundamentally meant to assess the activity of the soil organic matter in one or more of its edaphically important roles. These tests are of two kinds (*a*) those designed to measure the total carbon or total nitrogen (which may or may not be subdivided into organic nitrogen and mineralized nitrogen) in the soil, (*b*) those designed to measure biologically or otherwise the activity of the carbon or the availability of the nitrogen. Let us first consider those of type (*a*).

Chemical assessment of total carbon in soils

Of the numerous methods available for the estimation of the total amount of carbon in a soil sample, possibly the most widely used is the Walkley-Black method in which the amount of dichromate reduced by the organic moiety of the soil under standardized conditions is measured. This test is not one capable of giving absolute values for soil carbon because the amount of dichromate reduced by a given sample must necessarily depend on the state of oxidation of carbon in the sample. In practice, however, it works fairly satisfactorily (PEECH, 1948). On the other hand, the wet combustion method of HARDY (1929) in which the CO_2 evolved from dichromate oxidation of soil is measured is, in the writer's experience, as simple and rapid as the Walkley-Black procedure and is rather less open to theoretical criticisms of its accuracy. Possibly the best method for the measurement of total carbon in soils is, however, the Van Slyke manometric procedure which has been used by BREMNER (1949). Once the apparatus has been set up and the appropriate solutions made, estimates of soil carbon accurate to within 1% of the carbon present can be carried out at the rate of about four per hour. Moreover the same apparatus can be used to measure specific fractions of the soil organic matter, e.g. uronic acids (TRACEY, 1948). The main disadvantage of the Van Slyke method lies in the fact that the maximum amount of carbon permissible in the sample is 15 mgms. On highly organic soils replication between samples therefore becomes rather difficult.

Chemical assessment of total nitrogen in soils

Here the Kjeldahl incineration is pre-eminent and is probably completely satisfactory in most cases although the selection of a suitable catalyst (PRINCE, 1945; PATEL and SCREENIVASAN, 1948) may be of some importance. In analyses of the lower strata of soils, where nitrate-nitrogen may contribute significantly to the total

nitrogen present, the Kjeldahl determination of total nitrogen may be in error unless the nitrate is first reduced by, e.g. Fe or Zn. In such cases the nitrogen determination of EMMERT (1945) might well repay investigation, since in this procedure all the nitrogen is oxidized to nitrate and estimated as such.

The assessment of the activity of carbon in soils

The word "activity" in this subheading is meant to indicate the edaphic usefulness of soil carbon as opposed to its total amount. The concept is necessarily somewhat vague, but as an example we may take a soil to which (say) wood shavings had been added as a mulch. The total carbon in the soil would be high, but its soil organic matter status (as normally understood) would be low. The most common method for assessing the activity of the carbon in soil is the measurement either of the CO_2 output of the soil or (since the R.Q. of soils is usually necessarily about 1·0) its O_2 uptake. RUSSELL (1905), NELLER (1920), WAKSMAN and STARKEY (1924), MARSH (1928), LUNDEGARDH (1927), HUMFELD (1930), ROMELL (1932), have all made such measurements either in the field or in the laboratory. These measurements are of course an indication of the rate at which soil organic matter is breaking down and are thus, indirectly, an indication of the rate of nitrogen mineralization. Parenthetically, it is interesting that the great bulk of all the results obtained indicate that the QCO_2 (cu.mm. CO_2/g.soil/hr.) for most soils is between 1 and 10^{-1}. There is general agreement that the CO_2 output or O_2 uptake of a soil is correlated with soil fertility; this is probably due to the nitrogen mineralization already mentioned. JENSEN (1936, 1939) has made most detailed correlations between bacterial activity, mineralization of nitrogen, and CO_2 production. However, although laboratory tests have been carried out which showed good correlation between CO_2 production and fertility, these tests may sometimes be misleading. LEES (1949) and LEES and PORTEOUS (1950) working in Trinidad with an infertile clay and a rich loam of similar organic matter content found that the O_2 uptake and CO_2 output of the former soil were, when measured in the laboratory, considerably in excess of corresponding figures for the latter. This discrepancy was due mainly to the fact that in the field the infertile clay was badly aerated and, as a consequence, tolerably labile organic compounds had accumulated in it, these compounds being easily oxidized under the high aeration used in the laboratory. The fertile loam, on the other hand, being well aerated in the field had not accumulated such compounds. A method for assessing the activity of the organic matter in a soil, which the writer should like to suggest is worthy of further consideration, is one based on the fact that soil organic matter forms chelate complexes with trace elements such as copper (BREMNER, MANN, HEINTZE and LEES, 1946), and measurements of the amount of copper taken up by a soil in the presence of sufficient monovalent cation to saturate the base exchange complex of the soil gave results (LEES, 1948, 1950) that suggested that this method was indeed an easy and rapid method of assessing the organic matter status of a soil. Since one of the functions of soil organic matter in a soil is to provide a reserve of trace elements, the results given by the method may have some real biochemical significance.

The assessment of the activity of nitrogen in soils

These methods are, in general, tests of the ability of the soil to produce ammonia and/or nitrate from nitrogenous compounds present in it. The soil percolation technique (LEES and QUASTEL, 1946) has been found to give highly reproducible results for the nitrifying power of soils in such tests (MARTIN, 1949; CHASE, 1948). Unfortunately, despite their reproducibility, it seems likely that results obtained by the percolation technique do not bear any necessary relation to the nitrifying power of the soil in the field since the mere preparation of the soil for percolation and the technique of percolation itself are both intended to produce maximal nitrification; conditions in the field which might be expected to reduce nitrification (e.g. poor aeration) are therefore automatically masked. On theoretical grounds at any rate the ideal laboratory method for assessing the nitrifying capacity of a soil would be based on measurements of nitrate produced in deep core samples brought into the laboratory and left undisturbed at a constant temperature. The question arises, however, whether measurements of the nitrifying power of the soil are of primary importance in the assessment of the activity of the soil nitrogen. While the nitrifying power of the soil is often well correlated with the fertility of the soil, since the nitrifying organisms function best under those environmental conditions optimal for most plants, it should not be forgotten that nitrification is always subsequent to the primary process of ammonification. The writer feels that in most cases the activity of the soil nitrogen is best measured by the ammonifying capacity rather than by the nitrifying capacity of the soil. Measurements of ammonifying capacity are often complicated by subsequent nitrification of the ammonia produced, but it is sometimes possible to simplify the procedure by the addition of sodium azide to the soil. Sodium azide at a concentration of about M/1000 completely inhibits nitrification but does not influence ammonification (LEES and PORTEOUS, 1950), and therefore in azide treated soils ammonification can be measured directly. DR. E. A. FITZPATRICK of the Soil Science Department of Aberdeen University has had some success with this method.

In conclusion, the writer wishes to stress that this survey is not meant to be exhaustive, but is meant primarily to stimulate discussion as to how far it is possible, in the laboratory, to assess the carbon and nitrogen status of soils.

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ESTIMATION DE LA RICHESSE DES SOLS EN AZOTE ET ASPECTS PARTICULIERS DE CE PROBLEME DANS LA REGION MEDITERRANEENNE

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Introduction

L'estimation de l'aptitude d'un sol à fournir de l'azote minéral aux cultures est un des problèmes les plus complexes de la Science du Sol.

Il ne peut être traité que d'une manière fragmentaire. Nous n'envisagerons ici que l'utilisation des méthodes *directes* s'appuyant sur des analyses chimiques ou biologiques d'un échantillon de sol. Nous n'examinerons donc pas les méthodes indirectes basées sur la réponse des cultures aux fumures azotées sur un sol et dans une rotation déterminée.

Les méthodes directes sont essentiellement les suivantes :

1/ *Dosage de l'Azote Total* (KJELDAHL)

Cette méthode la plus anciennement utilisée ne donne qu'une estimation du stock d'azote, dans lequel l'azote organique représente souvent plus de 99 pour cent.

Ellé présente surtout un intérêt pédologique, en particulier lorsqu'elle est liée à la détermination du carbone total. Son utilisation pour l'étude de la dégradation des sols depuis la défriche est liée à une parfaite connaissance des roches mères. En effet les roches mères calcaires renferment des quantités importantes d'azote total difficilement utilisable.

Il en résulte que dans la région méditerranéenne les sols calcaires les plus dégradés conservent des teneurs en azote assez importantes 0,7 ou 0,8 pour mille avec un rapport C/N faible, parfois inférieur à 7, alors que les sols non calcaires, sur sables en particulier, ont un taux d'azote qui peut s'abaisser jusqu'à 0,2 pour mille avec un rapport C/N moyen de l'ordre de 11.

La valeur agronomique de cette méthode est actuellement considérée comme nulle sauf lorsque l'on étudie un type de sol déterminé, artificiellement enrichi en azote organique.

2/ *Dosage de l'Azote Minéral*

(*a*) *Azote nitrique.* Le dosage de l'azote nitrique a été largement utilisé et figure encore parmi les tests rapides. La variabilité dans le temps et dans l'espace de la teneur en nitrates des sols nus, la faible teneur en nitrates des sols cultivés lui enlèvent beaucoup de son intérêt.

(*b*) *Azote ammoniacal.* La détermination de la teneur des sols en azote ammoniacal est relativement récente. Elle a été subordonnée au développement de nos connaissances sur les échanges de cations. On sait maintenant que la teneur en azote ammoniacal peut être élevée dans les sols acides et riches en matières organiques, au cours de

l'hiver, et dans les sols soumis à des températures élevées. La possibilité de fixation de l'azote ammoniacal sous forme non échangeable doit également être considérée.

(c) *Azote minéral.* Le dosage de l'azote minéral (total azote ammoniacal + azote nitrique) présente certains avantages malgré l'ampleur des variations de cette somme dans l'espace et dans le temps.

Effectué sur l'extrait au chlorure de calcium au moyen de l'alliage de Devarda et de magnésie calcinée, il permet en outre de tenir compte des nitrites qui peuvent être présents en quantités non négligeables dans les sols calcaires (4—9). L'extrait au chlorure de calcium peut renfermer également des fractions azotées labiles susceptibles de libérer de l'azote minéral au cours de la distillation.

L'utilisation agronomique de cette détermination est subordonnée comme nous le verrons plus loin, non seulement aux conditions d'échantillonnage, mais encore à la connaissance du métabolisme de l'azote au cours de l'année, suivant la région.

3/ *Essais à l'Etuve*

De nombreux auteurs ont cherché à déterminer la quantité d'azote minéralisé pendant une période d'incubation variable dans des conditions d'humidité et de température favorables à l'activité microbienne. On détermine tout d'abord l'azote minéral présent dans l'échantillon de terre. Après incubation dans des conditions bien définies, on effectue un deuxième dosage d'azote minéral. La différence entre les deux résultats donne l'azote " minéralisable."

Cette technique a donné d'excellents résultats à BLACK, NELSON et PRITCHETT en 1946 et 1947 (10) pour des prélèvements effectués en Mars dans l'Iowa avec une durée d'incubation de 3 semaines. Ces auteurs ont indiqué que la réponse aux engrais azotés de champs de blé ou d'avoine était en raison inverse de la teneur en azote minéralisable.

HARMSEN (7) a présenté une étude critique des essais d'incubation en indiquant notamment que la quantité d'azote libérée à l'étuve pouvait varier suivant la teneur en azote minéral à l'origine. Cet auteur suggère que les essais d'incubation ne soient faits que sur des échantillons privés d'azote minéral. Cette objection s'ajoute à celles qui sont faites le plus souvent à cette technique ; variations de la structure au cours de l'échantillonnage, effet du séchage, humidité optimum, choix d'une durée d'incubation, comportement particulier des sols acides en présence ou en l'absence de carbonate de chaux.

Les essais d'incubation peuvent être envisagés sous une autre forme. GERRETSEN (6) a suggéré en 1950, la mesure du dégagement de CO_2 après apport de glucose. La décomposition de la matière organique assimilable et dépourvue d'azote qui a été ajoutée doit être fonction de l'azote disponsible. La valeur agronomique de cette méthode n'est pas connue.

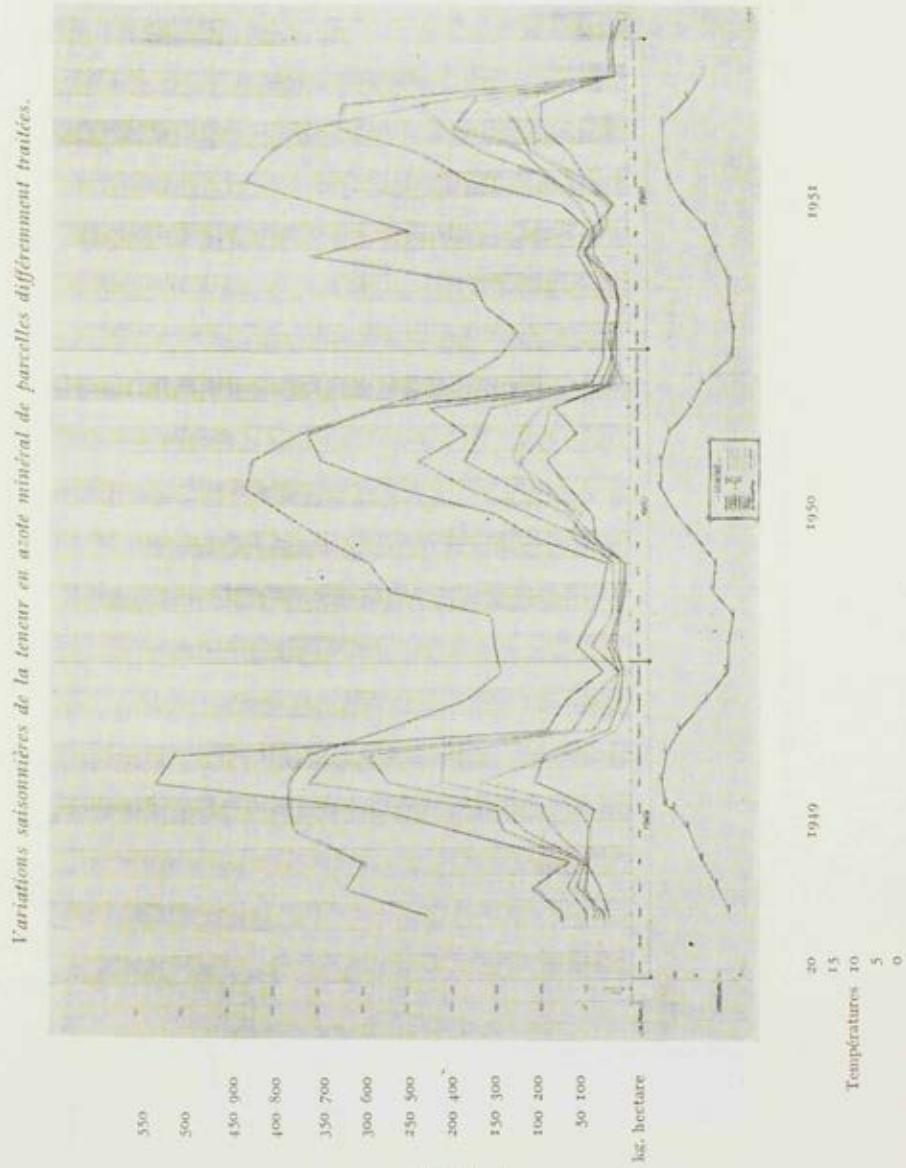
Les techniques biologiques d'évaluation de la fraction assimilable du stock d'azote paraissent supérieures aux techniques chimiques utilisant l'hydrolyse ménagée de la matière organique (autoclave ou traitements acides). La durée des essais d'incubation paraissant un obstacle majeur à leur utilisation pratique, la valeur du concept " azote minéralisable " et de son emploi n'a pas été assez discutée

jusqu'à ce jour, et nous devons reconnaître que nous manquons de travaux de base dans différentes régions du monde.

Nous ne pouvons que présenter certains aspects de cette question dans les sols calcaires sous le climat méditerranéen.

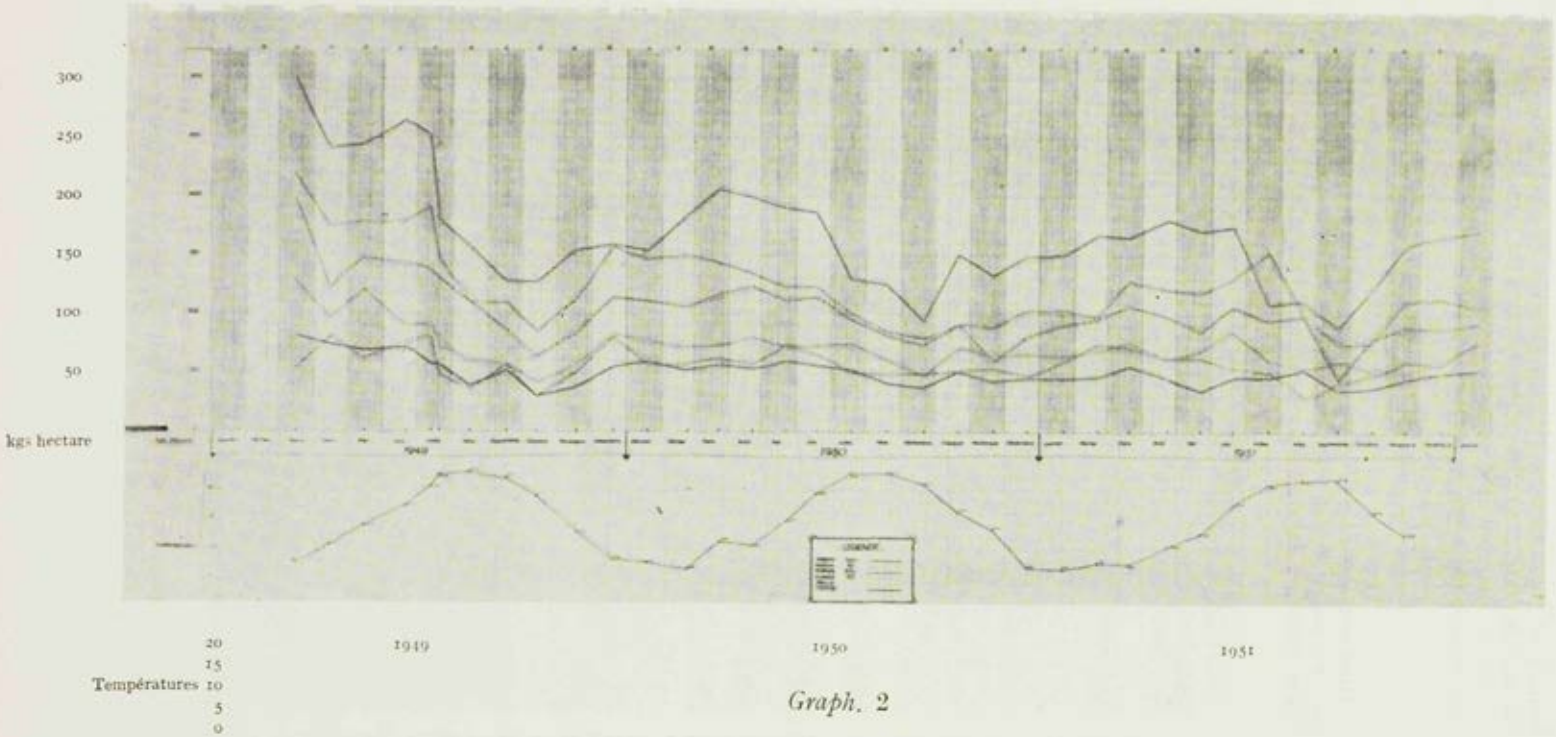
Variations de l'Azote Minéral et de l'Azote Minéralisable au Cours de l'Année

Ainsi que l'avait déjà noté YANKOWITCH (11), nous avons constaté que le climat méditerranéen exagère les variations saisonnières de l'azote minéral dans les sols nus (graphique n°1).



Graph. 1

Variations saisonnières de l'azote minéralisable de parcelles différemment traitées.



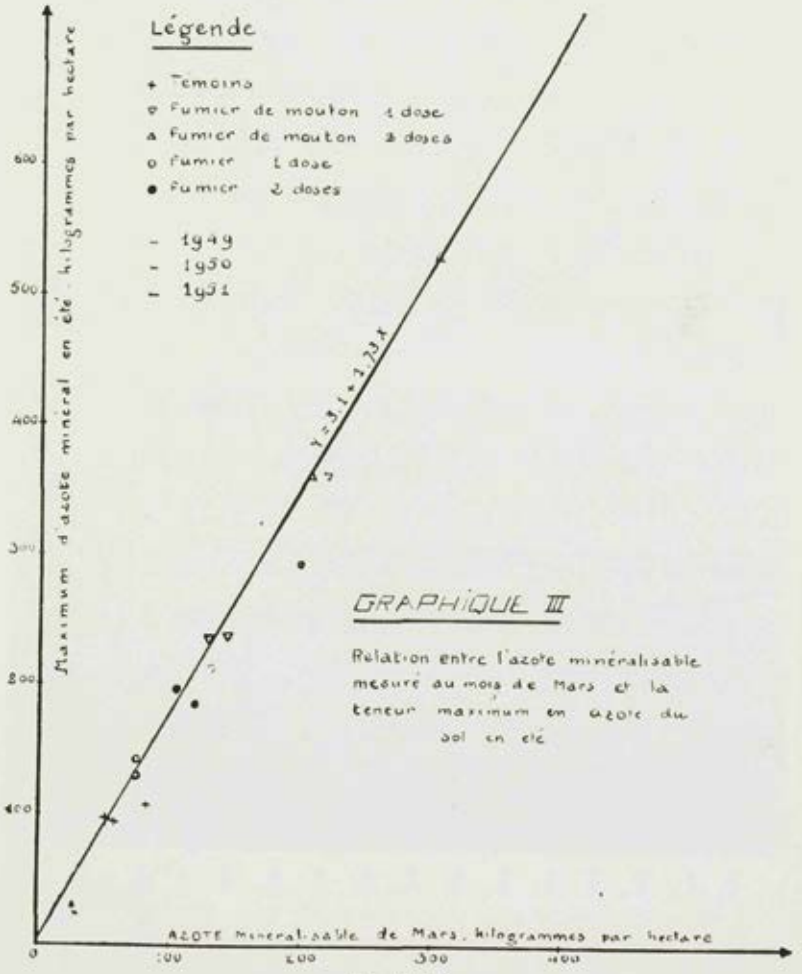
Graph. 2

Pendant l'automne et l'hiver la teneur en azote minéral reste très faible même dans les sols enrichis en azote organique. Les maxima d'été sont élevés et variables suivant les fumures.

Lorsque l'on effectue la détermination de " l'azote minéralisable " sur des échantillons prélevés mensuellement (voir technique dans 5), on constate également de fortes variations au cours de l'année. Les maxima se situent à la fin de l'hiver. Les minima en Octobre ou Novembre, après les pluies d'automne (graphique n°2).

La date de prélèvement n'est donc pas indifférente, et il parait avantageux d'effectuer dans la pratique ces déterminations en Février ou Mars. A cette date l'azote minéral se trouve d'ailleurs être très faible et n'est donc pas susceptible d'influer sur le résultat de l'essai à l'étuve.

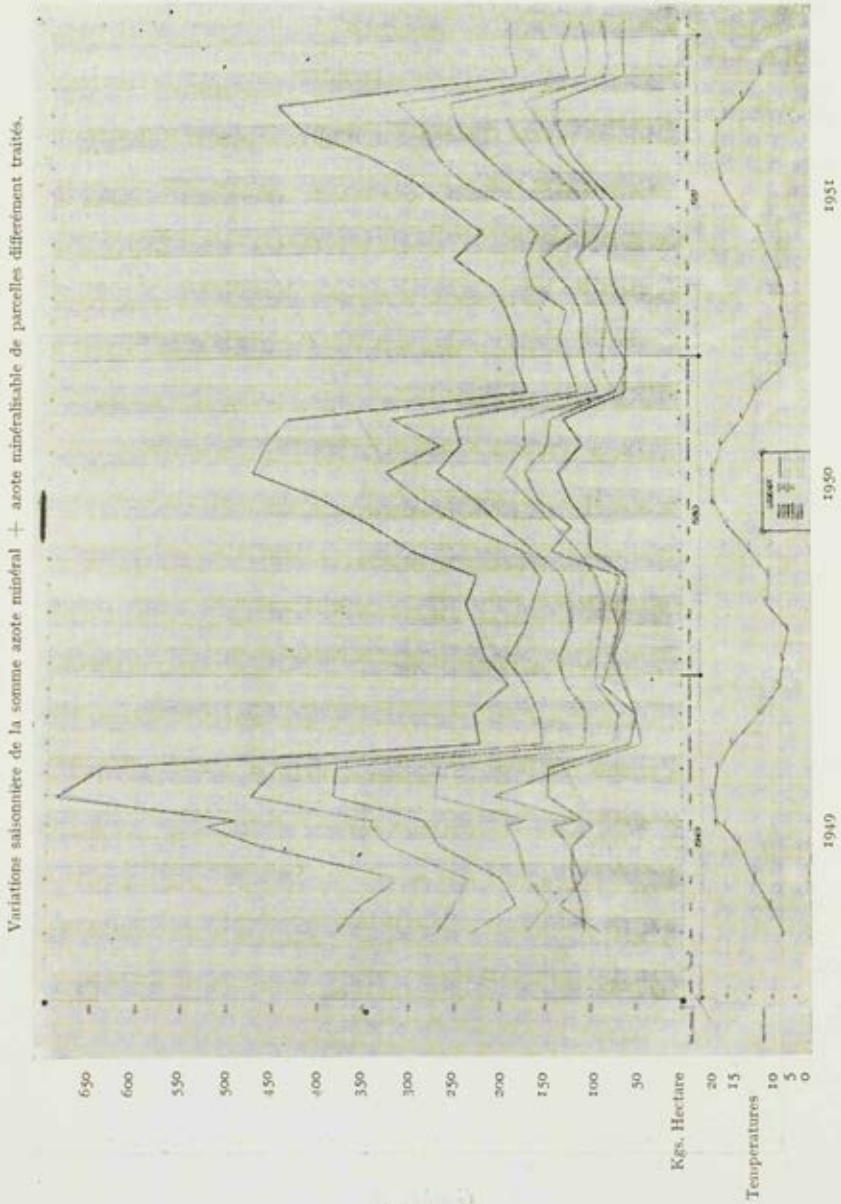
On peut également moter sur ces graphiques l'influence des traitements. Nous avons vu par ailleurs que la mesure de l'azote minéralis-



Graph. 3

able donnait une évaluation du même ordre que les autres techniques pour les arrière actions des légumineuses.

Dans nos observations effectuées sur des parcelles d'expériences de longue durée plus ou moins enrichies en azote organique, nous avons constaté une corrélation hautement significative entre l'azote minéralisable de parcelles diversement enrichies mesuré au début du printemps (Mars) et leur teneur maximum d'azote minéral en été (graphique n°3).



Graph. 4

Le total azote minéral + azote minéralisable qui pourrait être retenu comme la meilleure indication de l'aptitude d'un sol à fournir de l'azote aux cultures, est susceptible de variations également considérables au cours de l'année (graphique n°4).

Nous n'examinerons pas ici les raisons de ces variations liées, en l'absence de racines, à la fois au lessivage et aux variations de la libération et de l'utilisation de l' azote par la flore microbienne.

Nous voulons simplement souligner qu'il est indispensable de les connaître dans une région déterminée avant de songer à utiliser, en agriculture, les résultats des dosages d azote minéral et d'azote minéralisable.

Ces données fondamentales permettent également de connaître les périodes critiques en ce qui concerne la fourniture d'azote. Ainsi dans la région méditerranéenne, si l'humidité est suffisante, les blés à



Graph. 5

grands rendements présentent des besoins en azote minéral dans tous les sols pendant la période Décembre-Mars. La fourniture d'azote du sol sera beaucoup mieux liée aux résultats d'essais à l'étuve pendant la période d'été quand les besoins en eau sont satisfaits.

On peut critiquer cette méthode d'observation en sols nus, l'activité microbienne pouvant être très différente en présence des rhizosphères (2). Signalons simplement que les résultats qu'elle fournit peuvent être aisément contrôlés par des dosages de nitrates de la sève brute dans les tiges des plantes cultivées.

Libération d'Azote Minéral avec des Incubations de Durées Croissantes

La fixation arbitraire de la durée d'incubation à 3 ou 4 semaines pourrait être reconsidérée. Il est assez intéressant d'observer les courbes obtenues sur des sols différents et sur des sols ayant subi divers traitements (rotation, fumures organiques).

HARMSEN (7) et BARBIER (1) ont publié des courbes de ce genre.

Voici un exemple de ce que l'on peut observer dans un sol calcaire (graphique n°5).

Les courbes que nous obtenons sont bien différentes de celles qui ont été obtenues pour d'autres régions. Il est probable qu'une documentation plus complète sur cette question serait souhaitable et permettrait d'améliorer la technique des essais d'incubation dans une région déterminée.

Conclusion

La détermination de l'azote minéral et de l'azote minéralisable dans les sols parait intéressante et mériterait d'importants développements. Il est toutefois important de disposer au minimum pour une région déterminée de connaissances fondamentales comme celles que nous avons présentées. Ces connaissances permettraient de limiter les discordances entre les déterminations de laboratoire et les réponses à l'azote. Compte tenu des rythmes de besoins des récoltes, elles permettraient également une meilleure critique des expériences de fumures azotées minérales.

SUMMARY

With reference to the mediterranean Region (South-East of France) the basic data needed for a good utilization of results of N mineral and N mineralizable have been discussed in order to evaluate the ability of soils to supply nitrogen.

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METHODS FOR ASSESSING THE ORGANIC MATTER STATUS OF SOILS

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Introduction

Broadly speaking two lines of approach have been followed for assessing the organic matter status of soils. On the one hand the total organic matter may be estimated from the content of organic carbon determined by a direct or indirect method. On the other hand; since the organic matter of the soil is commonly divided arbitrarily into the humified material and the non-humified residues, the former fraction which possesses marked colloidal properties may be estimated separately. Where the primary interest lies in the effect of organic matter on such physical properties of the soil as structure and water retention, determination of the humus fraction may prove the more useful of the two but, where the major consideration is with organic matter in relation to the nutrient status of the soil, especially nitrogen, the determination of total organic carbon has assumed widespread importance for routine analysis.

Determination of the Humus Fraction

Numerous methods for the determination of the humus fraction have been described and the principal ones may be grouped as follows:

(i) extraction with alkalies such as ammonium hydroxide, sodium carbonate and sodium hydroxide solutions;

(ii) extraction with neutral salts such as sodium fluoride, oxalate or pyrophosphate which form complexes with polyvalent metal cations;

(iii) oxidation of humus compounds with hydrogen peroxide or solutions of permanganate or hypochlorite;

(iv) acetylation of non-humified fraction with acetyl bromide.

WAKSMAN in his book on Humus has given a critical review of such methods used prior to 1938 from which it may be seen that the first group involving alkaline extractions of the humus has been most widely employed. In this present account only this group will be considered in detail.

From the time of SPRENGEL (1826) it has been appreciated that extraction of humus by alkalies is enhanced when the soil is given a preliminary treatment with dilute mineral acid to remove base metal cations. The second group of extractions is employed with the object of avoiding this acid treatment. GRANDEAU (1877) used pre-treatment with acid and then extracted the humus with ammonium hydroxide solution. The filtrate was evaporated to dryness to obtain the *matière noire* and then determined from the loss in weight on ignition. HUSTON and MCBRIDE (1893), in America, modified GRANDEAU'S method and improved the conditions for extraction so that, for a while, it was adopted as an official method by the

Association of Official Agricultural Chemists. However, the extraction of humus by a single treatment with dilute ammonium hydroxide solution at room temperature is by no means complete and its use declined. Stronger alkalies, principally solutions of sodium carbonate and hydroxide were employed instead but again the proportion of the total organic matter extracted depended so much on the experimental conditions, ranging from as low as 15 per cent. for cold sodium carbonate to as high as 70% for 0·5N sodium hydroxide at 100°C.

Instead of tedious gravimetric determination of the dissolved humus, colorimetric methods were applied to the extracts to cope with the large numbers of soil samples involved in extensive field studies of soil fertility. It is interesting to note that LOUGHRIDGE, in an appendix to HILGARD'S book on Soils published in 1906, described short approximate methods of soil examination used at the California Experiment Station. These may be regarded as the first rapid soil testing methods and included the following procedure for humus :— 7g. of dry soil passing a 0·5 mm. sieve were boiled for 10 to 15 seconds with 15 to 20 ml. of a 10% solution of potassium hydroxide. After allowing the tube to stand, the colour of the supernatant liquid was observed to vary from light brown to black according to the supply of organic matter in the soil.

In 1912 BEAM published a method evolved in Khartoum as an alternative to ammonia extraction whereby the acid-leached soil was boiled with a 5% solution of sodium carbonate for 10 minutes. After dilution to a standard volume the soil suspension was allowed to stand overnight for clearing, or centrifuged, before matching with an extract prepared from a soil of known humus content. The following year the procedure was modified by direct extraction of the soil without preliminary treatment with acid. A method similar to BEAM'S first one was used in Germany by SPRINGER (1934) with permanent colour standards prepared from ferric chloride solution for matching.

Hot extraction with sodium hydroxide solution was adopted by ODÉN (1921) using MERCK'S acidum huminicum as a convenient standard for colour comparison. EDEN (1924) also described a method for the examination of mineral soils in which 5g. of soil was first leached with dilute hydrochloric acid on a GOOCH crucible and then extracted in a flask with 100 ml. of a 10% solution of sodium hydroxide by immersion in a boiling water bath for 15 minutes. A portion of the extract was filtered on a hardened filter paper in a BUCHNER funnel and an aliquot of the filtrate suitably diluted for visual matching against a standard in a colorimeter. An adaption of this method used in Australia with centrifuging instead of filtration was included by PIPER (1942) in his book on Soil and Plant Analysis.

ARNOLD and PAGE (1930), in their studies on the extraction of organic matter by alkali, found the ratio of colour tint to the content of organic carbon in the extract was by no means constant with different samples. Furthermore the colour of extracts, especially those prepared with hot alkali solutions, was unstable and thus it seems the value of such colorimetric methods for quantitative determinations is rather doubtful. SHOREY (1930) offered the following criticisms or such procedures :—

(*a*) it is impossible to prepare a colour standard representing a definite quantity of organic matter;
(*b*) colourless organic compounds which are present in soil organic matter are overlooked;
(*c*) the humus content of extracts is a variable fraction of the total organic matter;
(*d*) the colour of the extract varies with the soil and with the experimental conditions of extraction.

Determination of Total Organic Matter

(*i*) *Loss on ignition*

For a long while the loss in weight on ignition of an oven-dry sample has been used as a criterion of the organic matter content of soils. However, WARINGTON and PEAKE (1880) compared this method with the direct determination of organic carbon and concluded that the loss on ignition was quite unreliable for some soils. It is obvious that hydrated silicate minerals lose carbon dioxide during ignition and also calcareous soils lose carbon dioxide so that, except for sandy soils the loss on ignition may easily be two or three times the actual organic matter. Nevertheless, in spite of this, the loss on ignition has continued in use to the present time in some advisory laboratories as, for instance, at the soil testing laboratories in the Netherlands, but here, according to DECHERING (1950), a correction is made for the water and carbon dioxide from the determinations of clay and calcium carbonate respectively. RATHER (1918) introduced a very tedious method for removing the carbonate and silicate from soils by repeated treatment with dilute hydrofluoric acid prior to determining the loss on ignition, but this is much too cumbersome for ordinary use.

(*ii*) *Determination of total organic carbon by dry combustion*

From the time of LIEBIG the standard method has been that of the organic chemist in which the soil sample is burnt in a stream of air or oxygen and the carbon dioxide determined after absorption in a convenient train of apparatus. This may be regarded as the standard against which all other methods are compared. SPRENGEL reported that soil humus contains 58% of carbon and later SCHULZE (1849) obtained a similar value, from which it was suggested by WOLFF (1864) that the organic matter content of soils should be obtained by multiplying the carbon value by the factor 1·724. This has been widely used until the present time, in spite of quite wide variations which have been shown to occur in different soils, as WAKSMAN has emphasized.

It should be borne in mind when the dry combustion method is used on soils containing carbonate that this must either be carefully removed beforehand or determined separately and a correction made. Further, many soils contain elemental carbon as fragments of coal or charcoal and this will be returned as organic matter in the ordinary way, thus giving a false impression of the organic matter status of the soil.

(*iii*) *Determination of organic carbon by wet oxidation*

Two alternatives to dry combustion have been used quite extensively—oxidation with alkaline permanganate and with solutions of

dichromate in sulphuric acid. WARINGTON and PEAKE at Rothamsted made a careful comparison of these two methods with dry combustion and obtained average recoveries of carbon dioxide of 92% and 80% respectively for the permanganate and dichromate mixtures. The former have never proved so popular as the latter and numerous techniques have been devised for improving the oxidation with dichromate and the determination of the carbon dioxide evolved, by gravimetric and by titrimetric procedures. It is not the purpose of the present paper to review these in detail but mention should be made of a micro method recently described by BREMNER (1949). He employed the VAN SLYKE-NEIL manometric apparatus in conjunction with wet oxidation using the VAN SLYKE-FOLCH mixture of chromic, iodic, phosphoric and sulphuric acids. Very good agreement with the dry combustion method was obtained on nine different soils.

(*iv*) *Indirect determination of organic carbon from reduction*

ROBINSON, MCLEAN and WILLIAMS (1929) combined the determination of carbon with the estimation of nitrogen by the Kjeldahl digestion process. As the carbon is oxidized, sulphur dioxide is produced from the sulphuric acid and the gases issuing from the digestion flask are conducted through an absorption train containing standard iodine solution, the excess being titrated with standard thiosulphate solution. It was found that an average of 89·6% of the carbon was accounted for compared with dry combustion. However, this method does not appear to have been greatly used except at Bangor.

Over a century ago SCHULZE is reported to have determined carbon by titrating the excess permanganate remaining after alkaline digestion and this principle has been followed in a number of methods which have been used, principally in India and Japan. Thus PURI and SARUP (1937) boiled a 1 or 2 g. sample of soil with an excess of a normal solution of potassium permanganate in 0·05 N sodium hydroxide. After dilution to a standard volume an aliquot of the digest was treated with sulphuric and oxalic acids and the titration completed with permanganate. NOSTITZ (1936) used an acid permanganate solution, but in either case the procedure is prone to errors due to chemical side reactions with soil constituents, and titration methods with permanganate have not become popular.

In 1927 SCHOLLENBERGER, in Ohio, proposed a method for the short digestion of soil samples with a hot solution of potassium dichromate in concentrated sulphuric acid and then, after cooling and dilution with water the residual dichromate was titrated directly with a standard solution of ferrous ammonium sulphate. The mean recovery of carbon was reported to be about 90%. This simple procedure proved very attractive and formed the basis of nearly all the rapid methods for the determination of organic carbon in soils that are used very extensively at the present time. These will be discussed in some detail.

(*v*) *Rapid determination by oxidation with dichromate mixtures*

In SCHOLLENBERGER'S original method a small sample of finely powdered soil, usually 0·5 g. or less, was taken in an 8″ × 1″ Pyrex tube and treated with 10 ml. of a saturated solution of potassium

dichromate in concentrated sulphuric acid. The mixture was heated over a naked flame and stirred with a thermometer until the temperature reached 175° C, cooled in air and then diluted with water prior to titration with ferrous ammonium sulphate solution, using diphenylamine as indicator. Subsequently the method was revised in 1931 and again in 1945. According to the latest modification a weighed amount of pure potassium dichromate was mixed with the soil before adding sulphuric acid to the tube. Heating was done by immersion in a hot bath of sulphuric acid at 210°C so that the temperature of the reaction mixture was raised to 175°C in 1·5 to 2 minutes.

Sodium fluoride was added to the mixture after dilution in order to improve the end point of the titration by complexing ferric ions. SCHOLLENBERGER appreciated that soluble chloride in the soil causes inaccuracy through reaction with the dichromate to give volatile chromyl chloride and recommended that saline soils be given a preliminary leaching with water on a Shimer filter.

Weighing a separate quantity of dichromate for each determination is more tedious than a volume measurement and for this reason ALLISON (1935) in a careful examination of SCHOLLENBERGER'S method suggested the use of an aqueous solution containing 19·61 g. per litre of potassium dichromate, 10 ml. of which was pipetted into each tube and left to dry overnight in an oven at 80-85°C. He also suggested aqueous solutions of barium diphenylamine sulphonate or o-phenanthroline as alternative indicators. HESTER, BLUME and SHELTON (1937) of the Virginia Truck Experiment Station employed what is essentially SCHOLLENBERGER'S method for the routine determination of organic matter in their system of rapid chemical soil tests. Phosphoric acid was used in place of sodium fluoride for complexing ferric iron during titration.

The Russian worker, DEGTJAREFF (1930), developed two methods from SCHOLLENBERGER'S original idea. In one, a smaller quantity of soil, 0·2 g. instead of 0·5 g., was heated with 10 ml. of a solution of chromium trioxide in sulphuric acid by immersion in a hot bath of sulphuric acid at 165°C for 10 minutes. The chromic acid solution contained 16 g. of CrO_3 per litre and was "seasoned" by previous heating at this temperature for 0·5 hour after which no change in strength was supposed to occur. In the other modification the soil was treated first with 10 ml. of a 0·3% solution of hydrogen peroxide containing sulphuric acid. On adding 10 ml. of the above chromic acid solution considerable heat of reaction with the water developed and the mixture was shaken for 1 minute for the oxidation to proceed. After cooling and diluting with water the residual chromic acid was titrated and a correction made for the blank value without soil.

WALKLEY and BLACK (1934) showed that the inclusion of hydrogen peroxide to increase oxidation was entirely spurious and led to serious errors, but they retained the principle of using the heat of reaction for their own method. An 0·5 g. or 1 g. sample of soil is first treated with 10 ml. of a 1·0 N aqueous solution of potassium dichromate and then 20 ml. of concentrated sulphuric acid are added rapidly. The flask, a 500 ml. conical, is shaken for 1 minute while the temperature attains the peak of about 120°C and is then allowed to cool slowly before dilution and titration. This method gave a mean recovery of 77% of the carbon for the soils examined at Rothamsted. Despite

some variation from this figure quoted by other workers the method, because of its extreme simplicity, is still used more extensively than any other rapid method. PEECH and ENGLISH (1944) included WALKLEY'S 1935 revision of the method in their system of rapid chemical soil tests employed at Cornell.

The fact that oxidation of the organic matter depends so much on the temperature attained in the chromic acid mixture has prompted other workers to use methods giving definite temperature control. KELLEY and THOMAS (1942) compromised with WALKLEY'S method by placing the flasks on a boiling water bath for 15 minutes. One of the earliest attempts was due to TIURIN (1931) in Russia. He boiled the soil in a small flask for 5 minutes with a 0·4N solution of potassium dichromate or chromium trioxide in 1 : 1 sulphuric acid (S.G. 1·525). A small funnel was placed in the neck of the flask to reduce the loss of water during boiling, the temperature being about 140°C. MERKLE (1940) adopted this method for the system of soil testing in Pennsylvania and obtained a mean recovery of 88% of the carbon which agrees well with 86·8% quoted by TIURIN. This is rather higher than with the WALKLEY method but not quite so high as is generally obtained by SCHOLLENBERGER'S. SCHOLLENBERGER (1945) quotes mean recoveries of 0·790±0·019 for the WALKLEY method, 0·812± 0·015 for the equivalent of TIURIN'S method and 0·904±0·013 for his own. The three methods, with modifications of each, were tested critically by members of the Organic Carbon Committee of the International Society of Soil Science and their report was presented by CROWTHER (1935). Soils containing appreciable quantities of chlorides gave high results which could be corrected if the chloride content were known. Otherwise, the addition of silver sulphate to the sulphuric acid or the use of silver dichromate reduced this error but did not obliterate it completely. One noticeable feature is that silver appears to have a catalytic action in the oxidation since higher values are obtained with it in the absence of chloride.

There have been a number of other modifications especially designed for routine testing of large numbers of samples. PURVIS and HIGSON (1939) dissolved potassium dichromate in a 1 : 1 mixture of sulphuric and phosphoric acids and used an electric heater for standardized digestion of the soils at 175°C. WILDE (1943) used 2 ml. only of a 2N solution of potassium dichromate together with 20 ml. of a 4 : 1 mixture of sulphuric and phosphoric acids. The flasks were heated to 160-170°C for 5 minutes and then, after cooling and diluting with 20 ml. of water, the colour of the supernatant liquid was matched visually against standards in a series of tubes. A similar approximate colorimetric method designed for field use has been described by KHANNA, PRASAD and BHATTACHARYA (1949) of India. GRAHAM (1948) adapted WALKLEY'S method to a colorimetric estimation by diluting the digest, after cooling for 10 minutes, with 100 ml. of water and leaving it to stand for 5 hours to allow suspended material to sediment. The transmittancy of the supernatant liquid was then measured with a photoelectric instrument using a red 645 mμ light filter. The importance of a standard procedure and especially the effect of air temperature and concentration of acid was emphasized. CAROLAN (1948) in Ireland followed much the same procedure but recommended filtering the solution before measurement with an

orange filter in the instrument. The colorimetric finish seems likely to replace titration to a large extent in routine laboratories and just recently RAUTERBERG and SANDHOFF (1951) have reported good results with GRAHAM's method from Germany.

One of the chief difficulties with the titration procedure is the fact that 0·4N ferrous ammonium sulphate solution or a 1·0 N ferrous sulphate solution in dilute sulphuric acid as recommended by WALKLEY, do not retain their strength although, for routine use, much improvement is effected by storage under hydrogen. It has also been noted that the end point obtained with diphenylamine is not easily observed, but TINSLEY (1950) found that 2 ml. of a 10% solution of barium chloride saturated with barium diphenylamine sulphonate is very effective. Not only is it non-corrosive, but when added to the digest, after dilution with a saturated sodium fluoride solution, the barium forms a fine suspension of colloidal barium sulphate which acts as a background for observing the colour change from blue to green. THOMAS and WILLIAMS (1936) employed o-phenanthroline as indicator, thus making the use of fluoride or phosphoric acid unnecessary. In all other methods a small quantity of finely powdered soil is taken, but these workers chose to use 5 g. of an ordinary sample passing the 2 mm. sieve to which was added 25 ml. of a 4 N solution of sodium dichromate and an equal volume of concentrated sulphuric acid. After cooling, the reaction mixture was diluted to 200 ml. and a 10 ml. aliquot taken for titration. This method was adopted for soil testing on a large scale in North Carolina and the equipment complete with automatic levelling pipettes for the delivery of dichromate and sulphuric acid has been briefly described by CONSTABLE and MILES (1941). Other means of titration include the method of SMITH and WELDON (1940) in which a slight excess of ferrous sulphate solution is added and the titration completed with standard permanganate solution at a temperature of 80-85°C. GEE (1951), in Borneo, preferred an electrometric end point.

From the foregoing account it is clear that a great variety of methods exist for the rapid determination of soil organic matter with chromic acid mixtures. WALKLEY's method has proved the simplest to operate and is likely to remain popular with a colorimetric finish to the estimation. WALKLEY (1947) has himself presented a detailed examination of various factors which influence the results and it is clear that variation in the recovery of organic carbon may be due, apart from the nature of the organic compounds, to differences in conditions of digestion, to differences in strength of reagents and to the presence of inorganic soil constituents which react with the reagents. It is important to standardize the experimental procedure in the matter of size of flasks, and rate of addition and strength of sulphuric acid employed, as these factors affect the temperature attained during reaction. Even so, recovery increases about 1% for each 5°C rise in the air temperature. Most laboratories are subject to variation in temperature from day to day and with season of the year, but a good plan to check on variations due to any such factors is the inclusion of a standard soil sample of known carbon content in each batch of analyses. LEE (1939) drew attention to errors caused by reduced inorganic compounds in waterlogged soils, but WALKLEY considered these are rarely of much practical consequence if the soil samples are properly

dried in air before analysis, to allow oxidation of ferrous compounds. One practical advantage of WALKLEY's method is that inert carbon is but slightly oxidized during the digestion and therefore only the functional organic matter features in the analysis. For many purposes there is little or no advantage to be gained by attempting to improve the recovery of carbon above WALKLEY's level of about 80%. The ratio of 2 volumes of acid to 1 volume of dichromate solution appears to be about the optimum and, even by using 100% sulphuric acid and a 3 N solution of sodium dichromate with silver sulphate included, it is doubtful whether the recovery could be raised by more than 5% with little improvement in the standard error. The fineness of grinding of the soil sample does not appear so important as was once supposed. Provided the sampling error is satisfactory then a sample passing the 0·5 mm. sieve is adequate for ordinary use.

All the methods which involve external heating are less convenient for routine use on large numbers of samples. The critical factor is the thermal decomposition of chromic acid which appears to be catalysed by inorganic soil constituents. TINSLEY showed that an acid mixture comparable in composition with that of TIURIN, with a boiling point of 140°C can be boiled for as long as three hours with very little thermal decomposition, provided that a condenser is used to prevent loss of water and rise in temperature. A convenient form of condenser is the "cold finger" type resting in the neck of the flask and, under these conditions, oxidation of the organic carbon in soils is completed in two to three hours' boiling. The accuracy and practical value of such a method involving longer boiling remains to be established by trial on a wide range of soils.

SUMMARY

The determination of organic carbon and organic matter in soils has been reviewed with particular reference to rapid methods of soil testing.

Extraction of the humus fraction and its determination by colorimetric or other means is subject to considerable experimental variation, depending on the rather arbitrary choice of conditions.

A rapid oxidation of the soil organic matter with hot chromic acid solution followed by chemical estimation of the residual chromic acid forms the basis of most methods in use for the routine examination of soils in fertility studies.

WALKLEY's method, employing the heat of reaction of concentrated sulphuric acid with an aqueous dichromate solution, is the simplest and most popular procedure and gives a recovery of about 80% of the organic carbon of the soil.

Prolonged boiling under a condenser to maintain a temperature of 140°C achieves complete oxidation of the more resistant organic compounds.

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SESSION 2

EVALUATING THE PHOSPHORUS STATUS OF SOILS

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The term phosphorus status as applied to soils refers to their ability to meet the phosphorus requirements of crops. It is a function of the crop as well as the soil; since crops differ considerably in phosphorus requirement and in ability to utilize difficultly soluble forms, it is important not to lose sight of this fact. The direct and surest way of evaluating phosphorus status is to test the response of the crops in question to incremental dressings in field experiments. The yield and phosphorus content of the crop give an integrated expression of the phosphorus status, combining the inherent capacity of the soil to supply phosphorus, the physiological characteristics of the crop, and the effects of the many other factors, such as pH, moisture, aeration, biological activity and supply and balance of other nutrients, which regulate growth and directly or indirectly govern the supply and uptake of phosphorus. A properly planned field experiment tells whether the status is adequate and, if it is not, how much phosphorus should be applied to produce the yield and composition of crop considered to be optimal under the particular conditions prevailing. Valuable information can, of course, be obtained also from visual examination of growing crops for symptoms of phosphorus deficiency, and from analyses of whole plants or parts of plants at different stages of growth in the field (44), (77), (94).

Field experiments, however, are expensive and time-consuming, and give the information at the end of the growing season. Much attention has, therefore, been paid to the development of simpler and quicker methods. These fall into two categories: Biological and Chemical.

Biological Methods

These include pot tests, such as the MITSCHERLICH, WIESSMANN and NEUBAUER methods (74), (94), which employ indicator crops grown to various stages of maturity under standardized conditions. Other methods, such as the AZOTOBACTER soil plaque technique and the ASPERGILLUS NIGER method (72), (94), make use of bacteria or fungi. In the NEUBAUER method the phosphorus content of rye seedlings is determined, but usually the yield of the crop or organism is taken as an index of the phosphorus status of the soil. These methods were intended to approximate or simulate the behaviour of crops growing in the field and to bridge the gap between field experiments and purely chemical laboratory tests. But apart from possible deviations arising from the characteristics of the particular plant or organism used, the conditions during the determinations generally differ in several important respects from those obtaining in the field. To this extent, at least, the methods must be regarded as empirical, and their usefulness in practice depends on calibration against the results of field experiments. Since they are difficult to assess in any other way they will not be considered further in the present discussion.

Chemical Methods

It was soon realized that the total phosphorus content of a soil is generally useless as a criterion of phosphorus status. Following the classical work of DYER (26), who introduced 1% citric acid as an extractant for estimating the so-called "available" phosphorus, a wide variety of chemical soil tests has been introduced. They include: water and carbonated water (23); solutions of neutral salts such as KCl and $CaCl_2$ (49, 1, 2); strong acids of various concentrations, such as 25% HCl (45), 0·2N HNO_3 (30), and 0·2N H_2SO_4 (17); weak organic acids, such as 1% citric acid and 2·5% acetic acid (85); buffered dilute acid solutions, both organic and inorganic, such as TRUOG'S reagent (76), EGNÉR'S lactate solution (27, 28), and MORGAN'S solution (58, 75); and finally, alkaline solutions such as 2% K_2CO_3 (18, 78) and 0·1N NaOH (12). This list is by no means complete and is intended merely to exemplify the main types of extractant.

The use of dilute acids in general can be regarded as arising from the now largely abandoned idea of simulating the action of plant roots. Subsequently, the aim in most instances has been to obtain a suitable measure of the readily soluble inorganic phosphorus. Such considerations as the following have influenced the actual choice of extractant and the conditions of extraction: empirically tested suitability for certain soils and conditions; analytical convenience, particularly in relation to colorimetric estimation of phosphorus in the extracts; sensitivity in reflecting additions of phosphorus to soils; similarity in extracting power to carbonic acid solution; order of magnitude of the amount extracted compared with the phosphorus contents of crops; ability to dissolve compounds such as calcium phosphates known to be effective as fertilizers; convenience of combining the estimation of phosphorus and cations, especially potassium, in one extraction; prevention of wide fluctuations in pH; maintenance of a reasonably constant ionic strength; and the desirability of having present cations, particularly Ca, normally found in the soil solution.

Latterly, the emphasis has shifted towards the estimation of more specific categories of soil phosphorus, considered to be significant to crops. This approach is well illustrated in the introduction by Bray and his colleagues (22,9, 94) of neutral NH_4F as an extractant for adsorbed phosphorus and NH_4F—HCl for extracting adsorbed plus acid-soluble phosphorus. More recently, radio-active phosphorus has been used to estimate readily exchangeable phosphate (56, 34).

These tests are empirical, and before the results can be used as criteria of phosphorus status, limiting values corresponding to various degrees of adequacy or inadequacy must be established by correlation with the results of field experiments. The success of chemical tests must ultimately be judged from the closeness of this correlation, but a good indication of their interrelationships and significance can also be obtained from consideration of: (1) the categories of phosphorus in soils; (2) their extraction by different classes of extractants; (3) their significance in relation to phosphorus status; and (4) the limitations of laboratory values as criteria of field conditions.

Categories of Phosphorus in Soils

Several categories have been distinguished as a result of fractionation and retention studies (9, 10, 11, 14, 15, 16, 19, 20, 31, 32, 36, 46, 50, 51, 52, 54, 56, 60, 64, 65, 79, 81, 82, 86, 91). There can, however, be few sharp lines of demarcation between them. In most instances they constitute a dynamic system and grade one into another. The emphasis, number of distinctions, and nomenclature vary, depending on how much importance is attached to the mechanism of formation, type of binding, nature of binding agent, and solubility in various extractants. For present purposes it will suffice to distinguish organic and inorganic phosphorus (i.e., organic and inorganic compounds of phosphorus), three categories of inorganic phosphorus, and finally the inorganic phosphate in solution.

Organic Phosphorus

Up to one-half or more of the total phosphorus in soils may exist in organic combinations. The main constituents appear to be nucleic acids and phytin and their derivatives, but small amounts of phospholipids and other compounds may also occur, or have a transient existence (7, 8, 10, 64, 92). Phospho-humate complexes have also been reported (14). Inorganic phosphorus is subject to immobilization in organic form, and organic phosphorus to mineralization by enzymatic reactions. Both processes are significant in relation to phosphorus status, and both are associated with the activity of micro-organisms. They vary widely in importance, depending on the temperature, pH, nature of the clay minerals, aeration, moisture content, and nature and amount of the oxidizable organic matter present (8, 40, 62, 67, 68). Much progress has recently been made in understanding the reactions involved. For present purposes it will suffice to mention that phytin is stabilized by Fe and Al in acid soils, and by Ca in alkaline soils (38, 47), and that enzymatic hydrolysis is markedly inhibited by clay minerals (8, 59). Mineralization increases with temperature and is favoured by slightly acid to slightly alkaline conditions. The organic fraction is extensively soluble only in alkaline solutions, but there is often more organic than inorganic phosphorus in solution in soils.

Inorganic Phosphorus

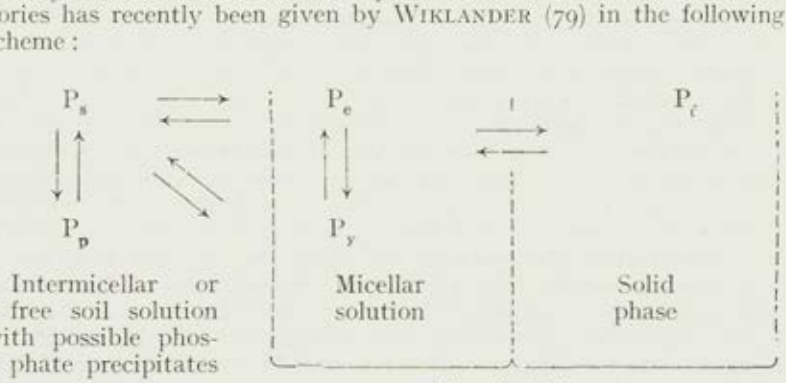
The inorganic phosphorus occurs in association with numerous soil constituents and in a variety of combinations representing widely different firmness of binding. From the point of view of reactivity and solubility, three broad categories can be distinguished: (1) A relatively inert category representing the P firmly held as an integral part of the crystal lattice of resistant minerals, such as apatites, which usually account for most of the phosphorus in the coarser fractions of soils. (2) An intermediate category of varying reactivity represented by (*a*) phosphorus fixed with varying degrees of firmness in the solid phase of complexes with hydrated Fe and Al oxides and clay minerals, and (*b*) simpler phosphates, of Fe and Al in acid soils (15, 16, 31, 32, 36, 46) and of Ca in calcareous soils (1, 2, 11, 52, 60). These may be of varying particle size and degree of crystallinity; they may also be precipitated as separate phases (15, 16) or may

be formed on the surfaces of other particles (6). In any case it is unlikely that there is any sharp demarcation between them and the more indefinite sorption complexes. (3) The adsorbed phosphate held in exchangeable form on the surfaces of soil particles.

It should be emphasized again that there will usually be no sharp boundary between these categories. They also vary greatly in relative abundance and importance in different types of soil. In acid soils, the phosphorus is predominantly Fe- and Al-bound, whereas in calcareous soils it is mainly Ca-bound.

Inorganic Phosphate in Solution

Depending on the conditions, inorganic phosphate may be contributed to the soil solution by mineralization of organic phosphorus, or it may be removed and immobilized in organic form by microorganisms. The concentration, however, is governed mainly by the inorganic categories, which tend to be in equilibrium with each other. But the passage of phosphorus from the resistant minerals is usually very slow and of significance only from a long-term point of view. A very instructive and concise representation of the other two categories has recently been given by WIKLANDER (79) in the following scheme:



P_s=phosphate in the free soil solution.
P_e=exchangeable phosphate adsorbed on the particle surfaces.
P_f=phosphorus fixed in the surface layer of the particles.
P_y=phosphate present as free salt in the micellar solution.
P_p=phosphorus precipitated as difficultly soluble compounds of Fe, Al, Ca, etc.

WIKLANDER makes the conventional distinction between the intermicellar or free solution, representing the bulk of the liquid in between the colloidal particles, and the micellar solution, representing the liquid close to the surfaces of the particles. There is, of course, no actual clear boundary between them, but the distinction is important because the filtrates normally obtained in soil extractions correspond to the intermicellar solution which may differ greatly in composition from the micellar solution.

A detailed discussion of these equilibria is given by WIKLANDER, and only the main features need be noted here. The important point

is that the phosphate in the free solution is governed by at least three processes: (1) The solubility of the precipitated phosphates, P_p, which is governed by a constant solubility product and may be markedly affected by the pH and temperature; (2) the equilibrium $P_e \rightleftharpoons P_f$ between the exchangeable and fixed phosphate which follows the general law of mass action, and (3) the equilibrium between the phosphate ions in the free solution and the micellar solution $P_s \rightleftharpoons P_y$ which follows, qualitatively at least, the DONNAN equilibrium (48, 49). WIKLANDER points out that transfer of micellar phosphate into the free solution can take place by exchange with other anions in the solution, by hydrolysis of the exchangeable phosphate, and by migration of the phosphate present as free salt, all of which are rapid processes. The dissolution of precipitated phosphates and the transfer of phosphorus between the exchangeable and fixed forms, on the other hand, may be very slow, depending on the conditions. The distribution of free phosphate ions between the free solution and the micellar solution is of particular interest and importance, because it is markedly affected by the presence of neutral salts, such as KCl, commonly used as fertilizers. Several workers have reported in recent years that neutral salts lower the solubility or increase the sorption of phosphate in the pH range commonly prevailing in acid to slightly alkaline soils (29, 42, 49, 80). A comprehensive theory, based on the DONNAN equilibrium, has been developed by MATTSON *et al.* (49) to account for the observed facts. Since the relationships involved have several important implications, some of the main features are qualitatively summarized below.

Salt Effects

When the colloids have a nett negative charge and a cationic atmosphere, as is usually the case in soils, the DONNAN distribution of the free phosphate anions is such that their activity in the free solution is higher than in the micellar solution, i.e. P_s is greater than P_y. This state of affairs is generally described by saying that the phosphate ions are negatively adsorbed. Other things being equal, the extent of the negative adsorption, i.e., the ratio P_s/P_y is greater, the higher cation exchange capacity of the colloid. Addition of neutral salts suppresses the negative adsorption and tends to make P_s equal to P_y. The phosphate activity in the micellar solution, however, is rather constant because it is controlled by the solid phase. The equalization of P_s and P_y is therefore brought about mainly by a decrease in P_s. Thus, in practice it is found that the concentration in solution is decreased by the addition of salts quite apart from any change in pH (49, 80). This is brought about by passage of phosphate ions from the intermicellar solution to the micellar solution, and from the micellar solution to the solid phase, i.e. $P_s \longrightarrow P_y \longrightarrow P_e \longrightarrow P_f$, i.e. absorption of phosphate by the soil. Other things being equal, the effect is greater the higher the valency of the cation of the salt; thus $CaCl_2$, for example, has a greater effect than KCl, especially at low concentrations. Should the anion of the salt be adsorbed by the soil to any appreciable extent, it will counteract the effect of suppressing the negative adsorption by displacing some of the exchangeable

phosphate from the micellar solution, i.e., $P_e \rightarrow P_y \rightarrow P_s$. In agreement with this, sulphates have a smaller effect than chlorides. When the anion has a strong displacing power, it becomes the dominant factor. This is discussed later in connection with the extraction of phosphorus from soils.

With positively charged colloids, the position is of course, reversed. In this case the colloidal particle has an anionic atmosphere. The salt effect is positive and dominated by the nature of the anion which displaces the "saloid-bound" phosphate ions from the anionic atmosphere (46, 85). Recent work by MATTSON *et al.* (53, 55) indicates that calcium phosphates in soils react in this way. There is also the more widely recognized effect of salts in increasing the solubility of sparingly soluble compounds. Provided there is no common ion effect, an increase in solubility is to be expected due to lowering of the activity coefficients of the ions with increasing ionic strength of the solution.

Extraction of Phosphorus by Different Classes of Extractants

The main factors governing the extraction of the different categories of phosphorus are: pH, nature and concentration of the cations and anions present, period of extraction, ratio of extractant to soil, temperature, and pretreatment of the soil sample. These factors are interrelated and vary in relative importance from one extractant to another and from soil to soil. The main features may be summarized as follows:

Water Extracts

The concentration of phosphate in water extracts varies inversely with the concentration of Ca (1, 2, 13, 49). In calcareous soils containing calcium phosphates this would be expected; but it is also true for acid soils in which there is no formation of calcium phosphates. It is readily explained on the basis that the phosphate concentration in the water extract, which represents the intermicellar solution, is controlled by the negative adsorption and is therefore higher the lower the electrolyte concentration. In leached soils containing little soluble salts the dominant factor is the exchangeable Ca because, as already mentioned, divalent cations are much more effective in suppressing the negative adsorption than are monovalent cations. The presence of anions, especially soluble organic constituents, capable of displacing adsorbed phosphate will, on the other hand, make for an increase in water-soluble phosphate. Since there is a seasonal variation in the electrolyte content of soils, corresponding variations are to be expected in water-soluble phosphate. Similarly, the electrolyte concentration may vary considerably with the ratio of water to soil, especially for soils containing appreciable amounts of soluble salts. It is not surprising, therefore, that the water-soluble phosphate is found to be so variable in practice.

Water extracts generally contain organic as well as inorganic phosphorus, the former often predominating. Usually, however, the phosphorus is estimated colorimetrically without any pretreatment to destroy organic matter, and the organic phosphorus is not included in the result.

Neutral Salt Solutions

MATTSON *et al.* (49) have suggested concentrated salt solutions, such as N KCl for assessing phosphorus status. In such suspensions the negative adsorption is suppressed. The concentration of phosphate in the extract should, therefore, be a good measure of the activity, P_y, of the free phosphate ions in the micellar solution at the colloidal surfaces. As will be explained later, there is reason for believing this to be an important criterion of phosphorus status. From rather different reasoning, SCHOFIELD and ASLYNG (1, 2, 70) have suggested 10^{-2} M $CaCl_2$. Since divalent cations are very effective in suppressing the negative adsorption, this solution may be expected to give comparable results. Such suspensions filter easily, but the concentration of phosphate is usually much lower than in water extracts and is difficult to determine for some soils.

Alkaline Solutions

The adsorbed phosphate is strongly displaced by OH^- ions. Depending on the period of extraction, the ratio of extractant to soil, the pH, and temperature, not only is the adsorbed phosphate largely or completely extracted by alkaline solutions but various amounts of the more firmly fixed Fe- and Al-bound phosphorus may also be hydrolyzed. Large amounts of organic phosphorus are also brought into solution, but the extraction does not usually approach completeness unless Ca is first removed and the suspension is strongly alkaline.

Acid Solutions

Most of the extractants commonly employed come under this heading, but the amounts extracted vary widely due to differences in the arbitrarily fixed pH, anion content, period of extraction, and extractant/soil ratio. The values generally increase with temperature, the effect being relatively greater for the milder extractants. The main features may be summarized as follows:—

Strongly acid solutions. The importance of pH is well-known from numerous solubility and phosphate retention studies (81). The stronger extractants, such as 0·2 N H_2SO_4 and 1% citric acid, give a final pH below 2. In this region not only are the adsorbed and difficultly soluble Ca-bound phosphorus extensively extracted, but the exchange-complex may be attacked, bringing into solution varying amounts of difficultly soluble Fe- and Al-bound phosphorus. The extraction of difficultly soluble forms increases with decreasing pH and is, of course, favoured by a wide extractant/soil ratio and a long period of extraction. Even at pH of 1 or less, mineral acid extracts usually contain only very minor proportions of organic phosphorus and it is not normally included in the result. But, in the writer's experience, considerable proportions of the total phosphorus in citric acid extracts may be in organic form. This is compatible with the results of YUEN and POLLARD (93), who found that nucleic acid and barium phytate, for example, are extensively soluble in 1% citric. The point is important because any organic phosphorus present in citric extracts is usually included in the result. Citric acid is also of particular interest because it illustrates the importance of taking account of the nature of the anion of the extractant.

Anion effects. Recent studies have emphasized that anions vary greatly in their ability to displace phosphate from soils (3, 4, 20, 42). In many instances, however, it is doubtful to what extent the displacement can be regarded as a simple anionic exchange comparable with cationic exchange. As would be expected, there is a trend for the displacing power to increase with increasing valency, but it is clear that there are other factors concerned also. Of the anions commonly found in extractants, chloride, nitrate, sulphate and acetate, especially the first two, have a relatively low ability to displace phosphate from negatively charged colloids. Certain organic anions, such as citrate, on the other hand displace large amounts. There is little doubt that they do so by virtue of their ability to form complexes with Fe and Al, and also Ca. This is supported by the fact that at the same pH and under the same conditions of extraction, citric acid extracts more Fe and Al as well as P than does a mineral acid such as HCl. The very high displacing power of the fluoride ion can be explained in the same way. It forms hexafluoro complexes with Al and Fe and also precipitates Ca. The Al_3F_6 complex is particularly strong and stable over a wide range of pH. This is borne out by the fact that even neutral NH_4F extracts considerable amounts of Al from soils. The values for Scottish soils (90) range from 0·1 to over 1·0% of Al_2O_3 and the results so far obtained suggest that they are useful criteria of phosphate sorption capacity. It seems clear that extractants containing such complex-forming ions bring into solution not only the adsorbed phosphate but varying amounts of difficultly soluble forms as well. The latter tendency can be counteracted by using a very short period of extraction, as in BRAY'S NH_4F–HCl method (94).

Dilute acid solutions. The final pH in the more widely used methods, such as the TRUOG, acetic, lactate and MORGAN methods, ranges from about 3 to 5. The anion exchange capacity of soils generally increases with decreasing pH and reaches its maximum somewhere in this range. As a result the extraction is often rather complicated. The amount extracted may vary greatly with small changes in the final pH, but unless the adsorption capacity of the soil is very small, it is usually low because it tends to be controlled by the adsorbed phosphate. In this pH range considerably more phosphorus may be dissolved than appears in the final solution. Thus, Ca-bound phosphorus is extensively soluble but its extraction may be greatly restricted by adsorption during the extraction. According to WIKLANDER'S representation, such an increase in adsorbed phosphate should induce conversion into fixed phosphorus. Alternatively, there may occur a gradual precipitation of phosphate by Fe and Al, especially when the period of extraction is long. The final concentration in the extract may, therefore, represent a balance between several processes which proceed to varying extents depending on their velocities and the period of extraction. This was clearly shown in the early work of RUSSELL and PRESCOTT (69), who found that the amount extracted by dilute acid solutions reached a maximum and then decreased with increasing time of extraction. In some Scottish soils, the redistribution of phosphorus brought about by dilute acid treatments has been found to result in greatly increased availability to plants (88). Adsorption during extraction will, of course, be counteracted by

the presence of anions with a high displacing power and by a wide ratio of extractant to soil which also favours desorption. The extent to which it occurs also depends on the period of extraction. Usually this is made very short with a view to extracting only the most rapidly soluble phosphorus or it is made long enough for the maximum amount extractable to be approached. This class of extractants undoubtedly gives a measure of the readily soluble inorganic phosphorus, but it is clear that their action is not so simple as this objective would imply. They reflect mainly the adsorbed and Ca-bound phosphorus, but the significance of the values may vary considerably in different soils. The lactate and MORGAN methods are in some respects comparable with neutral salt extractants. They contain high concentrations of anions not normally associated with soils, and are very strongly buffered and more drastic in their action, but the final pH values of 3·8 and 4·8 are similar to the values normally found in salt suspensions of acid soils. As suggested by DEAN and RUBINS (21), the values obtained by the milder extractants can, to some extent at least, be regarded as intensities rather than quantities.

The organic phosphorus content of dilute acid extracts is usually very small and not included in the result (84).

Pretreatment of Samples

The main question is the possible effect of drying on the solubility of phosphorus in mild extractants. Several workers have studied this point and it has recently been discussed by WIKLANDER (79) and KAILA and RYTI (41). Drying, especially at higher temperatures, would be expected to induce changes such as dehydration and favour the conversion of phosphorus into difficultly soluble forms. It appears, however, that the water-soluble phosphate generally increases (35, 41). A similar trend was found by ASLYNG (1) for $CaCl_2$ extracts, but the results for the common extractants such as citric acid, acetic acid, and lactate, are very variable (41, 73). Drying, even at moderate temperatures of 20–40°C. may produce considerable increases or decreases, or little change, depending on the extractant and the nature of the soil. There appear to be many factors concerned, such as content of organic matter, clay, active Fe and Al, and $CaCO_3$. As suggested by ASLYNG (1), increases due to drying are probably associated with increased solution of organic constituents which displace adsorbed phosphate. Since the limiting values are usually fixed on the basis of a standardized procedure including drying, the effect in the majority of cases is probably not big enough to affect the interpretation of results. Even so, the fact that the values can be affected in this way is still important because it illustrates the inherent limitations of the methods.

It is not customary to grind samples before extraction, but it has sometimes been done. Such treatment may alter the values considerably. The solubility as well as the rate of solution of difficultly soluble phosphates may be increased by grinding. Usually, however, this would be counteracted by an increased adsorption capacity due to exposure of additional active groups and surfaces (63, 71). Similar considerations probably apply to some extent to the effects of duration and vigour of shaking which may affect the degree of dispersion of the soil.

Significance of Different Categories in Relation to Phosphate Status

A critical and comprehensive review of the availability of anions, including phosphate in soils, has recently been given by OVERSTREET and DEAN (61), and only some of the main aspects need be noted here. For present purposes it is convenient to consider the main categories separately. Insofar as they exist as separate phases in direct communication with roots, the different forms may act as independent sources. Usually, however, the supply of available phosphate represents their resultant effect and tends to be dominated by one category. It must also be kept in mind that an adequate phosphorus status demands not only an adequate supply but also conditions favourable for its uptake by the crop.

It has been stated or implied by several workers at different times that the supplying power of a soil involves an intensity or concentration factor, a rate factor referring to the release of phosphate, and a capacity factor covering the reserves. On this basis, the phosphorus status could be inadequate due to any one of these factors limiting the supply to the crop. These concepts are useful in assessing the probable significance of the different categories and have recently been discussed and given a mathematical formulation by WIKLANDER (79).

Adsorbed Phosphate.

The adsorbed phosphate is a very important category, especially in acid soils. It seems reasonably certain that crops depend mainly on inorganic phosphate ions, principally $H_2PO^-_4$ (11, 37), taken up from solution. There is no direct evidence that the contact effect postulated by JENNY and OVERSTREET (39) for cations applies to phosphate uptake. Normally, however, there is close contact between the roots and the soil particles, and it is unlikely that the solution concerned corresponds to the free soil solution as obtained in analyses. The concentration of phosphate in the free solution is in any case controlled by the phosphate at the surface of the particles. As already explained, it fluctuates widely with the pH, and the nature and concentration of other anions and cations, especially Ca, present; it is not surprising, therefore, that it has often proved unsuccessful as an expression of the phosphorus status. The rate of release of the adsorbed phosphate is very rapid and unlikely to be a limiting factor.

Salt effects. Considerable light has been thrown on the uptake of adsorbed phosphate by plants as a result of the recent work of MATTSON *et al.* (48, 49) on salt effects. According to MATTSON (49), the soil and plant should be considered as a single system embracing two colloidal phases and one solution phase. In terms of WIKLANDER'S notation (79), this can be represented as follows:—

Soil particles	Micellar solution	External solution	Root membrane	Plant tissue
$P_f \rightleftarrows$	$P_e \rightleftarrows P_y \rightarrow$	$P_s \rightarrow$	$P'_y \rightarrow$	Org. P

In this chain, the adsorbed phosphate is the supplier of phosphate ions; the free phosphate in the micellar solution of the soil particles, P_y, supplies the phosphate in the external solution, P_s, and this,

in turn supplies the phosphate to the outside boundary of the root membrane, P'_y. Assimilation of phosphate ions into organic form by the plant causes a flux from left to right. The higher the level of P_y, the higher P'_y and the greater the uptake. The level of phosphate in the free solution, P_s, depends in the first place on the negative adsorption of phosphate from the negatively charged soil particles. As already explained, the ratio of P_s to P_y depends on the cation exchange capacity of the soil colloids and on the concentration and nature of the salts present. A similar relationship holds between P_s and P'_y, and in agreement with this the addition of salts has been found to increase the rate of uptake of phosphorus by young plants from culture solutions (48). Theoretical considerations show, however, that the nett effect of salts on the uptake of phosphate from soil is much more complicated. It depends not only on the nature and concentration of the anions and cations present but also on the relative cation-exchange capacity of the soil colloids and the root membranes, i.e., it depends on the qualitative nature of the crop. Theory predicts a zero salt effect on uptake when the cation-exchange capacity of the soil colloids and root membranes are equal, a positive effect when the capacity of the soil is the higher, and a negative effect when the capacity of the root is the higher. The root membranes of different plants are known to differ considerably in acidoid content and cation exchange capacity (24, 48, 49, 83), and the salt concentration is affected by the fertilizers applied and depends on biological activity, rainfall and drainage. Depending on the nature of the soil colloids and root membranes and on the conditions, all gradations of salt effect on uptake, ranging from strongly negative to strongly positive, may be expected. There are doubtless many other factors involved in the uptake of phosphate which may intervene to modify the course of events, and many of the theoretical predictions require experimental verification, but the theory of salt effects as developed by MATTSON accounts qualitatively for a diversity of known trends. It also illustrates very clearly the difficulties involved in evaluating the phosphorus status even when dealing with only one category. The salt effect on the availability of calcium phosphates will usually be positive, and where these are also present the nett salt effect becomes even more complicated and difficult to predict.

The above relationships suggest that the most significant criterion of phosphorus status is P_y, the activity of the free phosphate ions in the micellar solution. As already indicated, a good measure of it should be obtainable by determining the concentration of phosphate in a concentrated salt suspension, such as N KCl, where the negative adsorption is suppressed.

Other Inorganic Forms

The importance of the various forms of Ca–, Al–, and Fe–bound phosphorus depends on the amounts present and on soil conditions, particularly pH. Calcium phosphates are, of course, least soluble under alkaline conditions whereas Fe and Al phosphates are stable under acid conditions. In slightly acid to slightly alkaline soils, readily soluble Ca–bound phosphorus is probably an important source, but in acid soils only the resistant forms such as fluorapatite can normally be expected. There is evidence that micro-organisms can play an

important part in solubilizing difficultly soluble calcium phosphates (33), and this is probably important in calcareous soils where the solubility is low and markedly dependent on CO_2 production (11, 57). In many soils, and especially acid soils which have been limed, difficultly soluble Fe- and Al-bound phosphorus may also make significant contributions.

The solubility and availability of difficultly soluble forms increases with decreasing particle size. The rate of mobilization also increases with temperature. In agreement with this, VAN DER MAREL (45) found the rate of weathering of certain phosphorus-containing minerals in tropical soils to be rapid enough to meet the requirements of some crops. In so far as difficultly soluble forms come into direct communication with roots, they may contribute directly to crops and their availability may be enhanced by root action. Alternatively, they can be regarded as sources for the replenishment of the adsorbed phosphate. As pointed out by WIKLANDER (79), this may be important where the easily exchangeable phosphate is low.

Organic Forms

Organic forms may be directly absorbed by plants to some extent (10, 64), but the balance of evidence indicates that the organic fraction in soils is of significance mainly as a source of inorganic phosphorus. As already indicated, the rate of mineralization depends on many factors and can vary greatly depending on the conditions. Increased mineralization is probably a factor in the improvement in phosphorus status which often results when acid soils are limed. Temperature is particularly important, and VAN DER MAREL (45) found mineralization to be so rapid under tropical conditions that it was necessary to estimate the organic phosphorus in order to assess the status adequately. The bulk of the organic fraction in most soils is probably of long-term significance only. But this does not necessarily mean that mineralization makes no short-term contribution to the nutrition of crops.

Limitations of Laboratory Estimates of Phosphorus Status

Significance of different extractants. It is clear that the solutions commonly used, extract varying amounts of several different categories of phosphorus. Since there can be few, if any, clear demarcations between the categories this is inevitable. However, the methods in general reflect the categories of inorganic phosphorus which are the potential sources of supply to crops. They should, therefore, give some index of the phosphorus status. But there is no certainty as to the relative importance to crops of the categories in a given soil, nor of their relative contribution to the values obtained by different methods. The very weak extractants, such as water and neutral salts, give primarily measurements of intensities and the values are usually quoted as concentrations. The stronger extractants, on the other hand, give primarily measurements of quantities and are generally expressed as such. Usually, the intensity runs parallel to the total supply, but there can be serious divergences between them. It is to be expected that the relative and absolute usefulness of different extractants will vary according to the type of soil. In calcareous

soils, for example, the intensity as measured by extraction with water or carbonated water has been found to give a better index of the phosphorus status than do acid solutions, especially the stronger extractants which dissolve large amounts of the Ca–bound phosphorus present. In most acid soils also, the main consideration is probably the intensity of the supply and, as already explained, there are reasons for expecting that the concentration of phosphate in neutral salt extracts should provide a good index. But it may be that in some acid soils the more difficultly soluble forms, by virtue of root action for example, make a considerable contribution and are not adequately reflected by such weak extractants. In that case, better results might be obtained from dilute acid extractants. On the other hand, there is little doubt that in many acid soils the stronger extractants, such as citric acid, overestimate the significance of the difficult y soluble Fe– and Al– and Ca–bound phosphorus. But where the rate of mobilization of difficultly soluble forms is rapid it is necessary that they should be extracted. The extreme case is well-illustrated by the work of VAN DER MAREL (45), already referred to. He found the mild extractants used in temperate zones to be quite useless for tropical soils where the rate of weathering was high; to evaluate the phosphorus status of these soils it was found necessary to extract inorganic phosphorus with 25% HCl and to obtain an estimate of the total organic phosphorus. It is possible that mineralization of organic phosphorus contributes significantly under less extreme conditions also, and should be taken into account; some measure can be obtained by testing the increase in acid-soluble phosphorus after incubation (8). Only for citric acid extracts is there usually any organic phosphorus included in the result, but whether it has any significance is another matter. These considerations emphasize that each method must be calibrated against the results of field experiments, and that these should cover each combination of climatic conditions and soil type so that different limiting values can be established where necessary.

Recent results (34, 43, 56) suggest that much improved evaluations of phosphorus status are likely to result from the use of radio-active phosphorus in field, pot, and laboratory experiments. Its use in laboratory tests enables the amount of soil phosphorus in equilibrium with that in solution in soil suspensions to be determined very conveniently. Work along these lines should clarify greatly the significance of the values obtained by the conventional methods. The possibility of combining intensity determinations with quantity measurements in water or neutral salt suspensions is particularly attractive and promising. For four Swedish soils, GUNNARSSON and FREDRIKSSON (34) found remarkably close agreement between field and pot estimates and the total soil phosphorus in equilibrium with that in solution in water suspensions.

Phosphorus requirements of different crops. An evaluation of phosphorus status is required for two purposes: (1) to decide whether phosphorus fertilizer is required, and (2) to help decide how much fertilizer should be added if it is required. The answers to both these questions depend on the nature of the crop.

It is well known that crops differ a great deal in their need for phosphorus, and in their ability to uti ize difficultly-soluble forms.

For example, the phosphorus status of a soil that shows no response by cereals is not necessarily adequate for root crops. The reasons for such differences are not fully understood, but the factors usually quoted are differences in the type and extensiveness of the root system, in the excretion of organic acids, and in the rhizosphere population. Other relevant considerations are the length of the growing period and the intensity of uptake at different stages of growth. To these should be added differences in the acidoid content of the root membranes, because the theory developed by MATTSON *et al.* (49) indicates that, other things being equal, a plant will absorb soil phosphorus more readily the lower the cation exchange capacity of the root membrane. The extensiveness of the rooting system is obviously important because it determines the volume of soil from which the crop can absorb phosphate. It is clear, therefore, that the nature of the crop must be taken into account in establishing and interpreting limiting values, and possibly also in choosing the most suitable extractant.

The amount of phosphorus which should be applied is even more dependent on the crop and on agronomic factors, particularly the method of application (89). For example, other things being equal, a much lower dressing usually suffices to give the maximum or optimal yield of cereals than of root crops. Consideration must also be given to the relative importance of the yield and composition of crops, and to favouring production of the part or parts of the plant, such as grain in cereals, for which the crop is primarily grown. The effectiveness of applied phosphorus is also markedly dependent on its position and degree of concentration in the soil (87). As is well-known, the size of dressing can often be greatly reduced if it is suitably placed or concentrated near the seed or in the root zone (66). Even with broadcast applications, the fertilizer particles tend to produce pockets of highly saturated soil with locally high concentrations in solution. This effect is sometimes enhanced by applying soluble phosphates in granular or pellet form. These effects arise from the facts that phosphorus is not mobile in soils and that fixation is a time reaction. As a result a small application is often effective out of all proportion to its effect on the values obtained by conventional extraction methods. These effects also have obvious implications regarding the difficulty of obtaining representative samples of soil.

Effect of soil properties and conditions. As already indicated, the supply of available phosphorus in soils is governed by numerous interrelated factors, such as temperature, moisture content, pH, electrolyte concentration, presence of organic anions, biological activity and CO_2 production. These vary in importance from soil to soil and depend in turn on the weather and on various physical properties of the soil, such as texture, structure and drainage, and may be greatly modified by common operations such as cultivating, liming, fertilizing and manuring. The actual supply of available phosphorus, and particularly its intensity, may, therefore, vary widely not only from soil to soil and from season to season, but in the same soil during one growing season. It is, of course, customary to take account of the volume weight in translating laboratory estimations of quantity to field amounts. The values can also be

adjusted by means of empirically determined factors to make allowances for the effect of pH, plough depth, organic matter content, and mechanical composition (28). Considerable improvements in the practical usefulness of laboratory methods are possible in this way. But when it is considered that the uptake of phosphorus by the crop is governed directly or indirectly by all the factors regulating growth, it can hardly be expected that a relatively simple laboratory extraction can adequately integrate all the factors concerned. In practice sampling errors and seasonal variations have also to be contended with. Sampling errors can, of course, render the values useless.

Conclusion

Much progress has been made in recent years in understanding the nature, solubility, interrelationships, availability, and extraction of the different categories of phosphorus in soils. This has clarified many points in relation to the problem of eva'uating the phosphorus status, but it has also served to emphasize its complexity and the limitations of conventional extraction methods. It is clear that the conventional laboratory methods can be expected to give no more than an index of the phosphorus status and that their relative and absolute usefulness depends on the type of soil and must be judged ultimately from the degree of correlation with the results of field experiments. Improvements in laboratory estimates of phosphorus status seem likely from the application of radio-active phosphorus to measure solid phase phosphorus in conjunction with concentration determinations in neutral salt and water suspensions. But even so, it seems inevitable that the basis of any sound scheme of soil testing must remain an adequate programme of field experiments covering the requisite soil types, crops, climatic conditions, and agricultural practices.

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SESSION 2

THE EVALUATION OF PHOSPHORUS FERTILITY OF SOILS THROUGH THE MEDIUM OF RADIO-PHOSPHORUS

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The evaluation of the fertility status of soils is essential to any programme required to assess the changes in soil fertility or to predict the behaviour of crops as a result of the use of fertilizers or manures. The large number of methods proposed to determine the phosphorus fertility status of soils have met with varying degrees of success. Among the latest developments in this field has been the use of radio-phosphorus and it is the purpose of the present discussion to review the work involving these techniques in measurements of the phosphorus fertility of soils. It should be emphasized that the use of radiophosphorus greatly increases the technological requirements and generally should be employed only where other techniques are not adequate.

Biological Methods

Several hundred field and greenhouse experiments have been conducted in which fertilizers labelled with P^{32} have been used to estimate the relative amounts of soil and fertilizer phosphorus that are absorbed by the growing crop. These experiments have indicated that one of the factors affecting the proportion of soil phosphorus absorbed to fertilizer phosphorus absorbed is the amount of available phosphorus in the soil. This presents the possibility of using such experiments to determine the phosphorus fertility status of soils. A concept concerning the measurement of available soil nutrients has been discussed by FRIED and DEAN (3) and is briefly summarized below.

If it can be assumed that a plant presented with two sources of phosphorus, namely, the soil and the fertilizer, will absorb phosphorus from each in direct proportion to the amounts available, the following equation for determining the amount of available phosphorus "A" in the soil may be derived:

$$A = \frac{B(1-y)}{y}$$

where B = Amount of phosphorus in the fertilizer
y = Proportion of the phosphorus in the plant derived from the fertilizer.

This method for determining the amount of available phosphorus in soils involves the addition to the soil of a known amount of fertilizer (B) labelled with P^{32}, growing the desired crop, determining the proportion of the phosphorus in the plant derived from the fertilizer (y) and calculating the amount of available phosphorus (A) from the equation given above.

Actually, this proposed method closely parallels the well known technique of analysis by isotopic dilution. Addition of a phosphatic fertilizer to a soil can be regarded as dilution of the available phosphorus originally present in the soil. The proportion of soil to fertilizer phosphorus absorbed can thus be considered an index of the amount of dilution which has taken place. This application of the principle of isotope dilution has also been discussed by LARSEN (5).

The method, as described, is general. Its successful application depends upon one's skill in arranging experimental conditions suitable to meet the purpose at hand. Several factors, including properties of the fertilizer, method of fertilizer application, and choice of crop species grown, alter the apparent dilution of the soil phosphorus which accompanies a fertilizer application. A series of experiments aimed at defining more fully the most suitable conditions for determining the phosphorus "A" values of soils is currently in progress.

A method derived from the principles described above, and utilizing the metabolic activities of soil micro-organisms, has been developed by GORING (4). Fertilizer containing P^{32} is added to soil, which is then incubated moist for a short period of time. After incubation, soil phosphorus available to the micro-organisms can be calculated from the specific activity of the soil organic phosphorus and that of the original fertilizer.

Measurement of Surface Phosphate in Soils

One of the uses which has been developed for isotopic tracers has been the measurement of the specific surface of ionizable compounds. The method depends upon the isotopic exchange of the radioactive isotope with the stable isotope of the solid surface. For example, if $P^{32}O_4$ ions are introduced into a soil-water system without changing the total PO_4 concentration, the reaction would be as follows:

$$\text{(I) Surface } P^{31}O_4 + \text{Solution } P^{32}O_4 \rightleftharpoons \text{Surface } P^{32}O_4 + \text{Solution } P^{31}O_4$$

At equilibrium, the extent of the surface reaction can be estimated from the equation:

$$\frac{P^{31}\text{surface}}{P^{31}\text{solution}} = \frac{P^{32}\text{ surface}}{P^{32}\text{ solution}}$$

This principle has been applied to the measurement of surface P^{31} of soils (7) and apatites (6). It seems reasonable to assume that surface phosphate ions which are in free kinetic equilibrium with similar ions in the intermicellar liquid should be important in contributing to the phosphorus fertility of soils.

Measurements of the rate of reaction (I) indicate that there are at least two stages: an initial rapid reaction within 24 hours, followed by a slow reaction of longer duration. There is some evidence to support the contention that the rate of the latter reaction is limited by diffusion. In determining surface phosphate it has been convenient to select some arbitrary time of reaction, such as 24 hours. As measured under these conditions, the amounts of surface phosphate found in a variety of soils ranged from 5 to 200 ppm. These amounts

are quite similar in magnitude to values obtained by many of the common methods for determining available phosphorus. The correlations obtained will be discussed in a later section.

Correlation Studies

Evaluation of the adequacy of a given method as a criterion of the phosphorus fertility status of soils poses many problems. At present, there is no universally acceptable definition or standard of comparison. From a practical standpoint we are interested in crop yields, but many difficulties are encountered in using yield as a standard of comparison. A more satisfactory basis than is presently available would most certainly be helpful.

A series of phosphorus field experiments supplemented by greenhouse tests were conducted to aid in evaluating the usefulness of "A" value as a measure of the fertility status. A total of 69 were conducted in 24 States and Canada. They were of simple design with 6 replications of each of 4 treatments, the treatments being applications of concentrated superphosphate at rates of 0, 20, 40 and 80 pounds P_2O_5 per acre. The superphosphate used for the 40-pound rate contained P^{32}, thus making possible the determination of an "A" value for all locations. The crop grown varied; in the west, it was spring wheat; in the North Central and North-eastern States, it was oats, while in the south, it was cotton. Soil samples from all field experiments were sent to a central location. A greenhouse experiment using all of these soils was conducted with millet as a crop. Yield response and "A" value were determined for all soils in both the field and greenhouse.

A summary of the field experiments showed a significant yield response to phosphorus on the soils at only 25 locations. On the other hand, 37 soils showed a response to phosphorus when used in greenhouse experiments. For the most part, the soils that did not show a response in the field but did in the greenhouse were from locations reporting a shortage of rainfall during the growing season. There were four instances where a yield response to phosphorus was reported in the field but not in the greenhouse.

The correlation of yield response to phosphate fertilizers with other criteria of the fertility status is facilitated if a value indicative of the degree of response observed can be assigned each soil. For the purposes of the correlations reported in this discussion, the percentage yield method suggested by BRAY (1) and others was adopted. This was calculated in accordance with the following equation:

$$\text{Percentage yield} = \frac{\text{Yield without phosphate fertilizer}}{\text{Yield with adequate phosphate fertilizer}} \times 100$$

Correlations of percentage yield calculated for both field and greenhouse experiments with available soil phosphorus by the "A" value, BRAY (2) and TRUOG (8) methods are given in Table 1. The correlations with the observations from the field experiments are barely significant at the 5% level, indicating that the phosphorus fertility status of the soils was not an important factor associated with degree of yield response. The correlations using the greenhouse yield data are highly significant, but the r^2 values indicate that there is still a large proportion of the variance not accounted for.

TABLE 1 Correlations of Yield Response with Selected Methods for Determining Available Phosphorus

Percentage yield[1] for field experiments with	r	r^2
"A" value	·43	·18
Bray method	·39	·15
Truog method	·36	·13
Percentage yield[2] for greenhouse experiments with		
"A" value	·78	·61
Bray method	·78	·61
Truog method	·62	·38

[1]n = 25.
[2]n = 42.

Correlations with yield such as those given in Table 1 are limited to those soils showing a response to phosphorus. If the methods for determining soil fertility are to be used as a basis of predicting crop behaviour in relation to fertilizer use, then there should be equal interest in those soils that did not show a crop response. The frequency distribution data for the soils that did and did not respond to phosphorus, Table 2, are shown to illustrate this point. It becomes

TABLE 2 Frequency Distributions of Available Phosphorus Levels in Respect to Soils Responding and Not Responding to Phosphorus

	Number of Soils	
	Responding to Phosphorus	Not Responding to Phosphorus
Field Experiments		
"A" values lb. P_2O_5/A		
0–100	17	7
100–200	6	12
200–300	2	4
>300	1	14
Greenhouse Experiments		
"A" values lb. P_2O_5/A		
0–100	21	0
100–200	17	3
200–300	6	14
>300	0	14
Bray values lb. P_2O_5/A		
0–10	30	1
10–20	7	4
20–30	4	9
>30	3	17

apparent that only in the extreme cases, i.e., soils very low or very high in available phosphorus, is it possible to predict whether phosphate fertilisers will affect growth. The question might be asked: is this because of the inadequacy of our methods of determining the phosphorus fertility of soils, or is it because of the many uncontrolled factors inherent in our present methods of measuring growth response?

The soils comprising the group under consideration have a wide range of properties. Some were very acid while others contained free calcium carbonate. Many of the laboratory methods for determining available phosphorus are not equally applicable over this entire range, but the "A" value method should not be appreciably affected. The correlation coefficients given in Table 3 show that when all soils are considered there is a better correlation of "A" value with the BRAY than the TRUOG method. In another study designed to compare methods for determining the available phosphorus in soils of the arid and semi-arid regions of the western United States, the coefficients show the values best correlated with the "A" values to be the surface phosphate determined by isotopic exchange methods.

TABLE 3 Correlations of "A" Values Determined in the Greenhouse with Laboratory Methods for Available Phosphorus

"A" value for all soil (n=74) with	r	r^2
Bray method	·77	·59
Truog method	·56	·31
"A" value western soil only (n=25) with[1]		
H_2O method	·41	·17
CO_2 method	·13	·02
Bray method	·79	·62
0·5 M $NaHCO_3$ method	·86	·74
Surface phosphate	·94	·89

[1]Data of Dr. S. R. Olsen.

In conclusion, it can be stated that the use of P^{32} provides a new approach to the old problem of evaluating the phosphorus fertility of soils, although it is still too early to assess fully its utility.

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SESSION 3

THE AVAILABILITY OF NATIVE AND FIXED NONEXCHANGEABLE SOIL POTASSIUM

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Introduction

The potassium of soils occurs in a variety of forms whose availability to plants ranges from that of the water-soluble state to that of the interior of sparingly soluble potassium-bearing minerals. These forms include soluble, exchangeable, primary minerals, and secondary clay minerals. As used here, the term " nonexchangeable " refers to all the soil potassium not extracted by the usual exchangeable cation replacement procedures. The exchangeable potassium values include the water-soluble form except when it is removed previously or corrected for. Exchangeable potassium ions may be held by both inorganic and organic colloidal surface bonds. The general occurrence of substantial quantities of nonexchangeable potassium in soil fauna and flora (2, 38) and in non-living soil organic matter (40) remains unestablished.

With respect to the availability of potassium to plants, several forms have been emphasized at different times and by various investigators, for example, soluble, exchangeable, primary mineral, clay mineral, and fixed. This usage of the term " fixed " as it pertains to minerals refers to the entrapment of potassium ions subsequent to the formation of the mineral, either from additions by man or from other sources. Exchangeable potassium is arbitrarily defined here as that quantity replaceable by an ammonium salt ; the ammonium ion provides a sharp, rapid separation, whereas other cations effect a gradual replacement of either a lesser or greater amount, which increases with the period of contact (49, 70). The amount of moderately mobile potassium in any one form at a particular time is not independent of the other forms, but instead, the distribution of the mobile supply tends to be governed by an equilibrium, by which a change in the level of one component is reflected in corresponding changes in the other parts of the potassium system (5, 21).

The term " availability " has a biotic connotation. It is obvious that the definition of available potassium depends on numerous soil and plant factors, and that without detailed specification of growth conditions the term has no quantitative meaning. For the same reason, no chemical, physical, or biological assay method should be expected to agree precisely with the results of field availability measurements. The current prevailing value in use for the assessment of available potassium is the exchangeable quantity, as determined by laboratory procedures or estimated by rapid soil tests. For the immediate cropping season, this easily obtained value undoubtedly remains our most important single criterion of availability (14). There exists a growing awareness, however, that in the systematic planning of the role of potassium in soil management the rate of supply of native potassium, the fixation of fertilizer and manure potash, and the subsequent availability of fixed potash should be considered.

Primary Minerals

For over a century, soil, artificial soil, and sand culture experiments have been conducted to assess the availability of the potassium of primary silicate minerals, mainly feldspars and micas (45). These materials generally are ground very fine, and frequently the potassium thereby converted to soluble and exchangeable forms is not removed prior to planting. Despite this advantage, the minerals usually release only a small fraction of their potash content to the plants. Although conflicting evidence exists, the potassium of the two micas, biotite and muscovite, has been reported to be more available than that of the two feldspars microline and orthoclase (52).

TYNER (68) found that in sand culture, slow-growing plants such as alfalfa, alsike clover, red clover, and sweet clover, were able to utilize the potassium of microline more efficiently than were buckwheat, corn, oats, peas, rape, sorghum, and sudan grass; he concluded that slower-growing plants can absorb potassium from a more dilute substrate solution. From a comparison of 22 seed plants grown on a sandy loam with added orthoclase, LEWIS and EISENMENGER (44) concluded that plants of lower stages of development can better utilize mineral potassium, presumably because of their origin on relatively undecomposed rocks.

Native Soil Potassium

Experiments have shown that some soils, freed of exchangeable potassium by saturation with calcium (30), or even subjected to drastic hot acid extraction (37), can release sufficient potassium for the growth of plants. It was observed that for the soil of the Rothamsted Broadbalk field (50), some California soils (47), and some Texas soils (28) the decrease in exchangeable potassium during cropping did not account for all the potassium absorbed by the crops. STOLIAROVA (65) concluded that while plants on podsols and red earths obtain their potassium from the exchangeable form, those on chernozems use nonexchangeable sources primarily.

According to SCHACHTSCHABEL (59, 60) the mica minerals of the clay fraction are the main source of available nonexchangeable potassium of soils; the quantity of potassium absorbed by plants depends on the amount and kind of mica, its potash content, and its surface characteristics. On the other hand, DE LEENHEER (43) attributes the small response to potash fertilizer of sugar beets on soils of the Old Sea-polder region of Belgium to high contents of K-bearing feldspars. It was suggested by CORRENS (20) that the potassium-supplying ability of a soil is roughly correlated with its content of micas and feldspars. Determination of the mineral composition of soils is in current use in tropical regions as an index of the available supplies of potassium and other nutrients; its applicability is attributed to the rapid rate of weathering under hot and moist tropical conditions (46).

Fixed Potassium

Previous usage of the term " fixed potassium " included the rapidly exchangeable potassium but the current widespread usage is restricted to certain nonexchangeable forms. There remains a discrepancy

between the theoretical distinctions among the various forms of fixed potassium and the existing techniques for their actual separation.

DYER (23) and FREAR and ERB (29) reported evidence that in long-time field experiments a sizeable proportion of potash additions may be converted into forms not extractable by potassium availability reagents, in the first case 1% citric acid, in the second, 0·3 N NH_4Cl. River-clay soils of the Netherlands have become so depleted of potassium by centuries of grassland farming that fixation of current fertilizer potash precludes the commercial production of potatoes (24).

Studies of fixation by VOLK (69) emphasized its intensification by drying and by alkalinization, the role of the fine clay fraction, and the differing behaviour of various clay types. Within the soil potassium equilibrium system, fixation may be considered as both the replenishment of crystal interlayer potassium previously removed by cropping, weathering, or leaching, and the entrapment of potassium ions within expansible clay lattice interlayers by contraction in the presence of potassium or similar cations (5, 21). It appears that montmorin clay lattices require accompanying desiccation for appreciable fixation to occur, whereas illitic lattices do not (63, 72). The fixation of potassium and ammonium by vermiculite occurs readily even in the presence of water (9). ATTOE (3) concluded that the potassium fixed in a moist soil by liming was more soluble than that fixed upon drying.

It has been possible to show that a substantial fixation of potassium or ammonium is accompanied by an equivalent reduction in cation exchange capacity and an equivalent replacement of other cations (10, 12, 48, 67). For soils of high fixation capacities it is suggested that an ion which does not form a contracted lattice, for example, sodium, be used in the determination of exchange capacity (13). Fixation should be regarded as a cation exchange, in which the properties of the fixed ions, their interlayer location, and the strength of the negative lattice bonds make the ions of lower accessibility to replacing solutions than the remainder of the exchangeable cations.

GOUÈRE (33) observed that fixed potassium is slowly available to plants and that for the soils he studied it was more available than the native nonexchangeable sources. WALSH and CULLINAN (71) found that while fixation by drying cycles did cause severe potassium deficiency in the first crop, the ultimate effect was a liberation of much of the fixed form. During the greenhouse cropping of a cotton soil which had received 0, 24, and 48 pounds of K_2O per acre per year for 19 years, the "48 pound" soil sample released appreciably more nonexchangeable potassium than the other two samples (36). ATTOE (4) found that although Miami silt loam fixed about one-third to one-half of sizeable potash additions, seven oat crops were able to utilize an appreciable proportion of the fraction fixed. Field applications of potash in fertilizers, straw and manure not only raised the exchangeable potassium level of Caribou loam, but potash fixed therefrom increased the nonexchangeable supplying capacity by several fold, according to greenhouse experiments (54).

Availability Evaluation Methods

The quantitative definition of available potassium, as for other nutrients, is difficult because among other reasons, the feeding powers of plants vary widely. This applied to both exchangeable and non-

exchangeable forms. DRAKE and SCARSETH (22) observed that the responses of 13 plants to potash additions were inversely proportional to the plants' abilities to absorb native potassium from the soil; timothy grass utilized some potassium which was unavailable to other crops. Systematic attempts to correlate the nonexchangeable potassium supplies of soils to crops under field conditions with the results of laboratory and greenhouse availability techniques have been few. This contrasts with the extensive work done on the relations of yields of crops and their response to potash applications with measurements of exchangeable potassium. In most studies of nonexchangeable potassium the biotic comparison of soils has been based on greenhouse or NEUBAUER seedling procedures. Some of the investigations have included comparisons of results by such methods with those by laboratory assay procedures.

Because the nonexchangeable potassium generally is much less available than the exchangeable, it is difficult to assess its supply in the field to a single crop. On many soils, an appreciable delivery of nonexchangeable potassium cannot be expected unless the level of exchangeable potassium is relatively low. Single cropping in the greenhouse is similarly affected, and consequently the successive cropping of a soil by the same or by several plant species has been adopted. A number of experiments employing this technique have been reported, in which grasses and legumes have been used most commonly (1, 3, 4, 6, 11, 16, 19, 25, 31, 32, 34, 35, 36, 47, 51, 54, 64). In these experiments the release of nonexchangeable potassium is usually calculated as the total potassium content of the above-ground portions of the plants and of the roots, minus the decrease in exchangeable potassium occurring during the growth period. Soils of high supplying capacities may release potassium even when the exchangeable potassium level is high, whereas soils of low supplying power will not release important amounts even when it is low. During the course of prolonged intensive cropping with a single plant species, the exchangeable potassium tends to drop to a constant minimum value which is maintained thenceforward (6, 19, 35, 54). This persistence of some exchangeable potassium must be due at least partly to incomplete contact of roots with all the soil surface cation exchange sites (6). The rate of release occurring under this condition of minimum exchangeable potassium may be regarded as an index of relative supplying power, but this rate seldom stays approximately constant, for only on exceptional soils can plants long remain vigorous with nonexchangeable sources as their sole direct or indirect supply of potassium. Plant species differ with respect to their abilities to grow well and to utilize nonexchangeable potassium under conditions of artificially high plant population density and low exchangeable potassium; grasses appear to be more efficient than clovers (25, 54). A more complete review of this and of other evaluation methods has been presented elsewhere (53).

Numerous workers have made comparisons between exchangeable and NEUBAUER potassium values as indices of available potassium. In some of these studies, the NEUBAUER values of certain soils substantially exceeded the exchange values (8, 33, 57, 66). On the basis of this behaviour of some Illinois soil samples, THORNTON (66) concluded that fixation of fertilizer potash had increased the availability

of the nonexchangeable potassium. WIESSMANN and LEHMANN (73) observed substantial release of nonexchangeable potassium in three successive NEUBAUER seedling plantings on the same soil samples; the residual exchangeable potassium remaining after each NEUBAUER harvest was also determined. SCHACHTSCHABEL (59, 60, 61) also employed successive NEUBAUER plantings, up to five; in no case was the exchangeable potassium completely exhausted. He later (62) proposed the estimation of the availability of the reserve potassium of a soil by the use of different quantities of soil in the NEUBAUER procedure, for example 25, 50, and 100 grams. REITEMEIER *et al.* (54, 56) compared a number of United States soils on the basis of the release in a modified NEUBAUER procedure utilizing both the potash uptake by rye seedlings and the residual exchange value. Reduction of the soil mass from 100 to 25 grams permitted a greater draft on the nonexchangeable potassium and consequently a better appraisal of the effect of rotation systems on the supplying power of potassium-rich soils (55).

For a randomly selected group of soils, the exchangeable potassium-content usually is an inadequate criterion of the relative nonexchangeable supplying capacity. SCHACHTSCHABEL (59) observed a low correlation between exchangeable potassium and the uptake of reserve potassium by plants; ROUSE and BERTRAMSON (58) considered the exchangeable potassium a poor index of the potassium fertility status of Indiana soils; ABEL and MAGISTAD (1) found Hawaiian soils of low exchangeable potassium to release as much potassium as others of high levels; while CHANDLER, PEECH, and CHANG (19) concluded that the exchangeable potassium values of New York soils are not sufficient for prediction of the response of crops to potash. On the other hand, within a particular soil type, accumulations of exchangeable and moderately available fixed potassium from potash applications appear to occur concurrently (54), in accord with the equilibrium principle. The situation can be summarized by the opinion of BRAY and DETURK (15) that the level of exchangeable potassium is important primarily as an index of the soil's capacity to maintain it.

Attempts to associate closely the potassium supplying powers of soils with their total potassium contents have not been very fruitful. The relative range of total contents of soils within a limited geographic area often is small (51), and even where sizeable, the relationship cannot be expected to have adequate prediction value (64). Higher correlation might be obtained with the potassium contents of certain particle size fractions. For example, WOOD and DETURK (75, 76) stressed that the relative range of contents widened as the clay particle size decreased; this accompanied a reduction in the potash content of the smallest clay particles. The relationships of the content of potassium-bearing primary and clay minerals to the total potash content and to the evaluation of potassium supply to plants are of primary importance (54, 58), but no generally acceptable prediction method has been forthcoming.

Probably the most commonly used rapid method of assessment of available nonexchangeable potassium is extraction by strong inorganic acids. For this purpose, the procedure must involve either (*a*) the prior removal of the exchangeable potassium or (*b*) conditions sufficiently vigorous to extract both the exchangeable, and a portion of the nonexchangeable, forms. Under the first plan the following

acid conditions have been reported: 0·5N HCl (26); hot N HCl (6); and boiling N HNO_3 (21, 34, 58, 75); and by the second scheme, the following: 0·5N HCl (5, 26), 12% HCl (28), boiling N HNO_3 (51, 54, 56), and a variety of conditions (54). While some workers have obtained release of appreciable amounts of nonexchangeable potassium with cold acids, others have found them to be relatively ineffective, in some cases not even extracting all of the exchangeable form. Hot acids, however, are much more effective, but usually cause extensive decomposition of soil minerals. It is surprising that despite this vigorous action high correlation has been observed between results by hot acids and by plant growth methods. The following coefficients of correlation between release values by boiling N HNO_3 and by Ladino clover cropping have been obtained: 0·89 (34), 0·94 (56), and 0·96 (58); with alfalfa, PRATT (51) observed a corresponding value of 0·91. ROUSE and BERTRAMSON (58) observed that the acid-soluble potassium value for a particular soil series or type remained comparatively constant at different locations and that it was much less affected by cropping, fertilization, season, and drying than was the exchangeable potassium value. In a 25-harvest greenhouse cropping experiment completed recently, the release by the clay ($<2\mu$) and by the sand + silt (2μ—2mm.) fractions was compared with that of the whole soil; samples taken before and after the experiment were extracted with boiling N HNO_3 (Table 1). Although large amounts of nonexchangeable potassium, greatly exceeding the initial acid-soluble quantities, were removed from all the soils and fractions by the plants, this was not reflected in the acid-soluble values, which remained generally unchanged by the long period of

TABLE 1. Effect of Intensive Cropping of Soils and Soil Fractions on HNO_3 Soluble Potassium

Soil Particle Diameter	Extraction of Nonexchangeable Potassium by		
	Greenhouse Cropping	HNO_3 before Cropping	HNO_3 after Cropping
μ	lb. K_2O/Acre	lb. K_2O/Acre	lb. K_2O/Acre
	Decatur Clay Loam		
< 2000	560	259	205
< 2	663	222	183
2—2000	453	92	126
	Hagerstown Silt Loam		
< 2000	645	361	360
< 2	628	170	202
2—2000	509	221	264
	Sable Silty Clay Loam		
< 2000	1752	1053	751
< 2	1534	695	673
2—2000	751	425	358
	Wooster Silt Loam		
< 2000	859	411	398
< 2	874	288	214
2—2000	661	237	294

cropping. A suspicion is thereby aroused that, despite the high degree of correlation, the sources of potassium attacked in the acid and growth methods differ.

In the earlier use of electrodialysis for extracting soil potassium, the dialysis was continued for relatively short periods of time, and the usual goal was to have the amount extracted coincide with the exchangeable potassium. More recently, continuous dialysis for periods of 15 to 90 days has been found to extract, in addition to the exchangeable potassium, measurable, and in many cases large, quantities of nonexchangeable potassium (6, 7, 54, 56). In a MATTSON cell, under a potential difference of about 100 volts, a soil typically liberates potassium equivalent to the exchange value in 1 to 4 days, then a further amount at a continuously decreasing rate, and finally delivers potassium at a constant rate, whose value depends on the potassium-delivery status (Figure 1). The correlation coefficient of the relationship for 12 soil samples between the release of potassium in 30 days of electrodialysis and that in 740 days of Ladino clover cropping was 0·964 (56).

The moist storage of soils from which the exchangeable potassium has been removed by salt or acid solutions tends to effect a restoration of the exchangeable form. BRAY, DETURK and WOOD (15, 76) found that both native and fixed nonexchangeable forms are thereby released from H-saturated soils at ordinary temperatures during a period of months or years. YORK and ROGERS (77) observed that saturation with calcium, by liming, was more effective than saturation with hydrogen. This difference was obtained also by AYRES (6) on Hawaiian soils, of which the Ca-saturated samples liberated about three times as much potassium as their H-saturated counterparts, on the average ; for a group of 10 highly weathered soils, a significant correlation existed between release by moist storage while H-saturated and that by cropping. Alternate freezing and thawing of soils of relatively low exchange level has been found to release nonexchangeable potassium (27), but the process has not been investigated sufficiently to serve as a measure of availability.

Since several storage studies (6, 15) had demonstrated that the rate and extent of subsequent replenishment of exchangeable potassium increased as the exchange level was reduced, a more intensive or continuous leaching by solutions might be expected to liberate more potassium in the same period of time. WILLIAMS and JENNY (74) obtained the following order of effectiveness in the replacement of potassium from Ramona loam by concentrated solutions: $H > Na > Li > Ca > Mg > NH_4$. In the replacement of potassium from four New York soils by intensive leaching with 0·5 N acetate solutions, MERWIN and PEECH (49) observed the following general order of cation effectiveness: $Na > H > NH_4 > Mg > Ca > Ba$. (Three of the soils actually showed negative values for the Ca and Ba solutions because of adsorption of potassium impurity.) The ability of Na and H leaching solutions to extract appreciable amounts of nonexchangeable potassium in short periods of time is thereby demonstrated. The findings of abruptness of removal of potassium by ammonium solutions and the continuing extracting abilities of Na and H on these soils recently have been extended to other soils. The already apparent rough correlation of nonexchangeable potassium release by this

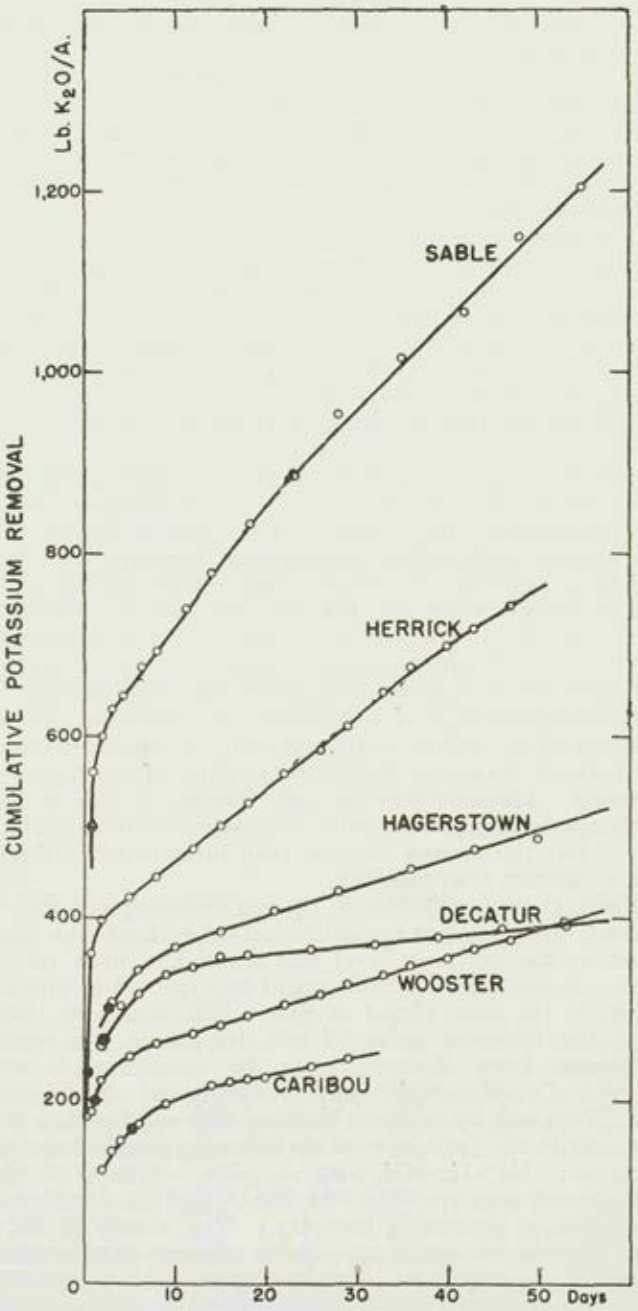


Figure 1. Extraction of potassium from soils by prolonged electrodialysis (exchangeable potassium indicated by black dot).

technique with that by cropping may lead to the refinement and elaboration of the method.

The use of synthetic cation exchange resins as extraction reagents for nonexchangeable potassium has been given attention recently. PRATT (51) compared the release from 13 Iowa soils by contact with a H-saturated exchanger with that by boiling N HNO_3 and that by nine cuttings of alfalfa. The resin and HNO_3 values agreed fairly closely with regard to order of magnitude; although the crop values averaged only about one-fifth as high as the resin values, the coefficient of correlation was 0·963. D. E. WILLIAMS (see JENNY (39)) found that during contact with NH_4- and Na-saturated resin Ramona loam released quantities of potassium intermediate between those liberated by 0·1N NaCl solution and by a NEUBAUER rye seedling procedure; removal of potassium by H-saturated resins was reported to be especially high.

Early in the investigative history of potash fixation it was established that drying at ordinary and elevated temperatures intensified the extent of fixation. Later BRAY and DETURK (15) definitely demonstrated that at 200°C not only was fixation augmented, but that in soils of comparatively low exchangeable potassium, release could occur, which they attributed to a hastening of the establishment of the equilibrium exchangeable potassium level. Subsequent studies showed that release can occur at about 50°C (17, 18) and that potassium liberated by repeated dryings at this temperature is rapidly available to plants (71). Air-drying at ordinary temperatures was found by ATTOE (3, 4) to be sufficient to increase substantially the exchangeable potassium content of many soils if initially low in exchangeable potassium. As potassium thus liberated was shown experimentally to be available to plants, he proposed a diagnostic method for the potassium supplying power of a soil comprising alternate air-drying and wetting and extraction with a salt solution. Similar increases in exchangeable potassium by air-drying have been reported subsequently (6, 41, 42, 54). Although some intensively cropped soils have exhibited relatively immense increases by air-drying, a large number of soils of high total potash contents display no measurable or important increase (54). This qualitative difference in soil behaviour may preclude the general applicability of drying as a technique for assessing supplying capacity.

Conclusion

Attention has been given here to various potassium extraction techniques which have been used or proposed as methods for the determination of the availability of nonexchangeable potassium. The difficulty of characterization of such a quantity as the slowly available potassium has resulted in the use of a wide range of extractants and extraction conditions. This leads to some loss of comparability of results obtained by different workers.

The successive cropping plan requires large expenditures of time and attention. Its restriction to infrequent use as a biotic standard of availability and its general supplanting by shorter methods offer advantages. Cropping by successive NEUBAUER seedling plantings is not generally applicable, because many soils do not produce satisfactory plants on second or subsequent plantings.

The apparent success of strong acid and hydrogen-resin extraction raises the question of the forms of soil potassium attacked by such reagents. Investigations of the extraction of potassium by exchange resins and salt solutions of various other cations are continuing.

The relationships between the potassium supplying powers of soils and their mineral composition require further investigation, both for the establishment of release mechanisms and for the possibility of using mineral composition as an index of availability.

The present dearth of quantitative information on the nonexchangeable potassium delivery powers of soils under field cropping conditions delays the adequate correlation of laboratory and greenhouse results with field behaviour. Wherever possible in field potash experiments, either specially planned ones or others established for a more general purpose, all measurements or estimates of the availability of nonexchangeable potassium which can reasonably be obtained should be compared with laboratory or greenhouse availability criteria.

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SESSION 3

PROBLEME DE LA FIXATION DU POTASSIUM CONSIDERE DU POINT DE VUE MINERALOGIQUE

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Le passage du potassium à l'état non échangeable constitue un fait agronomique d'une importance telle qu'il a donné lieu à de nombreuses recherches. Si le phénomène est certain, par contre ses causes et les conditions dans lesquelles il peut se manifester sont encore assez mal déterminées. La connaissance de la structure des argiles a montré que, dans certains cas, ces minéraux devaient constituter des pièges types. Cependant, si l'aspect géométrique de ce mécanisme est évident, par contre il ne semble pas que l'on ait examiné d'un point de vue assez critique les conditions dans lesquelles ils pouvaient fonctionner. C'est ce que nous allons essayer de faire dans cet exposé.

Nous rappelerons tout d'abord quels sont les différents types de pièges possibles. Nous examinerons ensuite dans quelle mesure le mécanisme de leur fonctionnement permet de les appliquer au cas considéré et nous essaierons de dégager de ces diverses remarques des possibilités d'application.

Les Pièges

La caractéristique principale des minéraux phylliteux qui constituent les roches argileuses est d'être constituée par un empilement de feuillets élémentaires d'une grande stabilité mais adhérant les uns aux autres par des forces d'attraction beaucoup moins intenses et parfois très faibles.

Les minéraux de la famille de la montmorillonite et de la vermiculite existent naturellement sous la forme d'un " hydrate " constitué par un feuillet de type " mica " d'une épaisseur d'environ 9,5 A séparé par des couches d'eau plus ou moins organisées. Il est hors de doute que les ions échangeables peuvent diffuser à travers ces couches d'eau et venir se situer au voisinage des charges négatives portées par les feuillets. Ces charges négatives sont dûes elles-mêmes à des déficits créés dans la structure par le remplacement d'un ion ayant une valence donée par un ion d'une valence inférieure ayant à peu près le même diamètre. Comme le mot remplacement peut prêter à confusion, indiquons tout de suite qu'il s'agit d'un phénomène qui s'est manifesté au moment de la genèse du minéral et qu'il n'y a pas de relation entre lui et les échanges de cations au sens courant du terme.

Ayant ainsi envisagé la structure de ces minéraux et la position des cations échangeables, on comprendra aisément que si on arrive à retirer l'eau qui est logée entre les feuillets de manière à ce que ceux-ci viennent au contact les uns des autres, les ions échangeables pourront se trouver bloqués et deviendront ainsi non échangeables. De telles transformations sont possibles.

G. W. GRUNER (1) en faisant bouillir de la vermiculite en presence d'eau oxygénée et d'ammoniaque a pu constater aux rayons X que les feuillets s'étaient refermés dans l'eau et qu'il obtenait ainsi, en définitive, un mica.

S. CAILLERE et S. HENIN (2) en traitant le même minéral par KOH en solution normale ont pu obtenir un phénomène voisin bien que moins net, le produit transformé donnant aux rayons X un halo à partir de 10 A au lieu d'une raie, ce qui montre qu'une partie seulement des feuillets s'est refermée.

G. W. WALKER (4), I. BARSHAD (3) ont obtenu des résultats encore plus démonstratifs puisque le simple traitement avec une solution de KCl a permis d'obtenir le mica.

D'autre part, traitant une montmorillonite K par KOH/N et faisant subir de temps à autre une dessication à 100°, S. CAILLERE et S. HENIN (5) ont obtenu le passage de la montmorillonite au mica. Le produit obtenu conservait son équidistance de 10 A environ après être plongé dans l'eau.

Plus récemment, C. E. WEAVER et Th. F. BATES (6) ont pu reproduire ce phénomène.

Une telle transformation est donc hors de doute. Mais nous soulignerons dès à présent que dans tous les cas l'évolution de la vermiculite et de la montmorillonite n'a été possible qu'en présence d'ions K. L'explication de cette spécificité est assez simple. On constate en effet que K et dans une certaine mesure NH_4 ont un diamètre qui leur permet de se loger exactement dans des cavités qui se présentent à la surface des feuillets mica. Les autres ions sont ou trop gros ou trop petits et l'on conçoit alors que l'on ne puisse obtenir avec ces éléments une configuration vraiment stable. Il est d'ailleurs remarquable que dans la nature la très grande majorité des micas contiennent principalement l'ion K entre leurs feuillets. Il existe exceptionnellement un mica calcique qui se caractérise d'ailleurs, outre ce fait, par l'existence d'un très grand déficit de charge dans le feuillet mica, ce qui assure évidemment une certaine stabilité à l'assemblage.

Cependant, le passage montmorillonite ou vermiculite à l'état de mica n'est pas le seul type possible de blocage qui puisse se présenter. En effet, S. CAILLERE, S. HENIN et J. MERING (7), S. CAILLERE, S. HENIN (8), J. LONGUET-ESCARD (9), R. F. YOUELL (10) ont pu établir qu'il était possible de précipiter des hydroxydes entre les feuillets de la montmorillonite. Suivant les conditions de préparation, le nouveau minéral ainsi obtenu ou bien ne se gonfle pas du tout dans l'eau, ou bien fixe une couche de molécules de liquide dans le mélange eau glycérol. Il s'en suit donc que très probablement les éléments échangeables peuvent se trouver bloqués sur le feuillet mica recouvert d'une couche d'hydroxyde. Ces travaux ont été effectués au laboratoire mais I. STEPHEN et D. M. C. MACEWAN (11) ont trouvé dans la nature des minéraux de ce type. Ils sont reconnaissables parce que leur diagramme de rayons X, quand ils sont à l'état sec, est très voisin de celui des chlorites. Et si comme la montmorillonite, ils peuvent gonfler dans l'eau, ils ne se referment pas par chauffage à 500° comme le ferait la montmorillonite ou la vermiculite. Ainsi, bien que la fixation à l'état non échangeable ou difficilement échangeable des ions portés par la montmorillonite n'ait pas été établie après un tel traitement, il est assez vraisemblable que cette fixation se produise. Remarquons cependant que le phénomène n'est plus spécifique en ce sens que tous les ions présents à l'état échangeable seraient bloqués par un tel mécanisme. S. CAILLERE et S. HENIN ont pu en effet obtenir une telle transformation non seulement avec NH_4OH et des

hydroxydes assez différents, mais encore avec KOH, NaOH, $Ba(OH)_2$ et $Ca(OH)_2$. D'autre part, si la fixation est possible par ce mécanisme, il doit jouer avec tous les minéraux argileux. En effet, les phénomènes qui sont suivis grâce à l'examen aux rayons X nécessitent que les transformations se produisent dans la structure elle-même, mais il ne semble pas y avoir de raison pour qu'ils ne se manifestent pas en même temps sur le pourtour des micelles et au contact des particules. Des phénomènes de cet ordre pourraient donc aussi bien servir à expliquer la rétrogradation se manifestant avec des minéraux du type vermiculite ou montmorillonite qu'avec des minéraux du type mica chlorite vraie ou kaolinite. Cependant, il ne semble pas jusqu'à présent que l'on ait pu observer des rétrogradations notables avec ce dernier minéral, et le rôle joué par les hydroxydes n'a pas été mis nettement en évidence. Enfin dans ce cas encore on expliquerait moins aisément que le phénomène d'adsorption non réversible paraisse se limiter à 2 ou 3 ions, potassium, ammonium et peut-être magnésium. Il existe encore un autre minéral argileux possédant une couche de molécules d'eau entre ses feuillets, c'est l'halloysite. Il s'agit cette fois d'un minéral dont le feuillet fondamental est du type kaolinite, dont l'épaisseur est de 7 A. La forme halloysite est assez instable et par chauffage à basse température, ou même par dessication dans un air assez sec, l'eau située entre les feuillets s'échappe et l'on obtient un minéral voisin de la kaolinite : la métahalloysite. Nous ne connaissons pas de travaux mettant nettement en évidence des blocages d'ions dans sa structure ; néanmoins, il est très vraisemblable qu'un tel phénomène ait lieu car les divers auteurs qui ont mesuré la capacité d'échanges de base d'halloysite, puis de métahalloysite provenant du même matériel par séchage sont tous d'accord pour admettre une réduction de la capacité d'échanges (12). Si la capacité d'échanges se trouve réduite, on doit normalement s'attendre à ce qu'il y ait blocage de cations. Cependant, dans ce cas encore, il est peu probable que le phénomène n'affecte que le seul ion K. En effet si l'on admet l'explication basée sur l'adaptation des ions aux cavités qui existent également sur une des faces du feuillet kaolinite tous les ions d'un diamètre inférieur à celui de K devraient pouvoir être bloqués.

Si les exemples que nous venons de donner représentent les modèles qui à première vue schématisent le mécanisme du blocage, il en existe d'autres pouvant également intervenir.

Considérons par exemple un minéral de type mica. Il a été démontré par I. BARSHAD (13), S. CAILLERE, S. HENIN (14) et J. L. WHITE (15) que les micas peuvent se transformer en vermiculite ou en montmorillonite, ceci par voie expérimentale au laboratoire. Il est à peu près certain dans ces conditions que l'on n'a pas affaire à une recristallisation. Cependant cette transformation exige qu'une partie au moins des ions K bloqués entre les feuillets du mica puissent s'en échapper pour être remplacés par un autre ion. L'opération demande un temps assez long, de l'ordre du mois. La lenteur d'un tel mécanisme d'échanges fait que les ions K ainsi libérés ne seraient pas considérés comme échangeables si on les avait évalués sur la base des méthodes actuelles. Ceci nous laisse entrevoir qu'il doit exister dans la structure des fissures à travers lesquelles les ions peuvent migrer plus ou moins lentement. Comme il n'y a pas de raison pour qu'un phénomène de ce type se produise dans le sens de l'extraction, sans se produire en

sens inverse, on peut donc considérer comme probable que certains ions apportés à l'état échangeable puissent s'infiltrer dans le réseau et passer ainsi à un état difficilement échangeable. Cette fois le diamètre des ions pourra intervenir et nous comprendrons que seuls certains ions puissent manifester ce comportement. Rappelons à l'appui de cette manière de voir que SCHACHTSCHABEL (16) a pu montrer justement avec les micas que l'équilibre des échanges de base dépendait dans une large mesure des cations utilisés pour l'échange.

Récemment (17) certains micas altérés ont été décrits qui présentaient cette particularité de ne plus contenir qu'une très petite quantité d'ions K. Ce fait ne peut être interprété qu'en imaginant un minéral ayant primitivement une composition normale, mais ayant perdu ses ions alcalins au cours de l'altération. Un tel matériel devrait présenter une capacité de rétrogradation considérable ; il suffirait pour cela que les ions K d'une solution reviennent prendre leur place entre les feuillets en s'échangeant au sens vrai contre les éléments probablement les ions H qui sont venus les remplacer. Il n'y aurait à première vue aucune différence avec un phénomène d'échange normal si la vitesse des remplacements n'était considérablement diminuée du fait que les ions migrent au travers d'une structure relativement compacte. Dans ces conditions, la teneur en potassium totale d'une argile de type mica pourrait être un des critères essentiels de sa capacité de rétrogradation.

Une telle explication pourrait peut-être étendue à d'autres minéraux comme la vermiculite ou la montmorillonite. Il fraudrait pour cela admettre que la couche octoédrique du minéral ayant été attaquée, il s'y est produit des cavités dans lesquelles le potassium est venu se loger. Il ne semble pas que le diamètre de cet ion s'oppose à cette possibilité et bien entendu il viendrait remplacer les ions H qui seraient nécessairement venu se fixer sur l'oxygène lié au silicium de la couche tétraédrique après que le cation constituant normalement le minéral en aura été extrait.

Un autre mécanisme auquel il a parfois été fait appel est celui de la genèse de nouveaux minéraux. Il est évident que s'il se constitue par exemple un mica, en même temps que le feuillet se forme une certaine quantité de potassium devra également être bloquée. Le rôle joué par un tel phénomène paraît cependant limité parce que même s'il s'en forme dans les sols, il est peu vraisemblable que des particules de mica se constituent en quantité suffisante au cours des expériences de laboratoire pour permettre d'interpréter les rétrogradations aussi considérables que celles que l'on constate.

Par contre, il existe une autre possibilité, c'est la formation de complexes. Divers auteurs dont S. MATTSON (18), A. DEMOLON et M. BATISSE (19) ont insisté sur le rôle que pouvait jouer les composés amorphes obtenus par coprécipitation d'hydroxyde par certains sels neutres, en particulier ceux de l'anion silicique. Il n'est pas exclu que dans la masse du précipité une certaine quantité de cations ne soit englobée et ne passe ainsi à l'état non échangeable.

JOFFE et LEVINE (20) ont pu montrer d'autre part que des minéraux comme la pyrophillite qui ne possèdent pas de pouvoir rétrogradant à l'état normal en acquièrent un par broyage prolongé. Dans ces conditions la structure d'une partie du mineral se trouve détruite

et l'on peut attribuer la propriété ainsi acquise aux éléments colloidaux résultant du broyage.

Il existe enfin une dernière possibilité qui n'est d'ailleurs pas strictement du domaine minéralogique. C'est le blocage de bases échangeables par l'adsorption de substances organiques à très grosses molécules. Ici encore la démonstration n'a pas été donnée d'une manière directe. Néanmoins quand on considère les expériences de S. B. HENDRICKS (21) on constate qu'une argile peut adsorber, sous forme moléculaire, certains grosses molécules d'amine. D'autre part, même dans le cas normal du replacement d'un cation inorganique par un gros cation organique il arrive qu'un autre cation inorganique non encore échangé se trouve recouvert par une partie du cation organique et devienne de ce fait non échangeable ou difficilement échangeable. A nouveau ce mécanisme ne rend pas compte du caractère de spécificité du phénomène.

Il est possible également que la fixation de matières organiques autres que les cations proprement dits masque une partie de la surface du minéral comme le feraient les colloides non organiques. De ce fait, ils pourraient être une cause de rétrogradation.

Le Fonctionnement des Pièges

La fermeture de systèmes hydratés types montmorillonite-vermiculite permet d'interpréter le blocage des cations K et l'on comprend également que seuls quelques cations puissent être ainsi rendus non échangeables. Cependant, le rapprochement même des feuillets reste un problème. En effet, si l'on déshydrate, par exemple en chauffant à différentes températures, une montmorillonite Ca ou une vermiculite, on n'observe pas de rapprochement des feuillets avant que la déshydratation ne soit très poussée. Il semble qu'autour de certains cations divalents 6 molécules d'eau soient organisées et forment des piliers maintenant les feuillets écartés. Au contraire, une telle organisation ne se manifeste pas avec l'ion K et l'énergie avec laquelle une argile saturée par cesions retient l'eau aux faibles humidités, est très inférieure à celle d'une argile Ca. On conçoit bien ainsi que le rapprochement des feuillets soit possible avec l'ion monovalent alors qu'il ne l'est pas avec l'ion divalent, mais *à condition* qu'une grande partie sinon la totalité des cations présents entre les feuillets soient monovalents (22). Dans ces conditions, les phénomènes de rétrogradation ne s'observeraient pas pour les premières quantités de potassium ajouté, mais seulement quand une quantité considérable de potassium a été fixée, c'est-à-dire exactement à l'inverse des résultats obtenus par la mesure directe de la rétrogradation.

Le passage de la montmorillonite à l'état de chlorite par précipitation d'hydroxyde et plus généralement la fixation sur la micelle d'un hydroxyde ou même d'une grosse molécule représentent des mécanismes assez compatibles avec les observations. Seulement, d'une part on n'a pas encore nettement mis en évidence qu'il y ait dans ces conditions réduction de la capacité d'échanges et blocage de cations, mais ceci est probable, et d'autre part il est assez difficile de comprendre pourquoi seuls quelques cations peuvent rétrograder par un tel mécanisme ; tous les cations devraient pouvoir ainsi rétrograder. Evidement, on peut dire là encore que les cations monovalents comme K en se collant plus étroitement dans les aspérités des feuillets, en

se déshydratant plus aisément, finissent par donner une configuration plus stable. Mais il ne devrait y avoir là qu'une question de degré et non pas un seuil assez bien délimité comme ça paraît être le cas.

Le même raisonnement vaut pour le passage de l'halloysite à la métahalloysite et d'ailleurs ce mécanisme est lié à la présence de tels minéraux dans le matériel étudié, et divers auteurs ont observé le phénomène de rétrogradation en utilisant des argiles comme la montmorillonite. Même s'il était démontré que cette hypothèse est exacte, elle ne permettrait pas d'interpréter l'ensemble des faits connus.

La diffusion des ions à l'intérieur d'une structure compacte, comme dans le cas du mica, représente un mécanisme assez satisfaisant en ce sens qu'il est possible et qu'aucune des objections que nous avons eu à formuler jusqu'à présent ne lui est applicable. Le seul ennui c'est qu'il est beaucoup plus difficile de prouver son existence en ce sens que l'on est privé des preuves cristallographiques que l'on peut utiliser dans les exemples précédents.

Nous ne reviendrons pas sur ce qui concerne la synthèse de nouveaux minéraux. Par contre, nous insisterons sur le fait que la formation de complexes représente un des mécanismes possibles. BASTISSE (23) par exemple a pu montrer que des complexes artificiels séchés à 105° pouvaient se dissoudre partiellement au contact de l'eau et bien entendu par dessication il pourra se reformer un complexe partiellement stable. Par conséquent, rien ne s'oppose à ce que les éléments nécessaires au blocage des cations soient mis en solution et partiellement rendus insolubles par des mouillages et des dessications alternées. Bien entendu il reste à prouver qu'une partie du potassium contenu dans un tel complexe est à un état peu ou pas échangeable. Le même mécanisme de dissolution que nous venons d'évoquer pourrait également permettre de comprendre l'existence de rétrogradation provoquée par l'adsorption d'hydroxydes et même de molécules organiques.

Conclusion

De mécanismes très variés peuvent expliquer la rétrogradation des cations échangeables. L'aspect minéralogique ou physico-chimique ne permet donc pas de délimiter clairement les hypothèses valables. Ceci d'autant plus qu'un mécanisme donné peut jouer dans un cas précis et pas dans un autre et il est vraisemblable qu'il n'y a probablement pas une, mais des solutions. Il n'en reste pas moins que si l'on s'arrête à un mécanisme plutôt qu'à un autre, on doit rassembler pour établir son existence, un certain nombre de preuves. Par exemple :

En admettant l'hypothèse d'un blocage par fermeture des feuillets, il faut être sur que l'argile étudiée est du type montmorillonite ou vermiculite. Si la quantité d'ions rétrogradés n'est pas considérable, il est possible qu'on ne puisse mettre en évidence par les rayons X, surtout si la technique n'est pas parfaite et qu'il s'agisse de mélange, la fermeture des feuillets. Mais on devrait au moins pouvoir mesurer une diminution de la capacité d'échanges de base ou de la surface du minéral.

Les mêmes remarques sont valables pour une transformation du type halloysite-métahalloysite.

Dans le cas où l'on estimerait qu'il s'agit d'une pénétration dans un cristal, par exemple dans une particule de mica ayant perdu

préalablement une partie de son potassium, la rétrogradation ne devrait pas s'accompagner d'une diminution de la capacité d'échanges, mais il serait probablement possible de montrer qu'à la pénétration de l'ion dans le cristal, correspond la sortie d'un ion que l'ion K est justement venu remplacer. Ce peut être, bien entendu, un ion H.

Quant au blocage par fixation d'hydroxydes ou de matières organiques, il devrait s'accompagner lui aussi d'une diminution de la capacité d'échanges.

C'est seulement le cas où les éléments rétrogradants seraient englobés dans un complexe colloidal qu'il serait difficile d'établir dans l'état actuel de nos connaissances, une convergence de preuves en faveur de cette thèse. Dans certains cas particuliers cependant, il serait peut-être possible d'entraîner par électrophorèse des éléments non cristallinés renfermant du potassium vers l'anode ce qui constituerait évidemment un favorable argument.

Il est évident qu'une telle liste n'est pas limitative et qu'on peut imaginer d'autres preuves en faveur d'une explication donnée. Ce qui apparaît néanmoins, c'est que l'on avancerait probablement plus sûrement vers une explication valable si chaque auteur établissait son programme de recherches en s'efforçant de confirmer ou d'infirmer l'un ou l'autre des mécanismes qui paraissent actuellement des plus vraisemblables. La discussion d'un tel programme de recherches permettrait probablement à un congrès de spécialistes d'aboutir à des conclusions constructives.

SUMMARY

On the basis of present knowledge of the crystalline structure of clay minerals, certain types of mechanisms can be visualised by which certain ions are brought into an unexchangeable state, e.g. the passage from :

montmorillonite and vermiculite into mica ;
halloysite into metahalloysite ;
montmorrillonite into chlorite.

This last mechanism offers an explanation for the fixation of cations both between the sheets of the montmorillonite and on the surface of each type of clay mineral through precipitation of hydroxide. Furthermore, the process could be considered as applicable also to the action of organic matter.

There are some other possibilities, for instance, the migration of the cations into the structure. This explanation may apply to mica and montmorillonite. It could also be visualised that the cations can become entrapped in a floc of the colloidal complex.

The possible actions of these different mechanisms are discussed, and it is suggested that in experiments concerned with the investigation of this problem a series of convergent proofs must be established.

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ZUM MECHANISMUS DES KALIUM-STOFFWECHSELS LEBENDER ZELLEN

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Die Notwendigkeit des Kaliums für das Pflanzenwachstum und seine Unentbehrlichkeit auch für lebende, tierische Gewebe ist seit langem bekannt und unumstritten. Ungeklärt sind jedoch die physikalisch-chemischen Ursachen, warum Kaliumionen in lebenden Zellen eine spezifische Wirkung entfalten, die von anderen Ionen nicht erreicht werden kann, worin diese spezifische Wirkung besteht und warum Kaliumionen in den lebenden Zellen bevorzugt vor anderen Ionen und gegen ein starkes Konzentrationsgefälle angereichert werden.

Im Folgenden soll versucht werden, einen experimentellen Beitrag zur Beantwortung dieser Frage zu geben.

Die spezifische Wirkung des Kaliums in den lebenden Zellen kann auch nicht anhaltsweise aus der grossen Zahl der Veröffentlichungen (1–7) über seine quellende Wirkung, seine Lipoidlöslichkeit, seine Ferment-aktivierende oder -hemmende Fähigkeit, seine Radioaktivität und seine leichte Elektronenemission ersehen werden, da andere Alkaliionen fast die gleichen Eigenschaften besitzen. Die hohe Anreicherung des Kaliums in den lebenden Zellen gegenüber anderen Kationem kann ebenfalls nicht ausreichend physikalisch-chemisch begründet werden, denn weder das chemische Massenwirkungsgesetz (8), noch das DONNAN-Gleichgewicht oder eine Aufeinanderfolge von DONNAN-Gleichgewichten (9), noch der Einfluss von Eiweissstoffen mit verschiedenen isoelektrischen Punkten (10), insbesondere der inneren und äusseren Plasmahaut von Zellen kann zu einer Erklärung herangezogen werden (11).

Einige Arbeiten sind jedoch in der Literatur enthalten, die vielleicht erlauben, etwas Licht in die ungeklärte, spezifische Wirkung des Kaliums in lebenden Zellen zu bringen: VERZÀR und Mitarbeiter (12, 13) fanden, dass Hefezellen unter aeroben Bedingungen aus einer Nährlösung Kalium aufnehmen, wenn zu dieser Nährlösung Glukose zugesetzt wird, und anschliessend das aufgenommene Kalium wieder ausscheiden. Der Natriumgehalt der Zellen und der Nährlösung bleibt hierbei vollständig unverändert. Die gleiche Erscheinung wurde von verschiedenen Autoren (14–21) auch noch an Colibakterien, Erythrozyten und Muskelzellen aufgefunden, so dass sie allgemeinere Bedeutung besitzen dürfte. HEVESY und Mitarbeiter (22, 23) folgern aus diesen Versuchen, dass Kalium zur Glykogensynthese benötigt wird, und berechnen, dass ein Kaliumatom auf vier Glukosemoleküle bei der Glykogensynthese benötigt wird, ohne jedoch anzugeben, zu welchem Zweck die Kaliumionem bei der Glykogensynthese dienen sollen. Interessant ist in diesem Zusammenhang, dass schon HELLRIEGEL (24) aus Analysen von Zuckerrüben vermutete, dass zur Synthese von drei Rohrzuckermolekülen ein Kaliumion nötig sei. Eine weitere wichtige Arbeit zur Klärung der spezifischen Wirkung des Kaliums wurde von HEVESY und Mitarbeitern geliefert (25). Sie fanden mit Hilfe von radioaktivem Kalium, dass Hefezellen in einer wässerigen

Suspension ständig intrazelluläres und extrazelluläres Kalium austauschen, eine Erscheinung, die allein durch Diffusion bedingt sein könnte. Der weitere Befund aber, dass diesser Austausch um so stärker ist, je höher die Atmungsintensität ist, stellt einen spezifischen Kaliumeffekt dar. Zu seiner Deutung nahmen HEVESY und Mitarbeiter an, dass in der Plasmamembran Trägersubstanzen (*carriers*) vorhanden seien, die eine spezifische Affinität zum Kalium besitzen und sich ständig innerhalb der Plasmamembran von aussen nach innen und umgekehrt bewegen, wobei diese Bewegung bei erhöhter Atmungsintensität beschleunigt ist.

Arbeitshypothese

Zur Deutung der Versuchsergebnisse von VERZÀR und Mitarb. sowie HEVESY und Mitarb. wurde folgende Arbeitshypothese aufgestellt: Es ist bekannt, dass in den lebenden Zellen Säuren auf verschiedene Weise (s.u.) gebildet werden können. Nach der klassischen Permeabilitätstheorie werden durch diese Säurebildung folgende Vorgänge ausgelöst: Die Wasserstoffionen dieser Säuren dringen wegen ihrer Kleinheit und hohen Beweglichkeit (Abb. 1) leicht durch die Plasmamembran nach aussen, während die Anionen in den lebenden Zellen verbleiben. Infolgedessen laden sich die lebenden Zellen negativ gegenüber ihrer Nährlösung auf. Kationen, die sich in der Nährlösung befinden, werden daher von den lebenden Zellen angezogen.

IONENBEWEGLICHKEIT ($CM^2 V^{-1} S^{-1}$) BEI 18° UND UNENDLICHER VERDÜNNUNG

H^+	315	K^+	64,6
Li^+	33,4	Rb^+	64,3
Na^+	43,5	Cs^+	68

Abb. 1

Wie Abb. 1 zeigt, bewegen sich die Kaliumionen etwas schneller im elektrischen Feld der lebenden Zelle auf sie zu als die Natriumionen und werden daher in ihr etwas stärker angereichert als die Natriumionen. Im ganzen betrachtet, findet also ein Austausch von Wasserstoffionen gegen Kaliumionen und Natriumionen statt. An diese Vorgänge dürfte sich vermutlich ziemlich zwanglos folgender Mechanismus anschliessen: Durch den Ersatz von Wasserstoffionen durch Alkalionen verändern sich die osmotischen Verhältnisse. Die Wasserstoffionen (H_3O) sind nämlich etwa ebenso gross wie die Wassermoleküle und können daher keinen osmotisch bedingten Eintritt von Wasser durch die ideal semipermeablen Poren der lebenden Zelle bewirken. Sind sie jedoch durch die viel grösseren hydratisierten Alkaliionen ausgetauscht, so findet durch die kleinen, ideal semipermeablen Poren ein osmotischer Eintritt von Wasser statt. Der hierdurch bedingte Anstieg des Turgordruckes bewirkt, dass Zellsaft (Wasser + gelöste Ionen) aus den grösseren Poren ausgepresst wird. Ein ähnlicher Vorgang findet in einer Pfefferschen Zelle statt (Abb. 2), die nicht nur ideal semipermeable Poren, sondern auch grössere Poren besitzt: Ist diese Pfeffersche Zelle mit Rohrzucker-

lösung gefüllt, und taucht sie in reines Wasser ein, so wird durch die ideal semipermeablen Poren Wasser osmotisch eingesaugt. Hierdurch steigt der hydrostatische Druck an, und dieser bewirkt, dass durch die grösseren Poren ein Auspressen von Zuckerlösung (Wasser + Zucker) erfolgt.

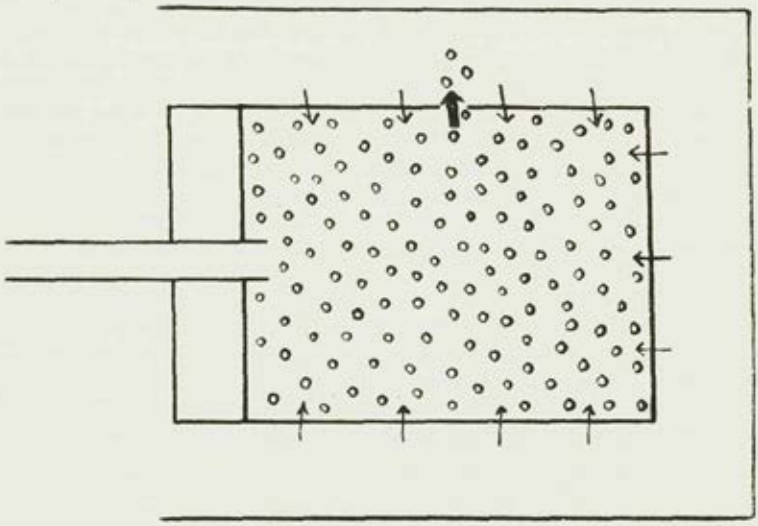


Abb. 2

Betrachten wir uns eine derartige grosse Pore einer lebenden Zelle, in welcher ein Ausfliessen von Lösung stattfindet, in starker Vergrösserung (Abb. 3). In ihr soll sich ein Kaliumion und ein Natriumion befinden, die beide mit der gleichen Kraft elektrostatisch von der negativ geladenen Zelle angezogen werden. Das ausfliessende Wasser schwemmt jedoch das grössere Natriumion bevorzugt vor dem kleineren Kaliumion aus. (Sehen wir nicht die Poren, sondern das ausfliessende Wasser als Bezugssystem an, so wird erkennbar, dass das bevorzugte Ausschwemmen des Natriums vor dem Kalium ebenfalls auf der verschiedenen Wanderungsgeschwindigkeit der Ionen im elektrischen Feld beruht). Insgesamt betrachtet, findet also ein bevorzugter Eintritt des Kaliums und ein bevorzugtes Ausschwemmen des Natriums vor dem Kalium statt. Bei oft wiederholtem Verlauf dieser beiden Prozesse kann also die in lebenden Zellen vorkommende starke Anreicherung des Kaliums vor dem Natrium erklärt werden.

Da das treibende Moment für den vermuteten Stoffwechselmechanismus des Kaliums die Entstehung von Säuren in den lebenden Zellen ist, kann eine Prüfung, ob dieser Stoffwechselmechanismus in den lebenden Zellen stattfindet, wie folgt durchgeführt werden: Die lebenden Zellen werden veranlasst, in ihrem Innern Säuren zu bilden. Gleichzeitig wird untersucht, ob

1. der Kaliumgehalt mit der Bildung von Säuren ansteigt und mit ihrer Vernichtung abfällt,
2. der Austausch von intra- und extra-zellulärem Kalium um so grösser ist, je höher die Säurekonzentration in den lebenden Zellen ist.

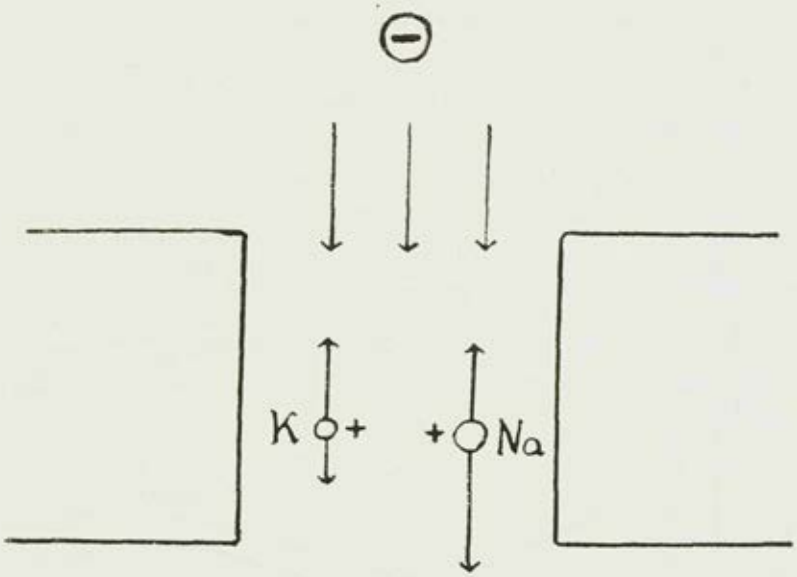


Abb. 3

Experimenteller Teil

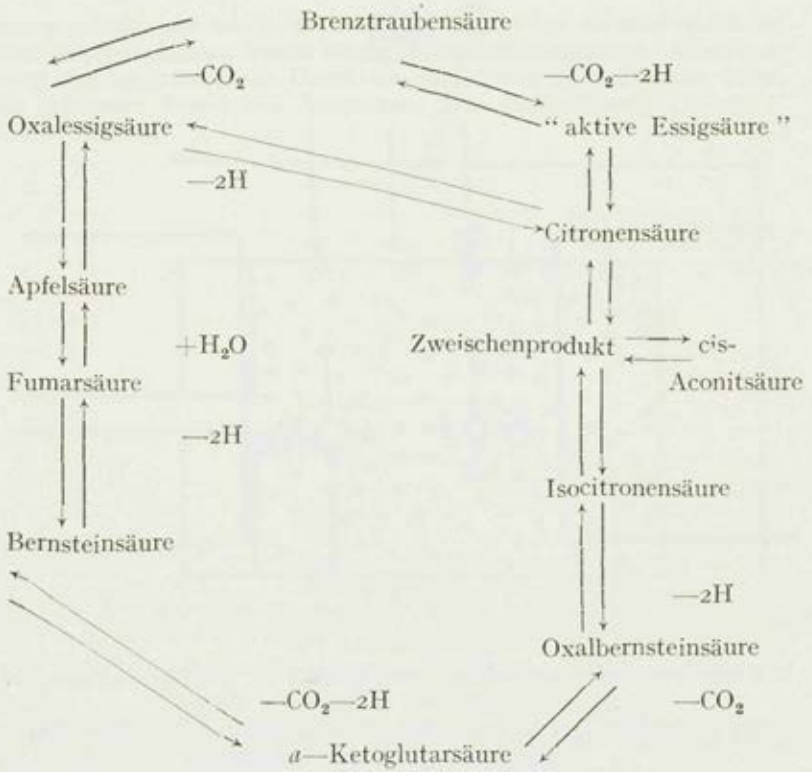
I. *Aufnahme und Ausscheidung von Kalium in Abhängigkeit von der Säurekonzentration in lebenden Zellen*

(A) Aufnahme und Ausscheidung von Kalium bei erhöhter und erniedrigter Atmungsintensität

Zunächst seien in Schema 1 die Säuren angegeben, die bei der Veratmung von Stärke (Glykogen) als Zwischenprodukte auftreten (26, 27).

Schema 1

Stärke (Glykogen)
$+H_3PO_4$ ↓↑ $-H_3PO_4$ (Phosphorylase) } Phosphorolyse der Stärke
Glukose–1–Phosphorsäure
↓↑ (Phospho-Gluco-Mutase)
Fruktose–6–Phosphorsäure
$+H_3PO_4$ ↓↑ $-H_3PO_4$
Fruktose–1, 6–Diphosphorsäure
↓↑ (Aldolase)
3–Phosphoglycerinaldehyd + Dioxyacetonphosphorsäure
↓↑ (Isomerase)
-2 H ↓↑ $+2$ H (Triosephosphorsäure-Dehydrase)
3 Phosphoglycerinsäure
↓↑
2 Phosphoglycerinsäure
$-H_2O$ ↓↑ $+H_2O$ (Enolase)
Phosphobrenztraubensäure
↓↑ (Phosphotransferase)
Brenztraubensäure + energiereicher Phosphorsäure-Ester



Man erkennt aus dem Schema, dass bei der Veratmung von Stärke (Glykogen) grösstenteils stärker dissoziierte Säuren in den lebenden Zellen auftreten, die durch Abspaltung von Wasserstoff (Dehydrierung) Kohlensäure, die bei der Atmung frei wird, entstehen. Ihre Konzentration in den Zellen ist um so höher, je höher die Atmungsintensität ist (28, 29). Es besteht daher die Möglichkeit, die Konzentration von Säuren in den lebenden Zellen zu verändern

1. durch Veränderung des Sauerstoff-Partialdruckes,
2. durch Zusatz von veratmungsfähiger Substanz, z. B. Glukose, zur Nährlösung, und gleichzeitig zu prüfen, ob eine Parallelität der Säurekonzentration und des Kaliumgehaltes in den lebenden Zellen besteht. Im einzelnen wurde wie folgt verfahren.

Durch 100 ccm einer 20% igen, wässerigen Suspension von frischer Bäckerhefe in einer Waschflasche wurde in verschiedenen Versuchsansätzen bei 30°

(*a*) ein kohlensäurefreier Stickstoffstrom oder ein kohlensäurefreier Luftstrom geleitet,

(*b*) abwechselnd ein kohlensäurefreier Stickstoffstrom und ein kohlensäurefreier Luftstrom geleitet,

(*c*) ein kohlensäurefreier Luftstrom geleitet, und während seines Durchleitens ein Zusatz von 0,3% Glukose zugefügt,

(*d*) ein kohlensäurefreier Stickstoffstrom geleitet, und während seines Durchleitens ein Zusatz von 0, 3% Glukose zugefügt.

Anschliessend passierten die Gase 2 mit Barytwasser beschickte Waschflaschen. Zu verschiedenen Zeiten wurden die in Barytwasser absorbierten Kohlensäuremengen durch Rücktitration mit Oxalsäure acidimetrisch bestimmt (30) und gleichzeitig aus der Hefesuspension Proben von 10 ccm herauspipettiert, in deren wässeriger Phase nach sofortigem Abzentrifugieren der Hefezellen die Kalium-und Natriumkonzentration flammenphotometrisch (unter Benutzung von Interferenzfiltern), die Glukosekonzentration jodometrisch (31) und der pH Wert elektrometrisch ermittelt wurde (Abb. 4–8).

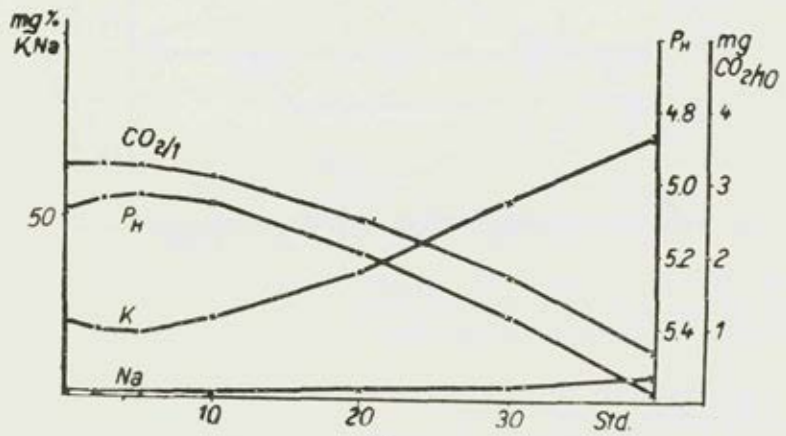


Abb. 4

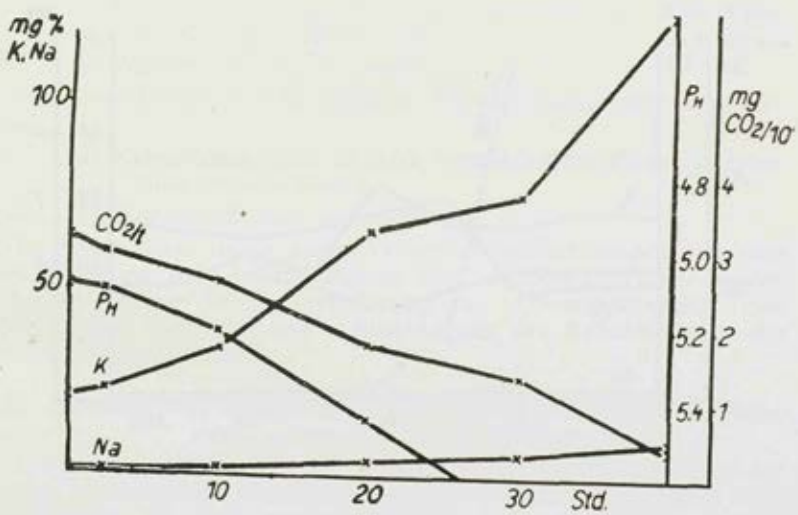


Abb. 5

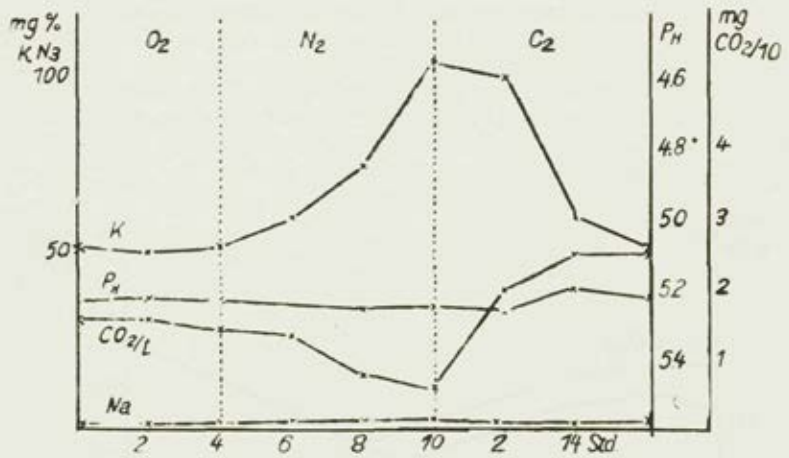

mg %
K,Na
100
50
O2
N2
C2
K
PH
CO2/L
Na
2
4
6
8
10
2
14 Std
PH
4.6
4.8
5.0
5.2
5.4
mg
CO2/10
4
3
2
1

Abb. 6

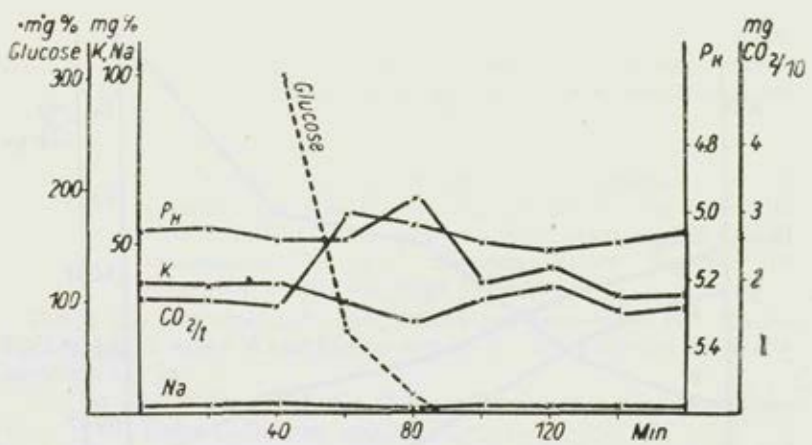

mg %
Glucose
300
200
100
mg %
K,Na
100
50
Glucose
PH
K
CO2/l
Na
40
80
120
Min
PH
4.8
5.0
5.2
5.4
mg
CO2/10
4
3
2
1

Abb. 7

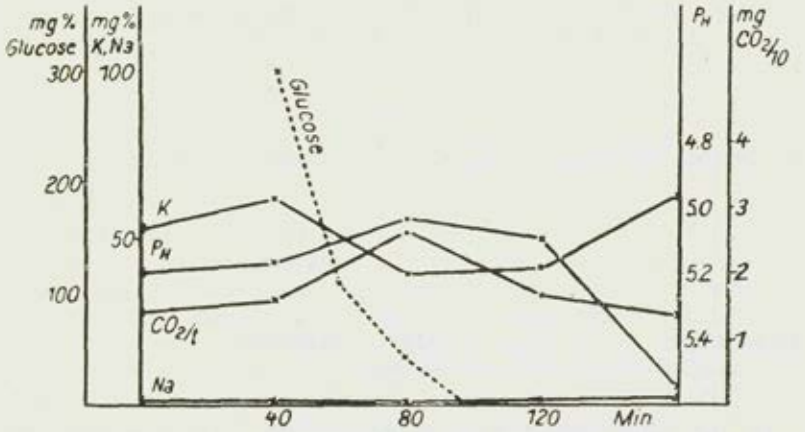


Abb. 8

Aus den Kurven ist ersichtlich:

1. Die Wasserstoffionenkonzentration der wässerigen Phase läuft in jedem Fall der Kohlensäure Entwicklungsintensität nahezu parallel.
2. Die Kaliumkonzentration der wässerigen Phase läuft in jedem Fall der Wasserstoffionenkonzentration der wässerigen Phase und der Kohlensäure-Entwicklungsintensität nahezu invers.
3. Die Kurven der Natriumkonzentration der wässerigen Phase verlaufen gleichsinnig wie die der Kaliumkonzentration, jedoch mit stark verminderten Amplituden.

Bei Erhöhung der Kohlensäure-Entwicklungsintensität werden also

(*a*) Kaliumionen (und in stark vermindertem Masse Natriumionen) aufgenommen,

(*b*) Wasserstoffionen ausgeschieden.

Bei Erniedrigung der Kohlensäure-Entwicklungsintensität werden also

(*a*) Kaliumionen (und in stark vermindertem Masse Natriumionen) ausgeschieden,

(*b*) Wasserstoffionen aufgenommen.

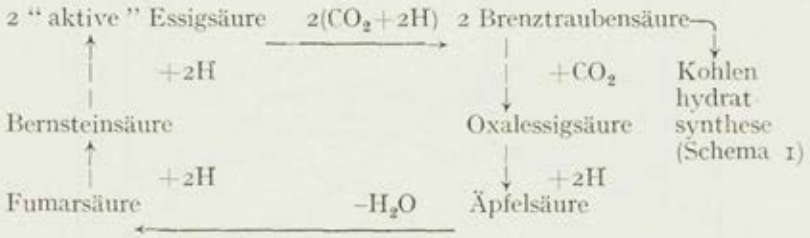
Es dürfte daher durch diesen Versuch aufgezeigt worden sein, dass bei Erhöhung bzw. Erniedrigung der Säurekonzentration in den lebenden Zellen durch Veränderung der Atmungsintensität eine gleichsinnige Erhöhung bzw. Erniedrigung des Kaliumgehaltes der Zellen aufgetreten ist.

(*B*) *Aufnahme und Ausscheidung des Kaliums bei veränderter Photosynthese-Intensität grüner Pflanzen*

Eine zweite Möglichkeit, die Säurekonzentration in den lebenden Zellen zu verändern, besteht darin, grüne Pflanzen verschieden stark zu belichten. Nach BENSSEN und Mitarb. (32, 33) entstehen nämlich

bei der Photosynthese ebenfalls in einem Kreisprozess verschiedene Säuren durch Hydrierung und "Assimilation" von Kohlensäure (Schema 2).

Schema 2



Da die Säurekonzentration in den lebenden Zellen parallel der Photosynthese-Intensität ist (34), kann weiterhin die Parallelität von Säurekonzentration und Kaliumgehalt lebender Zellen dadurch geprüft werden, dass bei verschieden starker Belichtung die Kalium-Aufnahme und Ausscheidung untersucht wird. Die diesbezüglichen Versuche wurden wie folgt ausgeführt:

In verschiedenen Versuchsansätzen wurden

(*a*) Chlorella pyrenoidosa-Algen in 100 ccm einer Nährlösung suspendiert (1,3 g Chlorella-Algen-Trockensubstanz je Liter enthaltend) und in 2 mm dicker Schicht bei 25° mit einer 100 Watt Halbwatt-Glühfadenlampe im Abstand von 20 cm belichtet und im Dunkeln stehen gelassen.

(*b*) 12 g Wasserlinsen (Lemna minor) auf 100 ccm einer Nährlösung (3 mm Schichtdicke) ausgebreitet und mit einer 100-Watt-Halbwatt-Glühfadenlampe im Abstand von 20 cm bei 29° belichtet und im Dunkeln stehen gelassen.

Nach verschiedenen Zeiten wurden die verdampften Wassermengen ersetzt und Proben von je 10 ccm aus den Nährlösungen entnommen, in denen nach sofortigem Abzentrifugieren der Algen bzw. nach Abtrennen der Wasserlinsen die gleichen Messungen wie oben in den Hefenährlösungen ausgeführt wurden.

Aus den Kurven ist ersichtlich:

1. Die Wasserstoffionenkonzentration der wässerigen Phase ist im Licht höher als im Dunkeln.
2. Die Kaliumkonzentration der wässerigen Phase ist im Dunkeln höher als im Licht.
3. Im Licht und im Dunkeln ändert sich die Natriumionenkonzentration gleichsinnig wie die Kaliumionenkonzentration, jedoch in weit geringerem Masse.

Bei Erhöhung der Photosyntheseintensität werden also

(*a*) Kaliumionen (und in stark vermindertem Masse Natriumionen) aufgenommen,

(*b*) Wasserstoffionem ausgeschieden.

Bei Erniedringung der Photosyntheseintensität werden also

(*a*) Kalumionen (und in stark vermindertem Masse Natriumionen) ausgeschieden,
(*b*) Wasserstoffionen aufgenommen.

Durch diesen Versuch dürfte weiterhin gezeigt worden sein, dass bei Erhöhung bzw. Erniedrigung der Säurekonzentration in den lebenden Zellen durch Veränderung der Photosynthese-Intensität eine gleichsinnige Erhöhung bzw. Erniedrigung des Kaliumgehaltes der Zellen aufgetreten ist.

(*C*) *Aufnahme und Ausscheidung von Kalium bei Bildung und Vernichtung von Oxalessigsäure*

Nach WOOD und WERKMAN (35) tritt in lebenden Zellen intermediär gebildete Brenztraubensäure mit Kohlensäure zu Oxalessigsäure zusammen, wobei die Wasserstoffionenkonzentration erhöht wird. Es ergibt sich daher zwecks Prüfung der Parallelität von Kaliumgehalt und Säurekonzentration lebender Zellen eine dritte Möglichkeit, die Parallelität von Kaliumgehalt und Säurekonzentration zu prüfen, indem Brenztraubensäure durch Atmung, z. B. in einem Luftstrom, in den lebenden Zellen erzeugt wird und mit und ohne Zusatz von Kohlensäure zum Luftstrom die Oxalessigsäurebildung verändert wird. Gleichzeitig wird gemessen, ob sich der Kaliumgehalt der lebenden Zellen mit der Säurekonzentration ändert.

Zum Versuch wurde durch eine 50%ige wässerige Suspension von Bäckerhefe ein kohlensäurefreier Luftstrom, anschliessend ein Gemisch von Luft und 5% Kohlensäure und darauf wiederum ein kohlensäurefreier Luftstrom geleitet. Nach verschiedenen Zeiten wurde nach Abzentrifugieren der Hefezellen die Kaliumkonzentration der wässerigen Phase flammenphotometrisch bestimmt (Abb. 9).

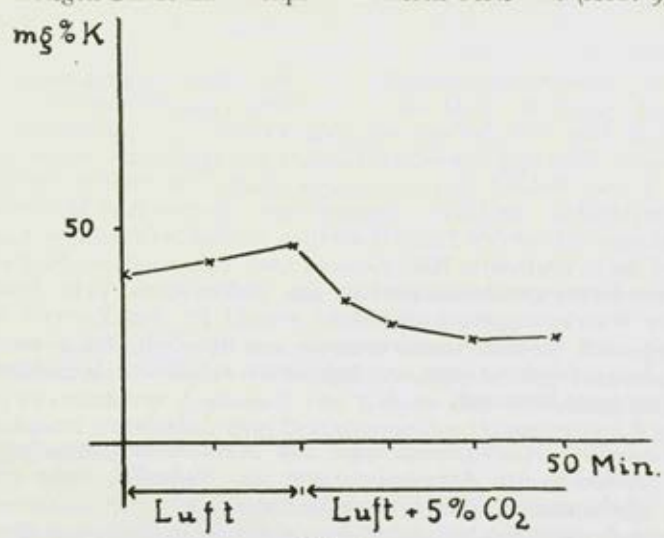


Abb. 9

Aus der Kurve ergibt sich, dass auch bei dieser Möglichkeit der Veränderung der Säurekonzentration in lebenden Zellen ihr Kaliumgehalt sich gleichsinnig verändert hat.

(D) Aufnahme von Kalium bei Bildung von "Extrakohlensäure"

Eine vierte Möglichkeit der Säurebildung in lebenden Zellen wurde von BROCK, DRUCKREY und HERKEN (36) aufgezeigt: Sie fanden, dass Speicheldrüsen- und Leberschnitte in Warburg-Apparat "fixe" organische Säuren nach Acetylcholinzusatz und nach Schädigung durch Abkühlen bilden. Gleichzeitig ergab sich eine "völlige Parallelität von Säurebildung und Kaliumaufnahme," die auch grössenordnungsmässig übereinstimmte.

II. *Austausch von intra- und extra-zellulärem Kalium in Abhängigkeit von der Säurekonzentration lebender Zellen*

Eine Prüfung, ob die oben angegebene Vermutung über den Stoffwechselmechanismus des Kaliums richtig ist, kann nicht nur aus dem Befund der Parallelität von Kaliumgehalt und Säurekonzentration der lebenden Zellen erfolgen, sondern auch durch den Nachweis, dass die Intensität des Austausches von intra- und extra-zellulärem Kalium um so höher ist, je grösser die Säurekonzentration in den lebenden Zellen ist. Die oben erwähnten Versuche von HEVESY und Mitarbeitern (25), dass eine Suspension von Bäckerhefe bei aeroben Bedingungen mit Zuckerzusatz (höhere Atmungsintensität, höhere Säurekonzentration) einen höheren Austausch von intra- und extra-zellulärem Kalium aufweist, als ohne Zuckerzusatz, könnte in Sinne der Bestätigung des Ablaufes des vermuteten Stoffwechselmechanismus in lebenden Zellen gedeutet werden. Eine weitere Prüfung, ob dieser Stoffwechselmechanismus in lebenden Zellen stattfindet, kann dadurch erfolgen, dass auch auf andere Art die Säurekonzentration in den lebenden Zellen erhöht bzw. erniedrigt wird, und gleichzeitig festgestellt wird, ob ein erhöhter bzw. erniedrigter Austausch von intra- und extra-zellulärem Kalium stattfindet.

Da ein Arbeiten mit radioaktivem ^{42}K wegen seiner kurzen Halbwertszeit (12,4 Std.) wohl nur in der Nähe eines Cyklotrons möglich ist, wurde von dem Befund von COLLANDER (37) ausgegangen, dass die lebende Zelle nicht zwischen Kalium und Rubidium unterscheiden kann. Dieser Befund von COLLANDER dürfte eine weitere Stütze für das Stattfinden des oben angegebenen Stoffwechsel-Mechanismus des Kaliums in lebenden Zellen darstellen, da das hydratisierte Kaliumion und das hydratisierte Rubidiumion nach Tab. 1 nahezu die gleichen Ionenwanderungsgeschwindigkeiten im elektrischen Feld besitzen, und die Wanderungsgeschwindigkeit sowohl für den Eintritt in die Zelle als auch für das Ausschwemmen aus der Zelle massgebend ist. Es ist daher möglich, statt des radioaktiven Kaliums Rubidium zur Markierung zu benutzen.

(A) Veränderte Austauschintensität von Kalium-Rubidium bei Veränderung der Atmungsintensität von Hefezellen unter aeroben Bedingungen durch Glukosezusatz

Es wurde zunächst versucht, den gleichen Befund, den HEVESY und Mitarb. (25) mit Hilfe von radioaktivem ^{42}K erhalten hatten, mit Rubidium wieder zu erlangen. Hierzu wurde in zwei Versuchsansätzen eine Aufschwemmung von einem Teil frischer Bäckerhefe in 50 Teilen Wasser in flachen Glasschalen mit und ohne Zusatz von 0,3% Glukose 2 Stunden lang stehen gelassen. Nach Zusatz von 40 mg% Rubidium

zu beiden Ansätzen wurden nach verschiedenen Zeiten Proben entnommen, zentrifugiert und in ihrer wässerigen Phase die Gehalte an Kalium und Rubidium flammenphotometrisch unter Zwischenschaltung eines Monochromators zwischen Flamme und Photozelle (mit Sekundärelektronen-Verstärker) gemessen (Abb. 10).

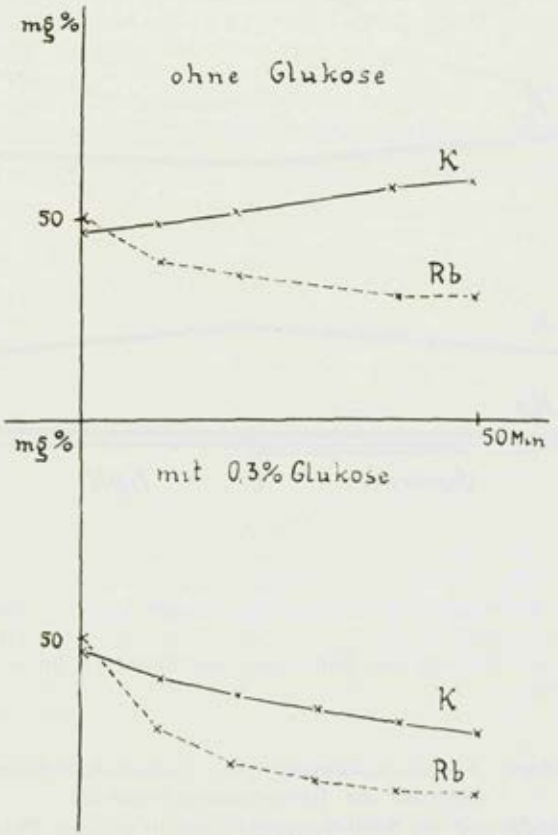


Abb. 10

Aus der Abbildung geht hervor, dass unter aeroben Bedingungen mit Glukosezusatz (höhere Atmungsintensität, höhere Säurekonzentration) ein stärkerer Austausch von Kalium und Rubidium als ohne Glukosezusatz stattfindet, eine Bestätigung des Befundes von HEVESY und Mitarbeitern.

(*B*) *Veränderte Austauschintensität von Kalium-Rubidium bei Veränderung der Atmungsintensität von Hefezellen durch verschiedenen Sauerstoffpartialdruck.*

Da die Atmungsintensität und somit die Säurekonzentration in den lebenden Zellen sich auch durch Änderung des Sauerstoff-Partialdruckes veränden lässt und gleichzeitig die Austauschintensität von Kalium und Rubidium leicht gemessen werden kann, wurde folgender

Versuch ausgeführt: Durch eine 20%ige wässerige Suspension von Bäckerhefe wurde in je einem Ansatz Luft bzw. Stickstoff geleitet. Nach 2 Std. wurden 40 mg % Rubidium zu den beiden Ansätzen gegeben, und nach verschiedenen Zeiten Proben entnommen, in deren wässeriger Phase die Kalium- und Rubidiumkonzentration flammenphotometrisch bestimmt wurde (Abb. 11).

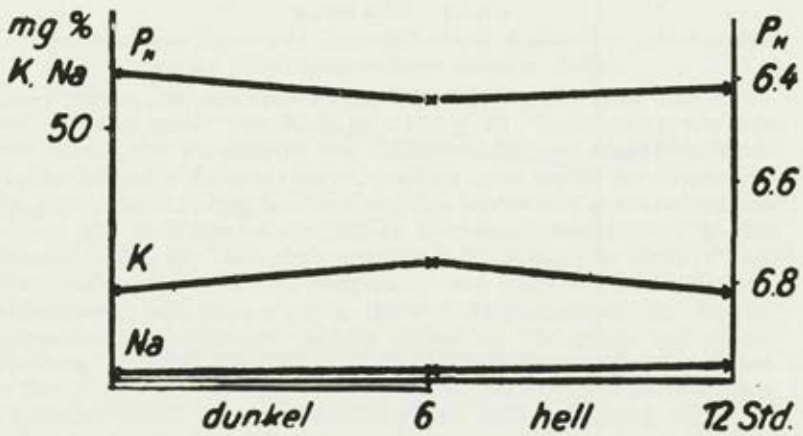


Abb. 11

Aus der Kurve ist ersichtlich, dass unter aeroben Bedingungen (höhere Atmungsintensität, höhere Säurekonzentration) ein stärkerer Austausch von Kalium und Rubidium stattfindet als unter anaeroben Bedingungen.

(C) *Veränderte Austauschintensität von Kalium-Rubidium bei Veränderung der Photosynthese-Intensität*

Die Veränderung der Säurekonzentration in grünen Pflanzen kann auch durch Änderung der Photosynthese-Intensität bewirkt werden, so dass hierin eine weitere Möglichkeit der Untersuchung der Abhängigkeit von Austauschintensität Kalium-Rubidium von der Säurekonzentration gegeben ist. Ein diesbezüglicher Versuch wurde wie folgt angesetzt: Eine Suspension von 0,5 g frischen Chlorella-Algen in 200 ccm Wasser wurde in 2 Hälften geteilt und in flache Glasschalen gefüllt. Eine Glasschale wurde bei 24° im Freien bei bedecktem Himmel (im August) aufgestellt, die zweite im Dunkeln bei 24° gehalten. Nach 2 Stdn. wurde zu beiden Suspension 40 mg% Rubidium zugesetzt und nach verschiedenen Zeiten Proben entnommen, in deren wässeriger Phase die Rubidium- und Kaliumkonzentration flammenphotometrisch bestimmt wurde (Abb. 12).

Auch aus dieser Kurve geht die höhere Austauschintensität Kalium-Rubidium bei höherer Säurekonzentration in den lebenden Zellen hervor.

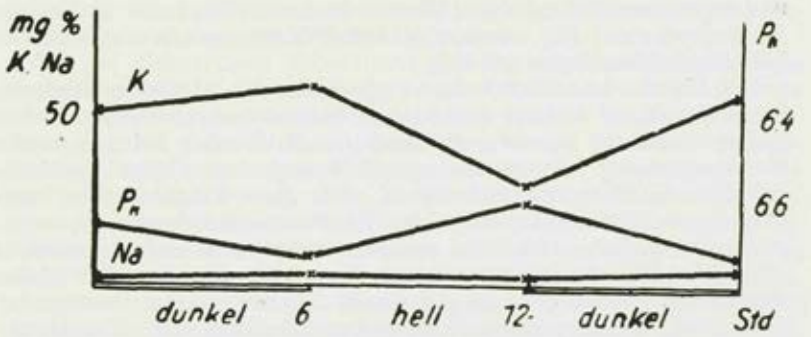


Abb. 12

Diskussion der Versuchsergebnisse

Aus den Versuchen ergab sich:

(1) Der Kaliumgehalt ist der Säurekonzentration lebender Zellen parallel.

(2) Die Austauschintensität von intra- und extrazellulärem Kalium ist der Säurekonzentration lebender Zellen parallel.

Diese Versuchsergebnisse wurden bei verschiedner Art der Säureerzeugung in den lebenden Zellen erhalten und dürften die Vermutung stützen, dass der oben beschriebene Stoffwechselmechanismus des Kaliums (bevorzugter Eintritt des Kaliums vor dem Natrium, bevorzugte Ausschwemmung des Natriums vor dem Kalium) in lebenden Zellen stattfindet und die starke Anreicherung des Kaliums vor dem Natrium bewirkt.

Es dürfte daher der Schluss berechtigt sein, dass das K a l i u m z u r N e u t r a l i s a t i o n v o n S ä u r e n mit impermeableu Anionen in den lebenden Zellen dient. Durch den Eintritt und Austritt von Kaliumionen wird bei veränderter Säurebildings-Intensität die Wasserstoffionen-Konzentration in den lebenden Zellen nahezu konstant gehalten, eine wichtige Voraussetzung für den Ablauf der vielfältigen fermentativen Umsetzungen in den lebenden Zellen. Wie wichtig die Einstellung eines bestimmten pH-Wertes in den lebenden Zellen für den Ablauf von chemischen Reaktionen ist, geht daraus hervor, dass in mechanisch zerstörten Hefezellen lediglich bei pH +6,2 fermentative Umsetzung vor sich gehen, während intakte Hefezellen in Nährlösungen von etwa pH=8 bis pH=2 leben können. So könnte z. B. auch die Bilding von weiteren Mengen Säuren des Intermediärstoffwechsels solange verhindert werden, bis durch den Austausch mit Kaliumionen die entstandenen Wasserstoffionen ersetzt sind und die Wasserstoffionenkonzentration wieder auf den physiologischen Wert gesunken ist.

Die von VERZÀR und Mitarb. (12) beschriebenen Versuchsergebnisse bestätigen diesen Schluss, so dass es nicht nötig erscheint, einen besonderen Zusammenhang von Kohlenhydrat- und Kaliumspeicherung in den lebenden Zellen zu vermuten. Ein Zusammenhang von Kohlenhydrat- und Kaliumspeicherung in lebenden Zellen wird durch das oben beschriebene Versuchsergebnis widerlegt, da unter aeroben

und anaeroben Bedingungen (also in beiden Fällen beim Abbau von Kohlenhydraten) ein verschieden hoher Kaliumgehalt der lebenden Zellen gefunden wurde (Abb. 5.).

Von HEVESY und Mitarbeitern (25) wurden ihre ähnlichen Versuchsergebnisse damit erklärt, dass in der Plasmamembran lebender Zellen Trägersubstanzen (*carriers*) vorhanden sind, die sich bei verschieden starker Atmung verschieden schnell bewegen und eine spezifische Affinität zu Kaliumionen besitzen. Ob diese Erklärung der oben dargelegten Vermutung über den Stoffwechselmechanismus vorzuziehen ist, kann entschieden werden, wenn der Wasseraustausch in Abhängigkeit von der Säurekonzentration in den lebenden Zellen durch Untersuchungen mit schwerem Wasser geklärt worden ist. Eine solche Klärung könnte vielleicht zur Deutung vieler Permeabilitätserscheinungen beitragen, die bisher durch die Annahme eines Trägermechanismus erklärt werden. Ein Hinweis, dass der Wasseraustausch das treibende Moment für den Alkaliionenaustausch darstellt, ergibt sich aus dem Befund von HEVESY und Mitarb. (38) sowie KROGH (39), dass durch eine Froschhaut, also eine Haut aus nebeneinanderliegenden lebenden Zellen, ein so starker Wassertransport stattfindet, dass das Wasser der Hydrathüllen der transportierten Ionen nicht zur Erklärung ausreicht (40).

Anhaltspunkte für die Parallelität von Kaliumgehalt und Atmungsintensität wurden schon früher aufgezeigt, ohne dass die Ursachen dieser Parallelität geklärt wurden: Es wurde festgestellt, dass in pflanzlichem Gewebe eine Kaliumanreicherung auftritt, die dem Sauerstoff-Partialdruck proportional ist (41).

Die in den oben beschriebenen Versuchen aufgefundene Parallelität von Kaliumgehalt und Photosynthese-Intensität grüner Pflanzen dürfte zur Klärung der oft behaupteten Beziehungen von Lichtwirkung und Kaliumdüngung beitragen: Sie bestätigt die Befunde, dass eine Kaliumdüngung zu landwirtschaftlichen Nutzpflanzen ihre höchste Leistungsfähigkeit erst bei vollem Tageslicht zu entfalten vermag (2) und dass Pflanzen in trüben, regnerischen Jahren weniger Kalium in ihrem Wachstun benötigen als in sonnigen Jahren (3). Sie stützt jedoch nicht die Meinung (42), dass das Kalium in den Pflanzen in der Lage sein soll, bis zu einem gewissen Grade den Mangel an Sonnenschein bei der Stoffproduktion auszugleichen, eine Ansicht, die bereits von anderer Seite widerlegt wurde (43). In pflanzenphysiologischen Versuchen wurde diese Parallelität von Kaliumgehalt und Photosynthese-Intensität weiter bestätigt (44, 45). ALTEN und GOETZE (46) fanden, dass Kalimangelpflanzen auch bei hohem Chlorophyllgehalt keine Kohlensäure assimilieren, und dass nach Zusatz von Kalisalzen in kurzer Zeit die Assimilation stark ansteigt, nach PIRSON (47) in einer halben Stunde um das 1 1/2 fache, so dass keine wesentliche Neubildung von Zellsubstanz angenommen werden konnte, sondern eine Reparatur der geschädigten "kolloidalen Plasmastruktur" durch das Kalium vermutet wurde. Sehr deutlich wurde die Parallelität von Kaliumgehalt und Photosynthese-Intensität weiterhin durch die Beobachtung gemacht, dass das Kalium, nachgewiesen als Kaliumkobaltinitrit, an der Oberflache der Chloroplasten angereichert ist (48) und bei der Photosynthese in diese eindringt (49). Durch die oben beschriebenen Versuche dürfte auch gezeigt werden, dass grüne Pflanzen am Tage Kalium aufnehmen und nachts aus-

scheiden, eine Erscheinung, die am Beispiel der Baummwollpflanzenblätter bereits experimentell bestätigt wurde (50).

Da die säureartigen Substanzen des Intermediärstoffwechels die Zwischenprodukte des Aufbaues und Abbaus der Polysaccharide und Eiweisstoffe (s.u.) darstellen, entstehen sie auch bei dem fermentativen Umbau der Stoffe in den Zellen, dessen Intensität infolgedessen ebenfalls mit dem Kaliumgehalt parallel gehen muss: So stellt schon ECKSTEIN (51) die Notwendigkeit des Kaliums für den Transport der Stärke aus den Blättern von Kartoffelpflanzen in die Knollen fest, welche später an den Blättern und Speicherorganen anderer Pflanzen bestätigt gefunden wurde (52). Die gleiche Erscheinung wurde von ALTEN und Mitarb. (53, 54) für den Eiweisstransport aus den Blättern in die Körner von Haferpflanzen gefunden, und aus dem gleichen Grund sind wohl auch die Speicherorgane der Pflanzen besonders reich an Kalium (55-57). Für das Bestehen dieser Parallelität spricht auch der bekannte Befund, dass Kalium in Pflanzenteilen mit hoher Umbauintensität (junge Triebe, Schosse), hohem intermediärem Stoffwechsel und somit auch hohem Gehalt an Säuren stark angereichert ist und aus älteren Pflanzenteilen abgezogen wird. Erklärt werden kann diese Beobachtung durch den Befund (58), dass Pflanzenteile mit hoher Stoffwechsel-Intensität einen niedrigeren ph-Wert als Pflanzenteile mit geringerer Stoffwechsel-Intensität haben, und daher der Austausch von Kaliumionen gegen Wasserstoffionen die Ursache der Kaliumanreicherung in den Pflanzenteilen mit hoher Stoffwechsel-Intensität sein dürfte. Störungen dieser Parallelität, z. B. infolge von Kaliummangel, müssten sich daher besonders dort auswirken, wo eine hohe Umbau-Intensität auftritt, und in der Tat bestehen einige Kaliummangelsymptome darin, dass die Blattspitzen vertrocken und sich einrollen. Umgekehrt müssen beim Absinken der Säurekonzentrarion von den lebenden Zellen Kaliumionen ausgeschieden werden, wie dies in den oben beschriebenen Versuchen gefunden wurde. Hiermit stimmt die noch umstrittene Beobachtung (59) überein, dass höhere Pflanzen nach der Blüte (Zeitpunkt der höchsten Stoffwechsel-Intensität) Kalium in den Boden ausscheiden, eine Erscheinung, die auf Grund der oben beschriebenen Versuche noch einmal überprüft werden sollte.

Die Aufgabe des Kaliums, das Neutralisationsmittel in der lebenden Zelle zu sein, geht auch daraus hervor, dass bisher noch keine Kaliumverbindungen in pflanzlichen und tierischen Zellen, sondern stets nur freie Kaliumionen aufgefunden wurden, die nach dem Aufhören der Lebenstätigkeit, z. B. Säurebildung, schon durch kaltes Wasser vollständig ausgewaschen werden können.

Der Ersatz von Wasserstoffionen durch Kaliumionen im Zellsaft wirkt aber nicht nur neutralisierund, sondern erklärt auch die Tatsache, dass ausreichend mit Kalium versorgte Pflanzen turgeszent sind und Kaliummangelpflanzen eine "Welketracht" zeigen: Bei ausreichendem Ersatz von Wasserstoffionen durch Kaliumionen und somit genügend neutraler Reaktion findet nämlich die enzymatische Bildung weiterer Säuremengen statt, deren Wasserstoffionen ebenfalls durch Kaliumionen ersetzt werden können. Die so zustandekommende Erhöhung des Kaliumgehaltes lebender Zellen bewirkt einen hohen osmotischen Druck des Zellsaftes und daher eine hohe Saugkraft gegenüber der Nährlösung (Bodenlösung) und eine geringe Transpira-

tionsintensität. Beide Faktoren wirken im Sinne einer Erhöhung des Turgordruckes und einer wassersparenden Wirkung des Kaliums.

Das weitere Ergebnis der oben beschriebenen Versuche, dass das Natrium gleichsinnig wie das Kalium, aber in bedeutend geringerem Masse, von den lebenden Zellen aufgenommen und ausgeschieden wird, dürfte aufzeigen, dass das Natrium nur eine geringe säureneutralisierende Wirkung in den lebenden Zellen ausüben kann. Hiermit stimmt die bekannte Erscheinung überein, dass bei Abwesenheit von Kalium kein Pflanzenwachstum durch Natriumgaben möglich ist, und dass bei Gegenwart von Kalium das Natrium höchstens eine zusätzliche Wirkung auf das Pflanzenwachstum hat.

Die meist säureartigen Substanzen des Intermediär-Stoffwechsels stellen nicht nur die Abbau- und Aufbauprodukte der Kohlehydrate, sondern auch der Eiweissstoffe dar, da sie mit Ammoniak zu Aminosäuren umgewandelt werden. Infolgedessen ist auch der Eiweissstoffwechsel von der Konzentration an Säuren des Intermediär-Stoffwechsels und damit von der Kaliumversorgung abhängig. Stickstoffmangelpflanzen enthalten daher höhere Kohlenhydratmengen (*carbonaceous plants*) (61, 62), während bei Stickstoffüberschuss grössere Mengen Aminosäuren gebildet und teilweise in Eiweissstoffe umgewandelt werden (*proteinaceous plants*) (61, 62). Hierdurch wird die bekannte landwirtschaftliche Erfahrung erklärlich, dass bei ausreichender Kali-Versorgung der Pflanzen der Gehalt an Zucker in Zuckerrüben, an Stärke in Kartoffen und Getreide und an Zellulose in Faserpflanzen vermehrt wird. Auch die bei ausreichender Kalidüngung verstärkte Halmsteifigkeit von Getreide, ebenfalls bedingt durch erhöhte Zellulose-Einlagerung, dürfte auf diese Art erklärt werden können.

Die Synthese der Polysaccharide und Eiweissstoffe erfordert wegen des regelmässigen Baues derartig grosser Moleküle aus thermodyamischen Gründen besonders hohe Energiemengen (62), die nur über die energiereichen Phosphorsäure-Ester zur Verfügung gestellt werden können. Da deren Bildung durch die Substanzen des Intermediär-Stoffwechsels erfolgt und deren Konzentration wiederum von der Versorgung mit Kalium abhängig ist, dürfte die bekannte Erscheinung erklärlich werden, dass bei Kaliummangel die Bildung von hochmolekularen Polysacchariden und Eiweissstoffen erniedrigt ist und sich Oligosaccharide und Aminosäuren in den Pflanzen ansammeln.

SUMMARY

The parallelism of potassium content and intensity of photosynthesis in green plants, found by the experiments described, might contribute to clear up the often-asserted correlation between the action of light and potassium fertilization: It confirms the findings that potassium fertilization for agricultural plants can show the highest efficiency only with full daylight (2) and that the plants need less potassium for their growth in dull and rainy years than in sunny years (3). But it does not support the opinion (42) that potassium in the plants would be in a position to compensate for lack of sunshine to a certain extent during the formation of plant substance. This

opinion has already been refuted by other scientists (43). This parallelism of potassium content and intensity of photosynthesis has, furthermore, been proved by experiments with regard to plant physiology (44, 45). ALTEN and GOETZE (46) found that plants with potash deficiency symptoms do not assimilate carbonic acid even when the chlorophyll content is high and that after supply of potash salts the assimilation soon increases considerably. According to PIRSON (47) this increase was 1·5 times within a 30-minute period so that it could be assumed that no essential new formation of cell substance but a repairing of the damaged " colloidal plasma structure " by the potassium took place. The parallelism of potassium content and intensity of photo-synthesis became still more evident by the observation that potassium in the form of potassium cobaltinitrite is accumulated at the surface of the chloroplasts (48) and that it penetrates into these during the photosynthesis (49). The experiments described also show that green plants absorb potassium during the day and secrete it during the night, a phenomenon that has already been proved by experiments with leaves of cotton plants (50).

As the acidoid materials of intermediate metabolism represent the intermediate products of the formation and decomposition of polysaccharides and proteins (see below), they also are formed by the fermentative transformation of the substances within the cell. The intensity of this transformation must consequently be parallel to the potassium content. ECKSTEIN (51), for example, has already proved that potassium is absolutely necessary for the transportation of starch from the leaves into the tubers of potato plants. The same phenomena were found later in the leaves and storage organs of other plants (52). ALTEN and his assistants (53, 54) found the same symptom for the transportation of protein from the leaves into the grain of oats, and for the same reason the storage organs of the plants probably have an especially high content of potassium (55 57). A further proof for the existence of this parallelism is given by the well known fact that potassium is accumulated in large quantities in plant organs with high intensity of transformation (young shoots, sprouts), high intermediate metabolism, and, consequently, high content of acids, and is removed from parts of older plants. This observation can be explained by the finding (58) that the parts of plants with high intensity of metabolism have a lower pH than parts with lower intensity of metabolism. Therefore, it may be assumed that the accumulation of potassium in the parts of plants with high intensity of metabolism is caused by the exchange of potassium and hydrogen ions. Disturbances of this relationship, caused by potassium deficiency, for example, must consequently be especially evident under conditions of high transformation intensity and, indeed, some symptoms of potash deficiency manifest themselves by drying and rolling of the leaf tips. Conversely, the living cells must secrete potassium ions when the acid concentration decreases as is found by the experiments described. The still disputed observation (59) that higher plants after blossoming (time of highest intensity of metabolism) secrete potassium into the soil also corresponds to this experience. The beforementioned phenomenon should be examined once more, having regard to the experiments described.

The role of potassium as a neutralizing agent in the living cell can

also be recognized by the fact that up to now no potassium compounds, but only free potassium ions, have ever been found in cells of plants and animals. These ions can be completely washed out by cold water after cessation of the vital functions, for example, formation of acids.

The substitution of hydrogen ions by potassium ions in the plant juice has not only a neutralizing effect but it explains also the fact that plants with sufficient supply of potassium are turgescent and that plants affected by potassium deficiency show inclination to wilting of leaves and blossoms. If hydrogen ions are sufficiently substituted by potassium ions so that a sufficient neutral reaction is possible, the enzymatic formation of further quantities of acids takes place, the hydrogen ions of which may in turn be exchanged for potassium ions. The resulting increase in potassium content of living cells causes a high osmotic pressure of the cell juice and, therefore, a high suction power in relation to the nutritive solution (soil solution) and a low transpiration intensity. Both factors result in an increase of the turgor pressure and a water economizing effect due to potassium.

The further result of the experiments described, viz., that sodium is equally absorbed and secreted by the living cells as is potassium, but in considerably smaller quantities, should prove that sodium has only a low acid neutralizing effect within the living cells. The well known fact that no plant growth is possible when only sodium is supplied and potassium is lacking, and that in the presence of potassium, sodium has at the best only an additional effect on plant growth, is also in conformity with the above observations.

The mostly acidoid materials of the intermediate metabolism represent not only the products that are necessary for the formation and decomposition of carbohydrates, but they are also necessary for these processes in proteids as they can be transformed by ammonia to amino-acids. Therefore, the protein metabolism also depends on the concentration of acids of the intermediate metabolism and consequently on the supplied quantities of potassium. Nitrogen deficient plants, in consequence, contain larger quantities of carbohydrates (" carbonaceous plants ") whereas with a surplus of nitrogen, larger quantities of amino-acids are formed and partly transformed to proteids (" proteinaceous plants ") (61, 62). Thus, the well known agricultural experience becomes comprehensible that with sufficient supply of potassium to the plants, the contents of sugar in sugar beets, of starch in potatoes and cereals, and of cellulose in fibre plants are increased. The increased stability of stalks of cereals after sufficient potash supply is likewise due to an increased storage of cellulose and might thus be explained.

The synthesis of polysaccharides and proteids requires especially large quantities of energy (62) for thermodynamic reasons, because of the regular formation of such big molecules. These quantities can only be forthcoming from the esters of phosphoric acid rich in energy. As their formation takes place from the materials of intermediate metabolism, and the concentration of the latter depends on the potassium supply, the well known fact might thus be explained, viz., that with potassium efficiency the formation of polysaccharides and proteids with large quantities of molecules is lowered and oligosaccharides and amino-acids are accumulated in the plants.

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SESSION 4

THE LIMING PROBLEM

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Introduction

Soil reclamation by liming has been known among farmers for centuries. The object of such a reclamation is to increase productivity of the land in question and it is a well-established fact that this in many cases is possible and that the increase in crop production is often very considerable.

The labour and money spent on liming are generally considered sound investments and in many countries are subsidized by the State.

It is, however, also a fact that often repeated or too heavy application of lime on certain soil types may cause severe injuries to crops and a decrease in soil fertility. Liming, as many farmers know from experience, is not always beneficial but may be just the opposite.

This point was emphasized when ÅSLANDER (1) a few years ago claimed that liming of ordinary soils should in no case be necessary; that crops like barley, alfalfa and sugar beets generally recognized as calceophile would develop satisfactorily even on soils very deficient in lime, if only the common fertilizers were supplied in suitable quantities and proportions; further, that since liming in many cases has proved to be directly harmful, this kind of soil reclamation should be immediately abandoned and considered rather as a non-justified taxation upon farmers for the sole benefit of lime manufacturers.

Even if this will not be true in general it seems well worth while to consider whether labour and money spent on liming could just as well be saved. In doing so, we will summarize a few important facts about the liming problem. Let us first consider

Definition and Causes of Lime Deficiency

We speak about lime deficiency if crop production may be increased by adding lime to the soil in question. Lime in this connection usually means calcium carbonate ($CaCO_3$), slaked lime ($Ca(OH)_2$) or burnt lime (CaO).

These compounds are all bases showing the characteristic properties of such substances, i.e., the ability to fix hydrogen ions when placed in certain mediæ (neutralization). A non-basic calcium compound like the sulfate ($CaSO_4$) has not this ability and will hardly in any case be of benefit to crops when spread on and mixed with the soil.

This leads to the assumption that the effect from liming is not simply nutritional caused by the calcium ion Ca^{++}. Logically, then, it must be due to the basic properties of the liming materials, and here the term *soil acidity* comes into the picture.

Acid soils, as we all know, occur commonly and are widespread over large areas. Their acid properties may easily be demonstrated by simple chemical methods, such as the litmus test, and by measuring the pH-value in an aqueous soil suspension. In districts where acid

soils are common, the pH, roughly speaking, shows variations between 4 and 8.

Soil acidity in nature is a result from leaching of the upper soil layer by rain water moving downward under the influence of gravity. (In places where no appreciable leaching takes place carbonates formed by weathering tend to accumulate near the surface, forming alkali soils). In its downward movement, the water takes up acids—chiefly carbonic—produced by plant roots and by microbial decomposition of plant residues in the root zone and the humus layer. This reaction may be visualized by the scheme

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO^-_3$$

From this it appears, that in a climate where the total evaporation is considerably less than the rainfall, the reaction will be directed from left to right, new carbonic acid and hydrogen ions being steadily produced.

In calcareous soils hydrogen ions react with calcium carbonate, according to the scheme

$$H^+ + CaCO_3 \rightleftarrows Ca^{++} + HCO^-_3$$

This reaction also goes on in the direction towards right, the soil thereby being gradually depleted of its content of calcium carbonate which is moved from the layers closest to the surface down below the ground water table as dissolved calcium bicarbonate.

As long as the soil still contains $CaCO_3$ in appreciable quantities, this substance acts as a buffer, preventing the reaction in the soil solution from turning decidedly acid.

BJERRUM and GJALDBÆK (2), nearly 30 years ago, demonstrated experimentally that the H-ion concentration in systems of water, calcium carbonate and carbon dioxide, when equilibrium has been established, will be determined by the formula

$$[H^+] = K \sqrt{pCO_2} \cdot \sqrt{Ca^{++}}$$

The numerical value of K when pCO_2 is expressed in atmospheres was found to be $10^{-5.02}$ at room temperature, i.e., 18°C. From this and from available solubility data pH may be calculated as a function of the carbon dioxide pressure pCO_2 and the molar calcium ion concentration $[Ca^{++}]$. Results from such calculations are given in Table 1.

TABLE I. Relationship between pCO_2, $[Ca^{++}]$ and pH in aqueous suspensions of calcium carbonate

pCO_2 at.	$CaCO_3$ in solution g per l	$[Ca^{++}]$	pH
0·0003	0·060	0·0015	8·3
0·0030	0·130	0·0032	7·9
0·050	0·361	0·0093	6·9
0·555	0·865	0·0217	6·2
1·000	1·008	0·0252	6·0

The figures show that an aqueous suspension in equilibrium with the normal atmosphere (pCO_2=0.0003 at.) will attain the pH-value 8·3 ; further, that the reaction in such systems will change in the acid direction with increasing CO_2-pressure, ending at pH 6 in an atmosphere consisting of pure carbon dioxide.

We may, therefore, expect in calcareous soils from which appreciable leaching takes place to find a slightly alkaline to neutral or slightly acid reaction depending upon fluctuations in CO_2-pressure and in their content of soluble calcium salts. This agrees very well with facts observed. We may further expect that $CaCO_3$ under such conditions, if present in the parent material, will now have disappeared from the upper horizons and will be found in the C horizon some distance below the surface.

This also agrees well with the observed facts. Where acid soils dominate, $CaCO_3$ is not a normal soil constituent but is very frequently found a few feet below the surface. Only in localities where the parent material has been highly calcareous (limestone) and where soil formation has not yet reached maturity, will this compound still be present.

Water that has been leaching through non-calcareous soils may contain appreciable quantities of dissolved calcium bicarbonate and show a neutral or slightly alkaline reaction. In such cases the calcium ions are generally assumed to have originated by an exchange reaction between H-ions and Ca-ions, the seat of which is the surface of the organic and inorganic colloidal particles found in varying quantities in all soils.

The mechanism of that reaction is not well known, but it may, as is often done, be conveniently pictured by the scheme

$$\begin{matrix}\mathrm{Ca}\\ \mathrm{Ca}\\ \mathrm{Mg}\end{matrix}\Big[\ \mathrm{Colloid}\ \Big]\begin{matrix}\mathrm{Ca}\\ \mathrm{Ca}\\ \mathrm{Ca}\end{matrix} + 2\mathrm{H}^{+} + 2\mathrm{HCO}_3^{-} \rightleftharpoons \begin{matrix}\mathrm{Ca}\\ \mathrm{Ca}\\ \mathrm{Mg}\end{matrix}\Big[\ \mathrm{Colloid}\ \Big]\begin{matrix}\mathrm{Ca}\\ \mathrm{Ca}\\ \mathrm{H}\\ \mathrm{H}\end{matrix} + \mathrm{Ca}^{+} + 2\mathrm{HCO}_3^{-}$$

which may serve as a useful working hypothesis.

According to this, H-ions from carbonic acid replace Ca from the surface of the ultramicroscopic colloids, calcium bicarbonate at the same time being formed. While the reaction goes on towards the right, calcium (and also magnesium) is gradually carried away dissolved in the drainage water as bicarbonate and hydrogen ions accumulate on the surface of the soil colloids.

When, according to the scheme, all " bases " have been removed in this way, the soil is said to be entirely base desaturated and has turned acid showing a pH-value around 4 and contains a reserve of dissociable hydrogen in the colloidal complex.

If soils are left uncultivated in such a state, the colloidal complex will gradually disintegrate, forming aqueous sols and slowly move downwards. The distance moved is ordinarily not great. Flocculation and precipitation take place and may cause the formation of hard pan. In this way the characteristic podsol profile develops with raw humus, bleached sand and hard pan layers.

If the soil is under cultivation, mature podsol profiles will not develop, but even so, drastic changes in its chemical properties

will result from leaching. It is quite evident that such changes may cause equally drastic changes in the soil's properties as a growth medium for the macro- and the microflora. Exchangeable calcium, magnesium, potassium and other important plant nutrients move away from the root zone. *Strongly leached soils are poor soils, containing but little available plant food.*

By deflocculation and breaking down of the colloidal complex, perhaps also by exchange reactions, iron, aluminium and manganese will pass into the ionic state. This is injurious to crops, because aluminium and manganese in small concentrations are toxic, in part directly and in part by disturbing the ionic balance in the soil solution or by rendering soil phosphates immobile and unavailable.

Changes in reaction, salt content and the ionic balance will greatly affect the soil's micropopulation and a number of highly important microbial processes, for instance those of the nitrogen cycle. In the most acid soils found, nitrification is very limited, and even a less acid reaction will favour the growth of soil fungi and depress bacterial action. For many reasons this is undesirable, among others because some of the fungi are parasites and may cause soil-borne diseases such as " black leg " in sugar beets and " finger and toe " in turnips.

Reduced microbial activity, caused by leaching and soil acidity, will often manifest itself in slow decomposition of manure and plant residues. Under such conditions the original structure of these materials may be distinguished over a long period, while peat-like humus particles are formed, indicating that mineralization and production of plant nutrients are also slow.

Adsorbed calcium, and calcium ions in the soil solution, keep colloidal clay in a flocculated state, thereby making heavy soils friable, more permeable to water and easier to handle than soils of a similar type, poor in adsorbed calcium and with a pronounced acid reaction.

(Adsorbed sodium is known to have a strong deflocculating effect upon colloidal clay. If adsorbed calcium in such soils is replaced by sodium, for instance by accidental flooding with sea water, they become nearly impervious, and will, when drying out, form a hard, stony crust. Sodium (alkali) clays, as already mentioned, occur commonly in areas where no appreciable leaching takes place ; the sodium ions here originate from slow chemical decomposition of felspars.)

There is little evidence that crops are affected directly to any large extent by hydrogen ions in the soil due to leaching, as described in the foregoing. H_2CO_3 is a weak acid showing in saturated solution, ($pCO_2=1$), pH around 4, the same value as found in soils where displacement of calcium by hydrogen is nearly complete.

The quantity of strong acids such as HNO_3 and H_2SO_4 produced in soils by micro-organisms is small compared to that of H_2CO_3, and their production will ordinarily cease before the buffering power of the soil has been diminished to such an extent, that they may accumulate and cause a strongly acid reaction.

Under certain conditions, however, such large quantities of sulfuric acid may be produced from sulfides by microbial oxidation, that the acid itself will accumulate and soil reaction turn strongly acid, with pH-values lower than 1, killing completely all vegetation on the spot. This happens rather frequently on low, newly-drained, formerly-

flooded areas from which the water has been pumped away. This acid is most likely to be produced by the sulphur bacterium Thiobacillus thio-oxidans which tolerates a high degree of acidity.

According to the statements above, it should be justifiable to assume that the cause of lime deficiency is leaching by which " bases," primarily calcium, in the adsorbing complex are displaced by hydrogen. This gradually changes the chemical properties of the soil, rendering it a less suitable growth medium for higher plants and micro-organisms. The resulting slightly acid reaction is probably not directly harmful to crops, but it depresses bacterial decomposition of organic materials, thus limiting the production and uptake of important plant nutrients.

Strongly leached and acid soils contain dissolved aluminium and manganese in quantities toxic to crops, whereas in slightly acid or neutral soils these elements are much less soluble and non-toxic.

The most logical way of correcting those defects seems to be a neutralization of the soil acidity by liming.

The Neutralization Process. Effects from Liming

When finely ground limestone is mixed with an acid soil, reactions pictured by the following schemes may take place :

$$\left[\text{Colloid}\right]\begin{matrix}\text{H}\\\text{H}\\\text{H}\end{matrix} + CaCO_3 \rightleftarrows \left[\text{Colloid}\right]\begin{matrix}\text{H}\\\text{Ca}\end{matrix} + H_2O + CO_2$$

$$\left[\text{Colloid}\right]\begin{matrix}\text{H}\\\text{H}\\\text{H}\\\text{H}\end{matrix} + 2CaCO_3 \rightleftarrows \left[\text{Colloid}\right]\begin{matrix}\text{H}\\\text{H}\\\text{Ca}\end{matrix} + Ca^{++} + 2HCO_3^-$$

In strongly leached soils with pH about 4 the first reaction will predominate. In less acid or neutral soils the reaction proceeds according to the second scheme. In both cases a neutralization takes place, i.e. dissociable hydrogen is removed from the surface of the colloids, being replaced by calcium. Hydrogen ions are fixed in the bicarbonate ion HCO_3^- while soil reaction changes in the alkaline direction. Part of the calcium goes into solution and will not be adsorbed by the colloids but will be leached away as bicarbonate.

If sufficient $CaCO_3$ is added, the reaction reaches a state of equilibrium in which the pH of the system is about 8, i.e. the originally acid soil, poor in adsorbed calcium, has been converted into a calcerous soil showing its characteristic properties.

If $Ca(OH)_2$ is added instead of $CaCO_3$ the reaction takes the course

$$\left[\text{Colloid}\right]\begin{matrix}\text{H}\\\text{H}\\\text{H}\end{matrix} + Ca(OH)_2 \rightarrow \left[\text{Colloid}\right]\begin{matrix}\text{H}\\\text{Ca}\end{matrix} + 2H_2O$$

Here, also, dissociable hydrogen is replaced by calcium, while instead of bicarbonate, water is formed in the neutralization process.

When using an excess of $Ca(OH)_2$ the system turns strongly alkaline with pH about 12·5, the same as that of a saturated $Ca(OH)_2$ solution. This, however, is only temporary, since $Ca(OH)_2$ will soon be con-

verted into $CaCO_3$ by the reaction $Ca(OH)_2+H_2CO_3 \rightarrow 2H_2O+CaCO_3$. carbonic acid always being present in the system. When this reaction is complete, the system will be identical with that resulting from the addition of a calcium carbonate surplus and its pH-value has dropped to about 8. That figure represents the final maximum pH-value obtainable in a soil by adding to it lime in any form and quantity. It seems, therefore, natural to use it for the definition of base saturation and base saturation degree, in connection with liming problems.

It has been stated that soil acidity is not chiefly due to exchangeable hydrogen ions, but rather to exchangeable aluminium ions Al^{+++} from the clay colloids. In an aqueous system this ion will always be hydrated with six firmly bound water molecules to $Al(H_2O)_6^{+++}$. This hydrate is an acid of the same strength as acetic acid and requires lime for neutralization. Therefore it makes no practical difference which of the two theories is accepted.

Neutralization by liming changes drastically the properties of an acid soil. Its hydrogen ion concentration will be greatly reduced. Aluminium and manganese precipitate, and their concentrations in the soil solution are so diminished that their toxic effects disappear. An increased bacterial activity will result from the reduced acidity, causing a more rapid decomposition of organic residues, accompanied by the formation of ammonium salts, nitrates, phosphates and other plant nutrients. Simultaneously the CO_2 production increases, making soil water a more active solvent than before, which again makes difficultly soluble minerals available to crops.

By the breakdown of organic residues under such conditions, a neutral structureless humus is produced which improves the structure of clayey soils. On heavy clays the structural improvement may be very pronounced, and is here chiefly caused by the flocculating effect upon clay colloids of the increased calcium ion concentration. Liming also, as shown by numerous field experiments, increases the availability of soil phosphates to plants. The mechanism of that process is not known in detail.

It is unlikely that such changes can be brought about only by the addition of comparatively small amounts of neutral salts in ordinary fertilizers. We may, therefore, conclude that liming in certain cases *is* necessary for the maintenance of soil fertility.

There can be no doubt that a suitable liming will improve growth conditions on many acid soils and increase their productivity. The increase in production as we know from field experiments may amount to 10–20% or even more. This means an increased consumption of plant nutrients, and that the crops, more than hitherto, will draw upon the soil's natural supply of these nutrients.

Therefore, in order to obtain full benefit from liming, it will always be necessary, in addition to lime, to add suitable quantities of fertilizers. If this rule is neglected, liming may gradually deplete the soil of plant nutrients and decrease its fertility. In such cases a renewed liming will be useless. Liming alone cannot replace the ordinary fertilizers, but it enhances their effect.

On the other hand a liberal supply of fertilizers to acid, lime deficient soils, may partly conceal the more common symptoms of that defect but will not remove its primary cause.

Overliming

Application of too much lime may on certain soil types lead to a decrease in fertility and sometimes to complete crop failure. In such cases we speak of *overliming*. These cases occur most frequently on humus sand and are usually accompanied by a characteristic change in structure, i.e. ability to form crumbs being lost so that the soil, when dry, turns into a powderlike dusty material.

The—often severe—injurious effect from overliming is due to demobilization of micro-elements such as manganese, copper, zinc, boron and perhaps others. This demobilization is presumably caused by the change in reaction together with an increased decomposition of the soil's organic material.

Injury to crops from overliming may be compensated for by direct application of the micro-element in question (manganese and copper sulfates, borax) and by the use of an acid fertilizer such as ammonium sulfate. Alkaline fertilizers as calcium cyanamide or basic slag must be avoided on all soils that have shown signs of overliming.

Detecting Lime Deficiency

Lime deficiency and soil acidity may be detected in different ways, by direct field observations and by chemical tests applied to soil samples.

The "lime status" of the soil is an important ecological factor, to some extent determining the distribution of wild plant species in nature. Among the weeds in our cultivated fields some species are most commonly found on acid soils, while others dominate on neutral or slightly alkaline soils.

Among cultivated plants in agriculture, sugar beet, barley and alfalfa are known as sensitive to lime deficiency, while potatoes, rye and lupines grow well on soils deficient in lime and with an acid reaction. Frequent occurrence of weeds of acid tolerant species in connection with poor growth of barley, beet roots and alfalfa on a soil, are strong indications of lime deficiency.

The most widely used chemical test is pH-determination on soil samples, made either in field or in laboratory. The last procedure seems preferable, since the necessary outfit for field work usually is slow to operate and difficult to handle.

The pH-measurements may either be carried out in aqueous suspensions or with the soil suspended in neutral salt solution, the first mentioned method being the more common. When measured in a salt solution, for instance 1M KCl, pH will generally be about one unit lower than the corresponding value from an aqueous suspension. This is due to exchange reactions of the type

$$\left[\text{Colloid}\right]\begin{matrix}\text{H}\\\text{H}\\\text{H}\end{matrix} + \text{K}^+ + \text{Cl}^- \rightleftharpoons \left[\text{Colloid}\right]\begin{matrix}\text{H}\\\text{H}\\\text{K}\end{matrix} + \text{H}^+ + \text{Cl}^-$$

or perhaps to displacement of acid reacting hydrated aluminium ions $Al(H_2O)_6^{+++}$. When using pH-measurements in the diagnosis for lime deficiency, it should always be stated whether they took place in pure water or in a neutral salt solution.

pH, Base Saturation Degree and Adsorbing Capacity

There is a rather simple relationship between soils' pH and their base saturation degree. According to HISSINK (3) $V=\frac{S}{T}.100$ where S designates milliequivalents of adsorbed bases (Ca+Mg) per 100 g. of dry soil and T the total adsorbing capacity (Ca+Mg+H), expressed in the same way.

In a large number of Danish soils, *the pH-value measured in an aqueous suspension was found to be a linear function of their base saturation degree* (4). Results of such measurements are shown in Fig. 1. This means that when pH is measured we know approximately the soil's base saturation degree. If T is also known, the quantity of lime which the soil must adsorb per weight unit for a certain rise in its pH, may be calculated.

(The above measurements were carried out according to the method proposed by BRADFIELD and ALLISON (5). In this the base saturation

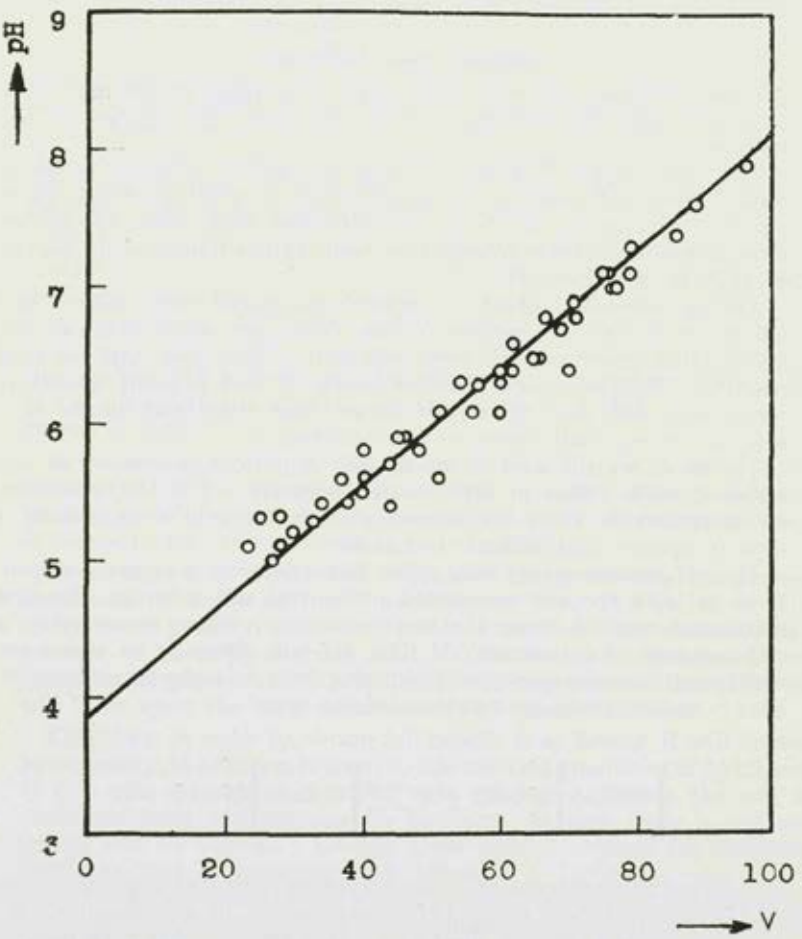


Fig. 1—pH-values and base saturation degree for 50 Danish soils.

degree differs from that of HISSINK on the point that V is arbitrarily fixed to 100% when the soil has been brought to equilibrium with an excess of $CaCO_3$ and a CO_2 pressure of 0·0003 at.).

The T-values (base exchange capacity at pH8·3) found in 50 clay loams varied between 10 and 63 increasing with their content of colloidal material. For most soils, T seems to be nearly constant, independent of its base saturation degree. In soil samples from a field experiment with increasing amounts of lime the figures seen in Table 2 were found. Lime was applied in 1921, the samples for investigation being drawn in 1934.

TABLE 2. S- and T- values in samples from a field experiment with increasing lime quantities

Lime application tons/ha.	Milliequivalents per 100 g soil				
	H^+	Ca^{++}	Mg^{++}	S	T
0	9·00	1·22	0·43	1·65	10·65
2	8·60	1·46	0·40	1·86	10·46
4	8·35	1·89	0·33	2·22	10·57
8	7·65	3·18	0·19	3·37	11·02
16	4·95	5·30	0·13	5·43	10·25

The adsorbing capacity (base exchange capacity), therefore, is an important soil characteristic. Contrary to the pH-value, it expresses a long lasting property and seems well suited for soil characterization. It may be determined in different ways and the pH-value, indicating full saturation, arbitrarily fixed. The point of neutrality, pH=7·0, is for convenience most frequently used. Since soils may adsorb considerable lime quantities above pH 7, it seems logical to select the value 8·3 to represent full base saturation.

Lime Quantities to be Applied

The ability of a soil to combine with basic lime compounds may be determined in the laboratory, for instance through its T-value or by titration with lime water and construction of the base titration curve.

From such figures, and from the volume weight of the soil, the lime quantities necessary for a definite change in "lime condition" may be estimated with reasonable accuracy. In practice, however, it would always be necessary to use appreciably more lime than the theoretical amount in order to reach the condition desired. This is because only a fraction of the calcium mixed with the soil as carbonate will be fixed by the soil colloids while the rest dissolves and is leached out as bicarbonate.

The figure by which the quantity theoretically found should be multiplied in order to obtain the desired change in soil reaction (the liming factor) is usually 1·5–2·5, the highest value being found in slightly acid soils. Lime will here be utilized to a smaller degree in the neutralization process than on more acid soils.

The most desirable lime condition in each case may not be found by any laboratory method but only by field experiments with increasing amounts of lime applied to different soil types. Such experiments have

been going on in Denmark for many years, and from the results gathered, the following advice is usually given to our farmers: Heavy soils cultivated chiefly with calceophile crops must be limed close to the saturation point, pH 7·5–8·0, clay loams to 7·0–7·5 and sandy clays to 6·5–7·0. In humus-sands pH 6·0–6·5 will be enough, and if manganese deficiency is to be expected, pH must be kept below 6 which, according to the above definition, corresponds to about 50% base saturation.

On newly-drained high-moor peat and meadows the symptoms of lime deficiency usually disappear after the application of relatively small lime quantities even if pH, on account of the high adsorption capacity, is not raised appreciably. pH-values of 5·0–5·5 will in such cases usually suffice.

In each separate case the necessary lime quantities are deduced from the pH-value of the soil and its lime adsorbing power. The adsorbing power may be determined indirectly from lime titration curves, but in most cases it is only estimated from the clay and humus contents. The quantity will, in nearly all cases, fall between 5 and 15 tons $CaCO_3$ per ha and in most cases below 10 tons per ha. On strongly acid heavy soils in the North Sea marshes, containing about 60% clay, it has in a few localities been necessary to use as much as 40 tons $CaCO_3$ per ha, in order to secure full crop production.

Liming Material and its Application

Materials used for liming must show such properties that the reaction between lime and the soil colloids proceeds quickly enough to secure full effect within a reasonable time.

If, as in most cases, calcium carbonate is used for correcting lime deficiency, this reaction takes place between solid particles with the soil solution as a medium. Its velocity will increase with increasing size of the reactive surface area per weight unit of calcium carbonate. This area depends upon the particle size of the carbonate and the extent to which it may be intensively mixed with the soil to be limed.

Since this area is inversely proportional to particle diameter, the active substance must be present in a finely subdivided state, and the liming material be of such a consistency that in suitable moist condition it is readily mixed with the soil.

In most varieties of marl, calcium carbonate is present in very small particles. Therefore, when marl is used as a liming material, neutralization will occur rapidly and be effective, provided a thorough mixing of marl and soil can be secured.

Different varieties of limestone show large differences in particle, size and mixability. Soft porous forms like chalk may be used directly from the pit without grinding, since they rapidly disintegrate and crumble under the influence of rain, frost and thaw.

A well-hardened compact limestone must necessarily be ground before it is used as liming material. The degree of fineness required is non-predictable. Information on that point must be gained from field experiments with lime of various particle size.

In a series of Danish field experiments with ground limestone, divided in fractions of different particle size, the fraction which was smaller than 0·5 mm. had raised the pH of the soil two years after the application decidedly more than the coarser fractions. After

four years, only a slight difference in effect was found for the fraction up to 2 mm. The coarsest fraction (2–3 mm.), however, was much less effective in neutralizing soil acidity.

Pot experiments, carried out earlier with ground limestone of different origins and divided into two fractions, one smaller than 0·5 mm. and the other 1–2 mm., had shown no clear indication of a better effect from the finer fraction (6). Similar results have recently been reported from U.S.A. (7, 8). The experiments, then, seem to indicate that extreme fineness is not required in ground limestone to be used as a soil amendment.

Slaked lime $Ca(OH)_2$ in a suitable moist condition is a dust-like material and much more soluble in pure water than is $CaCO_3$. Therefore we might expect this to be the ideal substance for neutralization of acid soils. When that material was compared with ordinary ground limestone in a series of Danish field experiments, no difference in effect was observed, either on soil or in crops (9, 10). The same has been found in Norwegian experiments.

This was probably due to the above-named fact that calcium hydroxide, when spread in thin layers, will rapidly be converted into carbonate by the action of atmospheric carbon dioxide and will then act as finely-ground limestone.

Under all conditions, a thorough mixing of soil and liming material is necessary for a rapid neutralization (11). This may be secured by spreading lime or marl late in fall on top of the winter furrow. When, next spring, the soil is suitably dry for cultivation it is worked down by repeated harrowing, eventually followed by ploughing.

If lime is applied to pastures where no cultivation is possible the liming material remains on the surface for a long time and neutralization will be very slow.

How often should Liming be Repeated? Rate of Leaching

Liming usually aims at a long or a permanent soil reclamation. The latter, however, is not obtainable, since lime and other bases are continuously being leached away from the root zone. The rate of leaching depends upon different factors, such as precipitation, infiltration, the permeability of the soil to water, CO_2-production, the quantities and kind of the fertilizers used and so on.

It is, therefore, not possible in each single case to predict how long the effect from a liming will last. The annual loss by leaching will reach maximum in well-drained calcareous soils, easily permeable to water, in which extensive decomposition of organic matter takes place. Under such conditions the content of dissolved calcium bicarbonate in drain water may easily correspond to 0·5g $CaCO_3$ per litre. If the annual leaching amounts to 200 litres per square meter (200 mm.) water will remove $0.5 \times 2 \times 10^3 = 1000$ kg $CaCO_3$ from one hectare each year. The magnitude of this figure agrees well with those found in various places by lysimeter experiments under similar conditions.

In a series of Danish field experiments (12), where increasing amounts of lime were used on acid soils, it was found that *the annual loss by leaching was directly proportional to the lime quantities applied* (4). Results from one of these experiments are shown graphically in Fig. 2. The field experiment was laid out on an acid, sandy, easily-

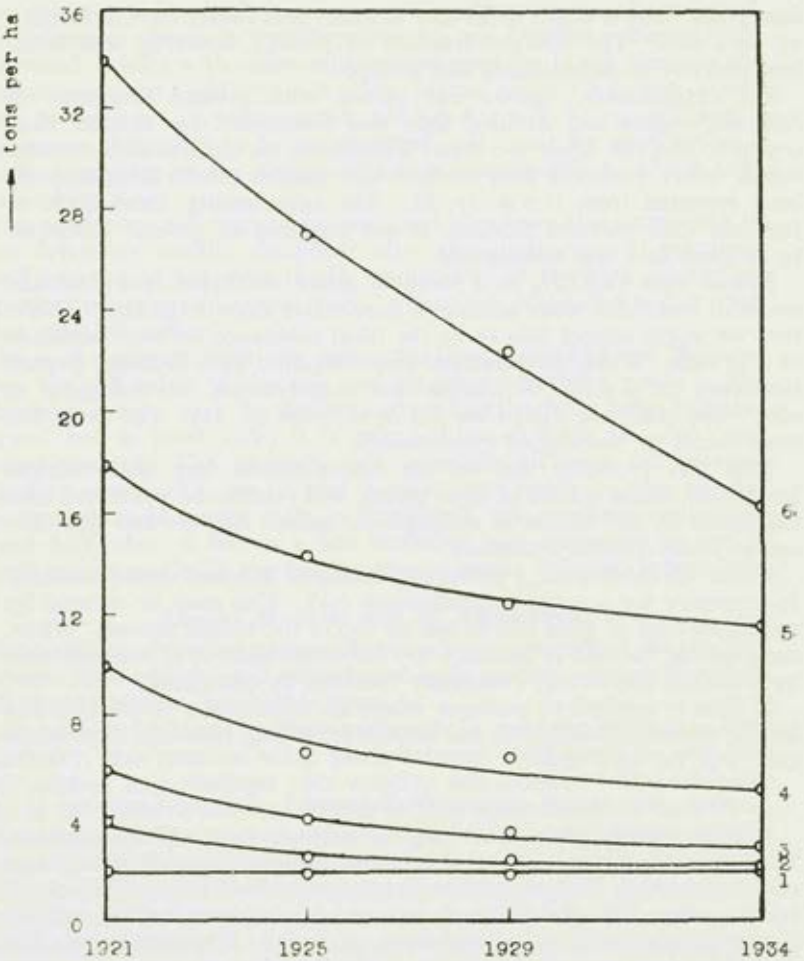


Fig. 2—Lime content in the upper 20 cm in the years 1921-34. 1) Unlimed. 2) 2 tons $CaCO_3$ per ha. 3) 4 tons $CaCO_3$ per ha. 4) 8 tons $CaCO_3$ per ha. 5) 16 tons $CaCO_3$ per ha. 6) 32 tons $CaCO_3$ per ha.

permeable soil in 1921; samples for analysis were drawn in 1925, 1929 and 1935. In the diagram the lime content of the soil adsorbed and as carbonate is plotted against time. In 1929, $CaCO_3$ had practically disappeared from all the plots except from the most heavily limed.

The shape of the curves shows that leaching proceeds with decreasing velocity while the soil is gradually being depleted of its base content; further, that on the unlimed plot (pH 5) a decrease in the soil's content of adsorbed calcium is hardly detectable over a period of 13 years.

Fig. 3 shows the leaching loss over the entire period of 13 years from the differently limed plots. As mentioned above, this is directly

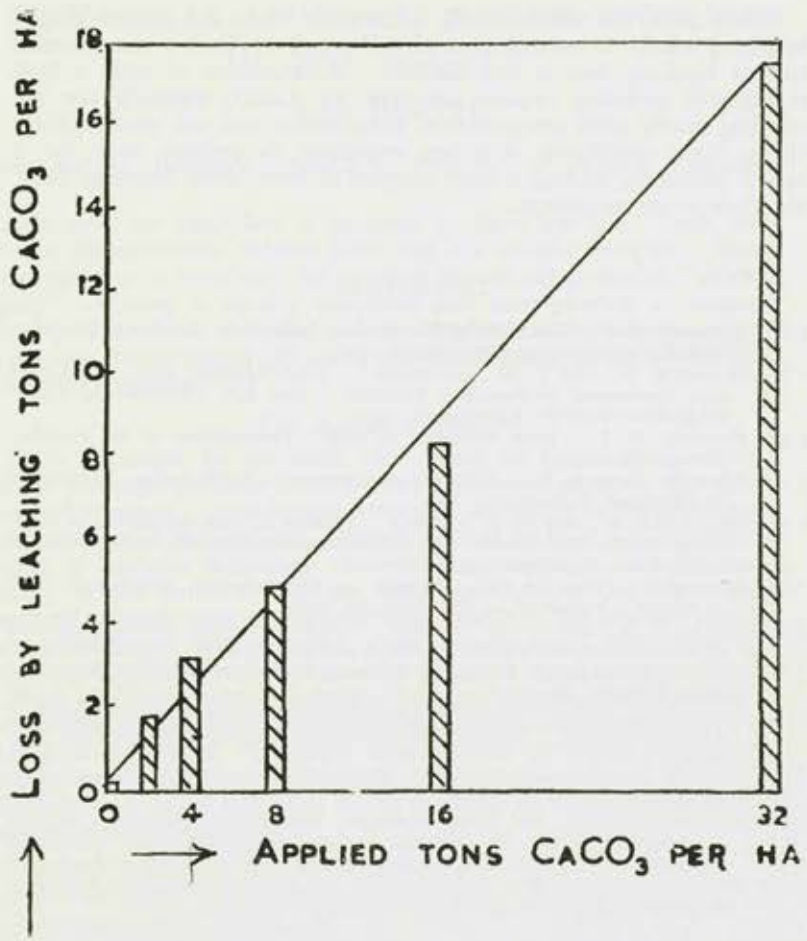


Fig. 3—Leachings over a 13 years period from differently limed plots in an acid sandy soil.

proportional to the lime quantities applied, averaging 1400 kg. $CaCO_3$ per ha annually from the most heavily limed plot.

Nearly one-third of the lime, which had disappeared from the upper 20 cm. of the soil, was found in the layer 20–40 cm., but very little in the layer 40–60 cm.

From the above statements we draw the following conclusions: Sandy soils, upon which calceophile crops are grown to only a small extent, may be kept at a favourable lime condition by small applications of lime at not too long intervals, for instance, once in the rotation. Applying large quantities of marl or limestone in order to reclaim such soils for many years to come is not advisable, since crop injuries from over-liming may occur and a large part of the lime applied will be lost by leaching. At pH 6, or below, that loss will only be small.

Heavy soils, on which chiefly calceophile crops are grown, should be limed nearly to saturation with pH 7·5–8·0. Then a considerable annual leaching loss is unavoidable. Maintenance of such a lime status will probably require 500–1000 kg. $CaCO_3$ annually per ha, varying chiefly with precipitation, evaporation and soil permeability. Under these conditions, it is less expedient to reclaim soils for a longer period by adding a large surplus of lime, since leaching, here, lies close to its maximum.

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SESSION 4

A BIOLOGICAL APPROACH TO THE PROBLEMS OF SOIL ACIDITY

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Acid soils are identified in practice by their low pH. Such soils have a characteristic natural flora and are usually infertile. Many crops growing in them may fail or show typical symptoms of "acidity injury". Liming is usually beneficial and may provide a complete control. The effects of liming may be complex and include the supply of calcium, correction of pH and a resultant change in the availability of several elements.

The Acidity Complex

Early attempts to elucidate the causes of failure concentrated mainly on single possible factors. Detailed visual study of the plants was seldom made. Considerable attention was given to the aluminium concentration in various soil extracts. Other factors, e.g. manganese excess or calcium deficiency received less emphasis, and the complexity of the problem was not appreciated. On the other hand chemical analysis may not satisfactorily indicate the relative importance of different factors which show simultaneous differences and some e.g. aluminium are not readily assessed by chemical means.

Work was begun at Long Ashton in 1945, using a new approach to the problem. In this method the respective crop plants served as biological indicators. Detailed observations of visual symptoms, already successfully applied to the diagnosis of mineral deficiency disorders (32), were extended to an analysis of the possible factors causing injury in acid soils.

The factors likely to be encountered may be summarized thus:

1. Direct injury by hydrogen ions (low pH).
2. Indirect effects of low pH.
   - (*a*) Physiologically impaired absorption of calcium, magnesium and phosphorus (1).
   - (*b*) Increased solubility, to a toxic extent, of aluminium, manganese, and possibly iron and heavy metals.
   - (*c*) Reduced availability of phosphorus partly by interaction with aluminium or iron, possibly after absorption.
   - (*d*) Reduced availability of molybdenum.
3. Low base status.
   - (*a*) Calcium deficiency.
   - (*b*) Deficiencies of magnesium, potassium or possibly sodium.
4. Abnormal biotic factors.
   - (*a*) Impaired nitrogen cycle and nitrogen fixation.
   - (*b*) Impaired mycorrhizal activity.
   - (*c*) Increased attack by certain soil pathogens e.g. "club-root".
5. Accumulation of soil organic acids or other toxic compounds due to unfavourable oxidation-reduction conditions.

Experimental

Methods

A wide range of important crop plants were grown in sand cultures. The levels of calcium, manganese, aluminium and phosphorus supplied were varied singly or factorally, and the effects were tested in some instances at different pH values. Calcium carbonate was used in some experiments as an alternative to the use of soluble calcium compounds. Molybdenum deficiency was also studied in several crops in relation to soil acidity problems.

The concentrations of calcium varied from almost nil to 200 p.p.m. (10 m.eq./L). Those of phosphorus ranged from 10—40 p.p.m. (1—4 m.eq./L). Aluminium was given at various ratios to phosphorus, up to 54 p.p.m. (6 m.eq./L). Manganese was tested at levels between 13·5 and 660 p.p.m. (0·25—24 m.eq./L) and usually at 27·5—81 p.p.m. pH values were normally 5·5—6·0 or 3·5—4·0 initially but were not closely maintained except by daily addition of nutrient solution. The nutrient solutions contained all elements including micro-nutrients known to be essential unless purposely omitted, and nitrogen was usually given as nitrate.

The levels of molybdenum in the deficiency tests were 0·000005 and 0·00005 p.p.m.; the latter was produced by addition of an appropriate amount of molybdenum to a highly purified medium.

The techniques used to provide suitable containers, sand, water and reagents are given in detail elsewhere (12) and summarized later in Volume II.

The visual behaviour of the respective crops and their relative growth under the different experimental conditions were recorded, and colour photography was extensively used. Results were compared carefully with the behaviour of crops in acid soils and especially with those grown in field trials by Dr. PLANT, and described elsewhere in Volume II.

Results

Effects of low pH. Sugar beet, cauliflower, savoy cabbage, swede, oat, barley and potato, were not appreciably affected by pH values of 4·5 in the nutrient solution as applied, but the plants usually caused the pH to rise to 5·5—6·0. In a few instances, nutrient solutions with pH values as low as 3·5 were applied. Under these conditions sugar beet was the first to show injury; cauliflower was next in sensitivity. Except for a tendency to chlorosis or red tinting of leaf margins in sugar beet no symptoms suggestive of the acidity complex were observed. Controlled pH values of 4·5 or over are often tolerated by culture plants (2), (8).

Calcium deficiency. Calcium deficiency symptoms were produced in a wide range of crops. Symptoms frequently included wilting, either in young leaves or petioles of cauliflower, or in pedicels and shoots at flowering time e.g. in flax, pea, clovers and lucerne. Marginal browning, tip burn, forward or backward folding of young leaves or leaflets, often producing a hooked appearance near the leaf tip, and death of the growing point were typical in Brassicas, potato, tomato, sugar beet and celery. Cereals were particularly resistant and only showed chlorotic rolled terminal leaves or tip die back with severe deficiency.

Field acidity symptoms apparently due to calcium deficiency most commonly appear in potato (34), where tubers may be irregular, or seed tubers may also show die back of the shoots (33). Calcium deficiency may occur in sugar beet when magnesian limestone is used instead of carboniferous limestone. "Wither tip", in flax, a wilting of the shoots at flowering, is also found in acid soils (20) and wilting may also occur in clovers. Leaf wilt and tip hooking have been recorded in cauliflower plants in acid soils and an isolated instance of failure of tomato plants in an acid soil was identified as calcium deficiency. These symptoms have not been found in cereals in acid soils.

Manganese toxicity. Most Brassicas were highly susceptible to injury by excess of manganese. Marrowstem kale and swede were most sensitive, followed probably by cauliflower, savoy cabbage and Brussels sprouts, whilst rape and hungry gap kale were relatively insensitive. Symptoms included leaf marginal cupping, marginal and intervenal mottling or chlorosis and necrotic spotting. French beans showed intervenal white or yellow chlorosis and profuse brown necrotic spotting.

Potatoes showed black necrotic stem streak, profuse leaf spotting and leaf drop. Tomatoes developed leaf vascular necrosis, leaf drop and dark brown stem lesions mainly around leaf bases. Barley showed brown necrotic streaks on the leaves. Celery, oat, carrot,



Plate 1a

Manganese excess as the soil acidity factor in kidney beans. White blotches, followed by intervenal chlorosis, necrotic spotting and later distortion.

flax and especially sugar beet were relatively tolerant to manganese toxicity.

In acid soils, symptoms resembling manganese toxicity have been identified commonly in French beans, whose susceptibility has been independently confirmed by LOHNIS (17), (18), and in marrowstem kale, Savoy cabbage and occasionally in cauliflower. These symptoms have been seen in potatoes and reported also in this crop by BERGER and GERLOFF (4) in the United States. Barley may also show apparent manganese excess symptoms according to the description given by PIERRE (25), and MANN and BARNES (19).

Oat, flax, celery, sugar beet and most legumes do not appear, however, to be affected greatly by the manganese excess factor in acid soils, although the element may still be accumulated at high concentrations (9).

Aluminium toxicity. Tolerance to aluminium also varied greatly, but different groups of crops were more susceptible. Sugar beet was especially so. Foliage became dark green, lustreless and apparently phosphorus deficient. Roots showed characteristic thickening at the tips and became brown and stunted. Germination and early growth were severely depressed. Barley was also easily injured by aluminium. Acute apparent phosphorus deficiency and stem blackening, lack of tillering and characteristic root injury were seen. Celery, carrot and flax were also injured, but were rather less susceptible. Potatoes showed slight phosphorus deficiency. Dwarf french beans behaved differently according to variety. "Masterpiece" tolerated aluminium even in excess of phosphorus level, whereas "Prince" was severely injured by aluminium at much lower concentrations when phosphorus supply was in excess. The effects of aluminium then greatly exceeded those of manganese. Oat, and most Brassicas, especially marrowstem kale and swede, tolerated aluminium levels sufficient to kill many crops.

In acid soils the behaviour of barley and sugar beet usually clearly suggested the effects of aluminium toxicity. Other effects of aluminium, e.g., in celery, have been only occasionally or less probably recognized.

Magnesium deficiency. Routine surveys of mineral deficiencies in crop plants showed that symptoms of magnesium deficiency were both characteristic and diverse in nature. The behaviour of oats was found to correspond in most details to a type of chlorosis found in acid soils. Lack of magnesium is also a principal factor in the Hooghalen disease of oats growing in acid soils in Holland, and described by SMIT and MULDER (30).

Magnesium deficiency has been seen in several other crops growing in acid soils but not as the dominant or characteristic acidity factor.

Complex factors. Two symptoms seen in potato in acid soils have recently been probably identified. One was seen only when potassium was also deficient. It was a central necrosis of upper leaves sometimes associated with dull purple or yellow tinting. The central necrosis factor appeared to be a combination of manganese toxicity and low potassium and calcium status according to the response of plants grown in sand cultures.

The other symptoms, more commonly seen in acid soils are the forward leaf rolling and general chlorosis suggestive of primary leaf roll symptoms (24) and occasionally basal intervenal chlorosis of



Plate 1b
Manganese excess as a soil acidity factor in marrowstem kale. Leaf marginal cupping, necrotic spotting, and interveinal mottling.



Plate 2a
Aluminium toxicity as the soil acidity factor in barley. Note root injury and enlargement of root tip.
Left : Excess Al with low calcium level.
Centre : Excess Al with extra calcium as $CaCO_3$.
Right : Excess Al with extra calcium as $Ca(NO_3)_2$



Plate 2b
Calcium deficiency as the soil acidity factor in potato. Leaf margins pale with black necrotic areas, and tip-burning of leaflets.

leaflets. These effects were reproduced unexpectedly by BOLLE-JONES (5) in experiments on nutrient balance in the potato. The symptoms occurred most frequently when high potassium status was combined with low phosphorus and high iron levels. The appearance of the foliage of these plants was also suggestive of normal calcium deficiency, and characteristic tuber irregularity and medullary necrosis reported elsewhere (29) in acid soils or under calcium deficiency conditions (10), (28) occurred. A combination of low calcium and excess manganese may also cause leaf rolling effects (11).

The behaviour of the potato in acid soils is greatly dependent on the manurial treatments given and deficiencies of calcium, magnesium, potassium, phosphorus and nitrogen may all occur in different combinations as well as the complex effects first described (34).

Molybdenum deficiency. Brassica crops, lettuce, tomato and sugar beet were found to be the most susceptible to molybdenum deficiency. Clovers and lucerne were less readily affected and large seeded legumes, oats, and potatoes usually had low requirements.

Most crops showed chlorosis, wilting and scorching of older and middle leaves. Lettuce plants in acid soils in Australia and Britain have been shown by WILSON (35) and PLANT (26) respectively to suffer from molybdenum deficiency as seen also in sand culture plants (13). " Scald " in beans has also been associated by WILSON (36) with molybdenum deficiency when once-grown seed from the same acid soil area is used, but plants grown in sand culture do not respond in the first season.

Probably the most widely recognized effect of acidity on cauliflower and broccoli crops is the condition known for many years as Whiptail (6). Clues to its origin in molybdenum deficiency were provided by DAVIES (7) and MITCHELL (21) in New Zealand. HEWITT and JONES (15), (16) first produced plants suggestive of Whiptail in molybdenum deficient sand cultures. The conditions required for its development as seen in the field were established in sand culture by HEWITT and AGARWALA (14). They comprised a high level of nitrogen supply, most readily provided as nitrate, and a low but critical level of molybdenum of 0·00005 p.p.m. All essential features of the disorder including long, narrow, irregular laminae, stunted, or bare vestigial leaf stumps, and death of the growing point in relatively large dark green plants were produced.

Interaction of Factors

In addition to the information provided from the study of individual factors, a number of interactions were revealed. These included the following:

Calcium/manganese: Additional soluble calcium depressed manganese uptake and often reduced or eliminated the symptoms of toxicity. Some crops, e.g. Brassicas seemed more sensitive than others to this relationship. Calcium carbonate was less effective in sand culture.

pH/manganese; Aluminium/manganese: Low pH or excess aluminium, which also produced a low pH, accentuated manganese toxicity symptoms and frequently resulted in greater soluble manganese content in the foliage.

Manganese/iron: In agreement with others (18), (22), (23), no

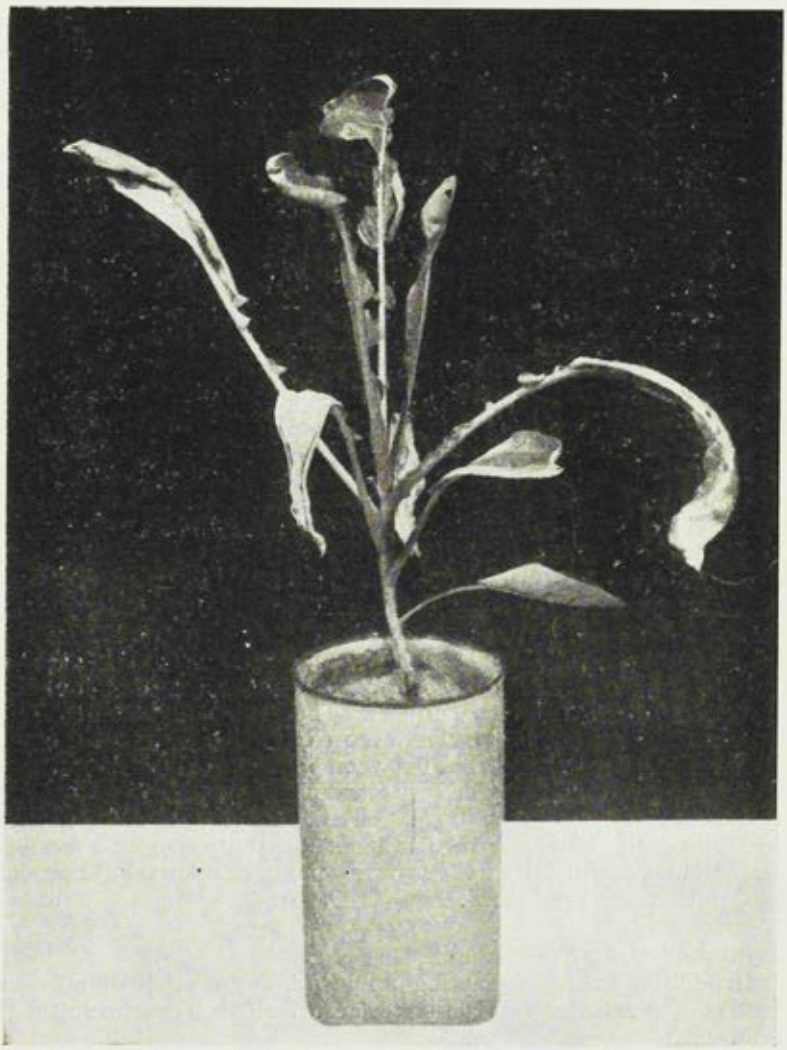


Plate 3a
Molybdenum deficiency as the soil acidity factor in cauliflower, showing Whiptail, leaf scorching and chlorosis symptoms.

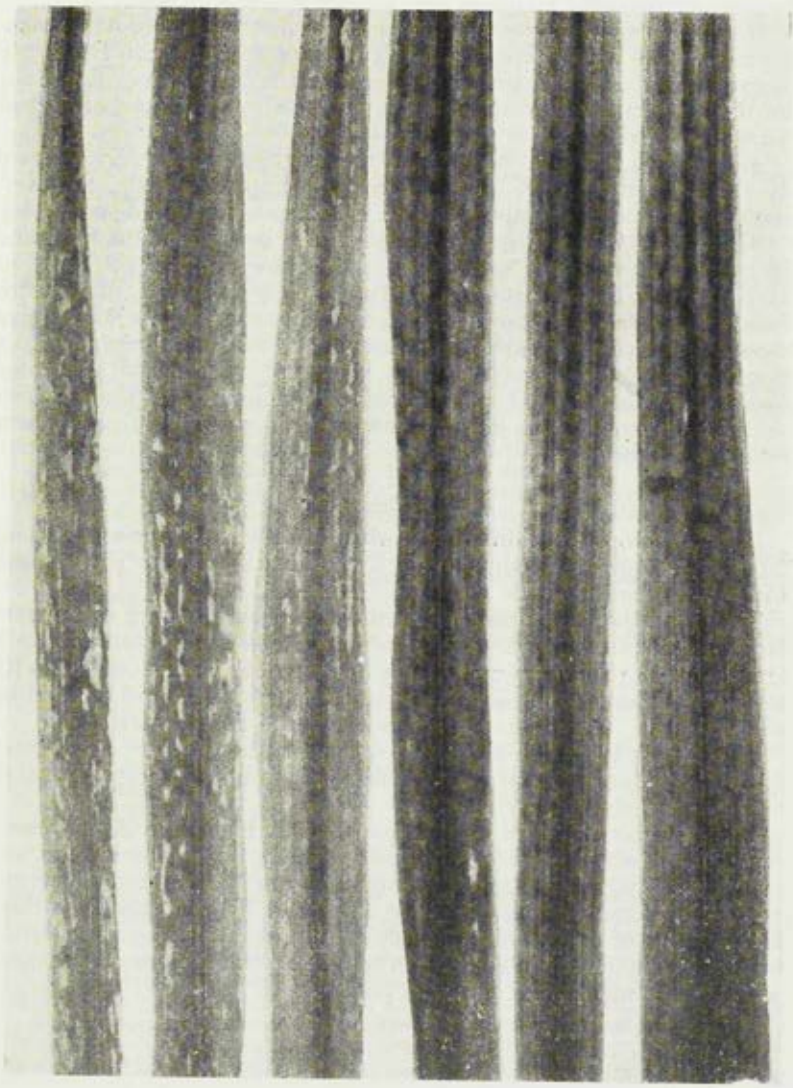


Plate 3b
Magnesium deficiency in oat as the soil acidity factor. Intervenal "beading" of light and dark areas followed by ivory tinted necrotic spotting.

evidence was obtained that the relationship between manganese excess and induced iron deficiency (31) was of significance in acid soils, or was in any way concerned in the development of manganese toxicity symptoms.

Manganese/molybdenum: Manganese deficiency reduced, and manganese excess accentuated certain effects of molybdenum deficiency in cauliflower. High manganese levels were not, however, important for the production of Whiptail which was readily developed at normal manganese levels (14).

Aluminium/calcium: Aluminium toxicity was not greatly affected by the concentration of calcium ions. Calcium carbonate, however, strikingly reduced the injury caused to roots of barley and sugar beet.

Aluminium/phosphorus: The relationship between aluminium and phosphorus availability was not simple. Some crops, e.g., carrot, or even varieties, e.g. Dwarf beanvariety Prince, were acutely phosphorus deficient in appearance, others, e.g., Swede or the variety Masterpiece showed no marked phosphorus deficiency with aluminium. Root injury and phosphorus deficiency were not necessarily associated together. The ratio of phosphorus to aluminium in the nutrient solution did not always determine whether symptoms of phosphorus deficiency were seen.

Conclusions

Different crops react differently when exposed to a single particular factor of the acidity complex and a characteristic order of tolerance can be assigned for each factor.

The respective crops show great differences in tolerance to different factors. Thus two highly sensitive crops, e.g. sugar beet and kale, are sensitive to aluminium or low pH, and to manganese toxicity respectively but are relatively tolerant to manganese and aluminium respectively. The order of tolerance to each factor varies.

The relative tolerance of crops to soil acidity described by ARRHENIUS (3) and RUSSELL (27) probably reflects their tolerance to a number of factors in the acidity complex.

The familiar order of tolerance observed in acid soils is closely reproduced when certain combined factors, e.g. aluminium and manganese excess with low calcium supply are tested and the visual responses of most crops are fully explained by the effects of these factors, and of deficiencies of molybdenum in Brassicas and lettuce, of magnesium in oat, and of certain complex combinations of potassium with iron or manganese status in potato.

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SESSION 4

SOIL ACIDITY AS CALCIUM (FERTILITY) DEFICIENCY[1]

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For all too many years our concept of the soil conditions called "soil acidity," and of the relation of these to plant nutrition, has been one which originated in the greenhouses and chemical laboratories dealing with solutions, and one mentally transplanted to the soil. It carried the belief that soil acidity *per se* is detrimental to plants. It provoked the conclusion of the converse, namely, that neutrality, therefore, must be beneficial. Such was the concept that gained wide popular acceptance, and unleashed in agricultural practice the extensive war on soil acidity with the carbonate of calcium as the ammunition for its annihilation.

Now that we have (*a*) found the hydrogen ion in potentially large numbers as a common cation part of the clay molecule, (*b*) measured this highly active element ionized from there in varying degrees to give different pH values, and (*c*) recognized its origin abundantly in the respiratory processes of the soil microbes and of the plant roots themselves, a newer concept is replacing this older one. We now consider those conditions called "soil acidity" as fertility deficiencies, of which calcium (and magnesium) is a prominent one.

We are coming to see the active hydrogen—even if it is not a plant nutrient when coming via the soil—as the major force in the many chemo-dynamics of the soil through which plant nutrition results. The activities of this ion are the major force in bringing about (*a*) the decomposition of the mineral reserves in the silt separates for increased availability of their nutrient contents, (*b*) the formation of the clay separate as a result of the mineral breakdown, (*c*) the adsorption on the clay of many essential nutrient ions made active as a consequence of that mineral decomposition, and (*d*) the exchange of these from the clay-organic-colloid to the microbes and the plant roots for nutritional services to these living forms.

When the world's population has located itself mainly on what is considered the "acid" soils; and when life is scant on those of alkaline reaction, even those of much less degree of this opposite to the acid; it seems high time to re-examine the simple chemical solution concept of acidity-neutrality-alkalinity, considered as bad-good-bad condition, respectively, for plant nutrition. This reconsideration seems especially necessary when these reaction differences, as only such with no other accompanying differences, are transplanted into the soil. It is, therefore, proposed here to defend the thesis (*a*) that an acid reaction of most soils is not a hindrance, but rather a help, to plant nutrition via the provision of the essential nutrient ions, (*b*) that it is only under significant hydrogen ion activity that the processes of mineral breakdown, clay formation and fertility

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delivery can be carried on, and (*c*) that the respiration of plant roots and microbes generates active hydrogen to maintain the flow of nutrient cations from the soil's rocks and minerals in the assembly line of agricultural production.

Soil acidity is not a hindrance when fertility is present

At the outset, let us accept the widely experienced and correctly interpreted observation, namely, that in Nature there are less and less of the more nutritious herbages, especially the legumes serving for growing young livestock and for multiplying its numbers, according as the natural degree of soil acidity goes higher. Let us also note that in waging the fight on soil acidity, it was probably more good fortune than wisdom when the carbonates of calcium and magnesium rather than of sodium or other alkalies and alkaline earths were chosen for soil treatments to drive the hydrogen out. After the years of growing concern about soil acidity, there is gradually dawning the broader concept, namely, that the increasing degree of acidity is merely the reciprocal of the real trouble, namely, the decreasing store of the soil fertility. While the earlier concept of soil acidity as the hydrogen's damage may now be slowly going into the discard, it has served, nevertheless, as the means by which the later one evolved, and, with it, our concept of at least some of the mechanisms—including the hydrogen as a part in them—by which the soil, rather than a solution within it, serves to deliver its fertility and to nourish the plants.

It was the modified Comber method (16)* of testing soils for the degree of acidity (the thiocyanate method) which served early to point out that liming a soil is helpful in growing clovers and other legumes because it applies the plant nutrient calcium and not because it applies carbonate for bringing about a reduction of the degree of acidity. Two fields, failing to grow clover, on the same farm were tested for their degree of acidity and were found highly acid. Two tons per acre of ten-mesh, agricultural limestone, were applied on each of them in the autumn ahead of the wheat seeding. The clover seeding followed the next spring with an excellent stubble crop of this legume as the result the next autumn. The soil test, repeated at that season, showed the soil nearly neutral for the one upland field of silt loam. The test, however, for the bottomland, a clay soil, showed still the same degree of acidity after liming and clover establishment as that which prevailed before the soil treatment. Here the clover had resulted from the same kind of liming which removed the acidity in the one field of upland soil with its low exchange or buffering capacity, but which brought about no change in reaction in the other field of bottomland soil with a high exchange or high buffering capacity. Here was some of the first evidence that it is an erroneous explanation of the effects of liming the soil, when we say that this practice is beneficial because it reduces the degree of acidity or lowers the pH value. Here was evidence that the presence of acidity is not a hindrance to clover growing if the fertility (calcium) is present.

As a test of this error in reasoning, a field of "acid" soil was put to soybeans—a supposedly acid-tolerant legume—by using calcium

*Numbers in parenthesis refer to references in the "Literature Cited".



Applications of calcium chloride, calcium nitrate, and calcium hydroxide (right to left) gave improved growth and nitrogen fixation by soybeans on this "acid" soil, irrespective of the resulting increase in its acidity by the first two and the decrease of it by the third of these treatments.

chloride, calcium nitrate, and calcium hydroxide as successive treatments applied through one side of the fertilizer attachment of the drill at seeding (1, 2). Each of these treatments applied calcium. Regardless of whether the soil was made more acid in case of the first two, or reduced in its acidity in the case of the last one, of these treatments, the soybean plants grew larger, were greener, gave better nodulation and nitrogen-fixing, and brought about more stable nature of the plant tissues under microtomic sectioning wherever any one of these calcium-carrying salts was applied.

As additional test of the physiological effects of the lime because of the calcium going through the plant rather than the carbonate through the soil for acid neutralization, some finely pulverized limestone was drilled with clover seedings of inoculated seeds on acid soils (4). Clover was well established by drilling limestone with the seeds. Nodule production occurred on the roots in the soil at significant depths below, and distances from, the location of limestone in the drill row. Determinations of the pH around the nodules at these depths found this as low as 5·0. Here were legume root growth and excellent nodulation on all roots in soils of high degree of acidity as the result of merely growing some of the roots in contact with calcium in limited soil volumes or in only a few focal points. If lime is required for nodulation, this certainly occurred not where the acidity of the soil around the nodule was neutralized, but where the nodule-producing bacteria met a root of nutritional contents for mutual benefits, to which the calcium, taken by the plant roots in some other part of the soil made its contributions.

Separation of the lime's effects as a nutrient from those as neutralizer of acid makes the soil's exchange capacity a major factor in fertility

By means of electrodialized colloidal clay (7), which is a hydrogen-saturated clay at a pH of 3·6 when free of cations other than hydrogen, it is possible to titrate this to any desired degree of calcium (or other cation) saturation, or to any pH figure between 3·6 and 7·0 with all the cations adsorbed and none in solution. Since the amount of clay in the suspension can be controlled, then by taking a given volume of known concentration of clay to be mixed with sand, any given amount of exchangeable calcium (or other cation) can be so offered per plant. One can, then, choose the degree of acidity, or pH and keep it under control, and independently of that can also control the amount of supplied calcium by merely putting into the sand more or less of the clay of the chosen pH. By means of this colloidal clay technique, nitrogen fixation and other physiological processes of plants have been studied to segregate the various effects of the hydrogen ion on plant nutrition.

It was by means of this technique that the exchange capacity of the soil demonstrated its significance in the effects on the soil and the plants when liming to fertilize with calcium or to fertilize with any other nutrient element. For example, by putting into given constant amounts of sand, increasing amounts of clay of any chosen pH, or thereby a clay of any chosen degree of calcium saturation, this gives

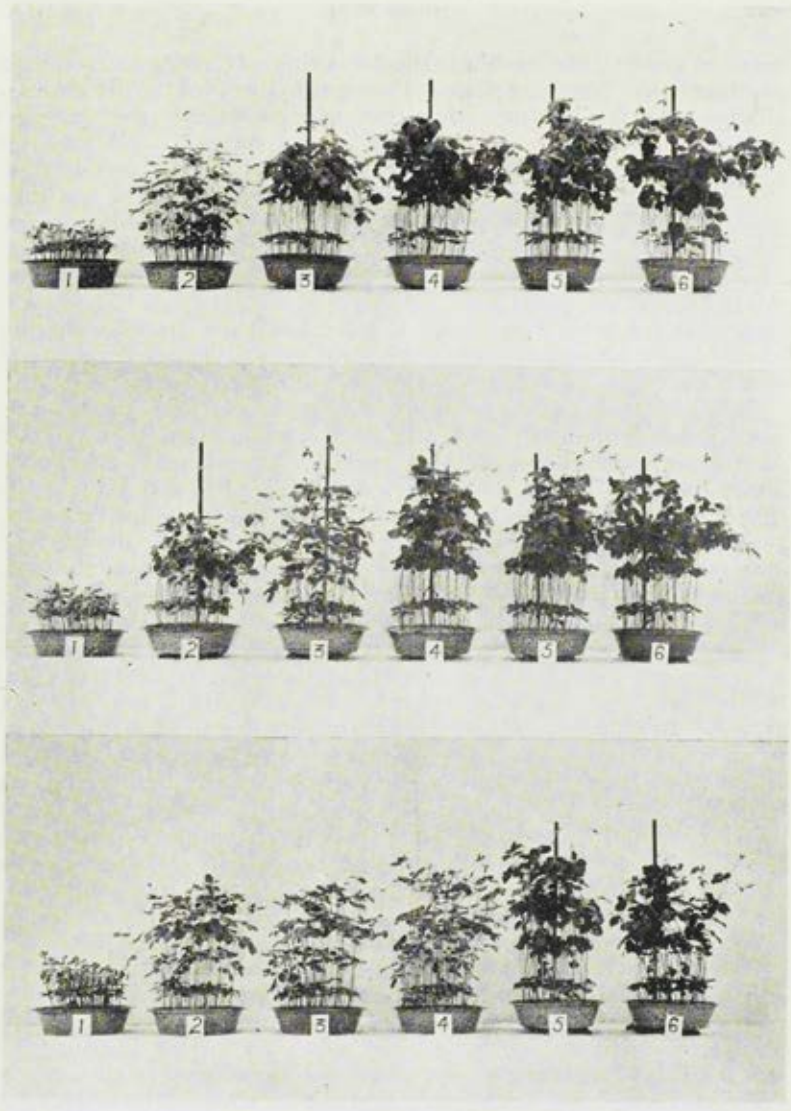


Increasing the amount of calcium offered the plants by increasing the colloidal clay (pH 4·4) in the quartz sand (left to right) in the glass containers made the difference between poor and good growths, and between attacks by a fungus and immunity to it.

an increase in the exchange capacity of this artificial soil and by that means the amounts of calcium (or other nutrients) offered the plants can be increased while the pH remains a constant. Thus, the pH is eliminated and is consequently not mistaken as a measure of the amounts of calcium (or of other nutrients and hydrogen) offered to the plants growing in the given soil volume. By this it is demonstrated that the pH cannot be construed as of any value in determining the amount of lime to be supplied either as nutrition or as neutralization of soil acidity. This points out, then, that a knowledge of the soil's exchange capacity is necessary if the degree of hydrogen saturation is to be quantitatively interpreted as total hydrogen and conversely as totals of the cations other than hydrogen exchangeable from the soil. The exchange capacity of the soil becomes the important property when quantitatively interpreting soil tests of exchangeable ions.

By means of this colloidal clay technique, permitting varied control of the pH of the clay as well as varied control of the amounts of calcium or other cations on the clay, studies of plant nutrition in relation to the hydrogen ion have been extensively carried out (3). When a series of the clays was prepared to include the pH values going from 4·0 to 6·5 by increments of ·5 pH, and the amounts of each of these six clays were taken so as to give ·05 milligram equivalents of calcium per soybean plant, the plant growth was poor at the four pH values of 5·5 and lower, but it was good at the two pH values of 6·0 and higher. When twice as much of each of these clays was put into the sand to offer ·10 milligram equivalents of calcium per plant, the corresponding pH values differentiating between poor and good plant growth as above were 5·0 and 5·5, respectively. But when four times as much clay was put into the sand offering ·20 milligram equivalents for root contact, the dividing pH figures between poor and good plant growth were 4·5 and 5·0.

Thus, had one seen the plant growth of only the first series, it would have been logical to report that the soybean plant is " disturbed by," or " sensitive to," a pH of 5·5, and " requires " a pH of 6·0. Had one seen only the second series, it would have seemed logical to refute these reported figures and to contend that this plant species is disturbed by a pH of 5·0, but not by the required one of 5·5. Then, similarly had one seen only the third series, the contradiction of both preceding sets of figures given above would have been expectable, and the claims anticipated that soybeans are not disturbed seriously by soil acidity until the degree of it becomes as severe as pH 4·5. Here would have been apparent grounds for claiming that the soybean is an " acid-tolerant " crop. However, in this third series, which exhibited higher " tolerance " of a degree of acidity by ten times more than that " tolerated " in the first series, this " tolerance " was brought about by merely quadrupling the exchange capacity in the constant volume of sand-clay soil. Increasing the nutrition as calcium by four times was the counteraction or the antidote for an increase of degree of acidity, or hydrogen-ion concentration, by ten times.



Decreasing degrees of acidity (increasing degree of saturation of the clay by calcium) were offered the soybeans (pH, left to right, 4·0 ; 4·5 ; 5·0 ; 5·5 ; 6·0 ; 6·5).
There was an increasing amount of calcium offered as a constant per horizontal row by putting more clay into the sand-clay medium in going from the lower to the upper one, viz.: ·05 ; ·10 ; *and* ·20 *milligram equivalents per plant.*

Plants lose fertility back to acid (infertile) soils or gain it from these according to their degree of saturation

Equally as interesting as this preceding observation of what has erroneously been called " toleration " of acidity by plants, were the changes in the reactions, or pH values, of these colloidal clays as a

result of growing the soybean crop for a time extending scarcely from planting to the blooming stage. The measurements of the pH values of all the sand-clay mixtures after they had grown the crop showed a shift of the reaction toward neutrality from the initial pH values of 4·0, 4·5, and 5·0, and a shift toward more acidity from the initial pH values of 5·5, 6·0, and 6·5. These shifts were greater in the last three cases according as the initial value was higher. As a consequence, the pH in these soils resulting finally from the crop's growth in them was almost the same, namely, near 5·5, for all the different sand-clay mixtures that originally were pH 5·0, 5·5, 6·0, and 6·5. The first of these resulted from a decrease, and the last three from an increase in the degree of acidity. Here the plant growth modified and determined the degree of acidity of the soil, and not vice versa.

Chemical analyses of the crops, in comparison with those of the seed, showed that they had all taken calcium from the clay-sand mixture in consequence of their growth. The amounts taken were about the same for all those cases of pH 4·0, 4·5, and 5·0. If this calcium removal represented an exchange of it to the plant for hydrogen from the roots, this hydrogen added to the clay should have lowered its pH figure below the initial values, and to about the same amount for all these three of them. The amounts of calcium taken from the soil, however, by the soybeans growing at pH values 5·5, 6·0, and 6·5 increased with these increasing pH values. This was not in agreement with, but was more than the equivalence represented by, the increasing degree of acidity of the soil resulting from the crop growth. In only one case was the increasing degree of acidity equal to or slightly more than the increasing degree of calcium removal. In only one case was there a suggestion that the hydrogen going from the root to the soil was replacing nearly exactly the calcium taken from there by the root. The extra cations, besides the hydrogen, going in the reverse from the root to the soil in exchange for the calcium were shown in later studies to include potassium and nitrogen (10), since in respect to these two elements, the total crop (tops and roots) contained less than was in the planted seed.

Here, then, there was an interchange of cations, including hydrogen and others from the roots to the clay as well as from the clay to the roots. The final hay crop contained less nitrogen, potassium, and phosphorus than was in the planted seed. As for the calcium, this was found moving only in one direction, namely, from the clay to the roots, when the plants were growing or even barely surviving. Calcium was moving into the plants in larger total amounts at any given pH of the soil when the exchange capacity of that soil was pushed higher by increasing the clay in the sand-clay soil. Calcium was taken both in larger totals from, and at larger percentages of, the same exchangeable supply offered, according as there were increasing degrees of saturation of the clay by that calcium, or with higher pH values, only when these were 5·5 and above. Thus, the delivery of calcium from the soil to the crop was more efficient in terms of the applied calcium according as the soil was more highly saturated by it, or of higher pH values above this figure of pH 5·5 for this particular clay. This suggests that the efficient use of a given amount of lime calls for its application so as to give highly saturated, limited soil volumes rather than an infinite distribution throughout the soil of



Increasing calcium saturation (40, 60, 75, 87·5 *and* 97 *per cent., left to right) of the clay colloid in the clay-sand soil offering the same amount of exchangeable calcium per plant, gave increasing plant growth accordingly, but irrespective of the accompanying decrease in soil acidity (upper row) or the accompanying neutrality (lower two rows).*

the entire root zone. Drilling the lime well down into the soil for root contact and for fertilizing effects is suggested as better practice than mixing it throughout the entire soil body for effects in acid neutralization.

Relative degree of saturation of the colloid by the different ions, and this of each in relation to the others, influences their activities in plant nutrition

Because the degree of saturation of the colloidal complex by calcium exhibited its significance in the efficiencies with which the constant amount of exchangeable calcium was passed to the plants, studies of the increasing degree of calcium saturation with reciprocally decreasing degrees of saturation of other cations were undertaken, using constant amounts of exchangeable calcium offered to the soybean crops grown by means of the colloidal clay technique (14). In the first trial, the percentages of calcium saturation were 40, 60, 75, 87·5, and 97 reciprocally combined (*a*) in one series with hydrogen, (*b*) in another with magnesium, and (*c*) in another with barium. In the hydrogen series, this increasing degree of calcium saturation represented a corresponding decreasing degree of hydrogen saturation or decreasing degree of acidity as increasing pH values, namely, 5·10, 5·50, 5·90, 6·45, and 6·85, respectively. In the other two series this increasing calcium saturation represented no ranges in degree of acidity, since all the clays were made nearly neutral by means of cations other than hydrogen, namely, (*a*) magnesium, a nutrient, and (*b*) barium, a non-nutrient, and both similar to calcium in many of their properties.

The plant growth increased nearly 50%; the nodule production increased by more than 50%; and the calcium uptake increased by more than 100%, as a result of the increase in calcium saturation, regardless of whether there was at the outset a range in the degree of acidity in the series or whether all the soils were nearly neutral. Since the increasing efficiency of calcium, as measured by the increase of plant growth, of numbers of nodules, and of calcium taken from the same exchangeable amount in the soil, resulted from the increasing degree of saturation of the colloid by it, regardless of whether the soils were of differing degrees of acidity or all nearly neutral, there can scarcely be much disturbing significance, either hindrance or help, ascribed to the hydrogen ion as an acidity factor when these other active inorganic cations of fertility or non-fertility values are associated with it.

As a comparison of the behaviour of calcium when associated with the highly active hydrogen in contrast to its behaviour when associated with a much less active or less ionized cation, the large, positively charged ion of methylene blue was adsorbed on the clay with the calcium as the reciprocal to it in its increasing degrees of saturation of the clay colloid. There were three series, similar to the preceding ones, as regards the constant amounts of total exchangeable calcium as increasing percentage saturations, but this combined with decreasing percentage saturations of (*a*) hydrogen in one series, (*b*) potassium in another, and (*c*) methylene blue in still another.

In the first two series, the plant growth increased by nearly 50%,



Increasing calcium saturation (40, 60, 75, 87·5 and 97 percent., left to right) of the clay colloid in the clay-sand soil offering the same amount of exchangeable calcium per plant, gave increasing plant growth accordingly when the inorganic hydrogen and potassium were the accompanying ions. But the saturation degree was without effect and the plant growth reflected the constant amount of exchangeable calcium when methylene blue was the accompanying ion.

the nodulation by the same degree, and the uptake of calcium by almost 100%, according to the increasing calcium saturation and the reciprocally decreasing saturation of these other two accompanying active, inorganic ions, one of which made the soils in the series decreasingly acid and the other made all of them nearly neutral. But in the third series, where the reciprocally decreasing saturation was the result of the inactive, large, organic ion of methylene blue, also making all the soils in the series neutral, the constant amounts of exchangeable calcium, regardless of the differing degrees of saturation by it, gave nearly constant weights of crops, constant numbers of

nodules, and delivery of calcium suggesting larger amounts as the saturation degree of the colloid by it was smaller. All these results from the calcium in this series were nearly the equal of the maxima in all the other series for it, regardless of whether accompanied by hydrogen, magnesium, potassium, or barium.

In these two trials with the six plant series, there was again demonstrated the increase in the degree of acidity of the soil resulting from the crop growth. This demonstrates the fact that the removal of fertility from the clay in the clay-quartz medium increases the hydrogen presence there or increases the degree of its acidity. For the two series in which the decreasing hydrogen saturation of the clay, or the increasing pH values, accompanied the increasing degree of calcium saturation, the growth of the crop for the six weeks lowered the initial pH values by the following amounts, ·20, ·20, ·60, 1·10, and 1·65 respectively for the units of decreasing hydrogen saturation. In the three neutral series, made so with decreasing degrees of saturation by (*a*) magnesium, (*b*) barium, and (*c*) potassium accompanying the increasing calcium saturation, the pH values were lowered as a result of the crop growth by amounts varying from 1·10 to 1·60. In the case of the series with methylene blue, here, too, the crop growth made the soils more acid by pH amounts as much as 1·30 to 1·60. By the growth of a single crop for six weeks on these soils that were initially neutral, the degree of acidity was increased by amounts approaching even a hundred times. Acidity can scarcely be much hindrance when the very crop growth itself increases the degree of acidity to such magnitudes.

Hydrogen, or acidity, helps in mobilizing other cations (possibly anions) from the soil colloid into the plant roots

The association of the active calcium with the inactive methylene blue molecule reported above, presented the concept that the activities of any adsorbed ion resulting in its entrance into the plant are determined not only *per se*, that is, by its chemo-dynamics, but also according as these are modified by the activities of other ions by which it is accompanied. From these results there arose the concept that not only the activity of the hydrogen ion deserves measurement by its glass electrode, but that plant nutrition in terms of calcium will be better understood when the calcium activity can be measured by a similar electrode, or if we can have a pCa as an activity measurement for calcium, and similar measurements for other ions just as we have pH for activity of the hydrogen ion.

As a partial measure of the influence on the calcium activity by some of the cations associated with this element in the suite of ions on the colloidal complex of the soil, some calculations were made of the efficiency with which the exchangeable calcium on the colloidal clay was moved into the soybean plants in some studies (*a*) using increasing degrees of saturation of a constant amount of clay by calcium and thereby offering increasing amounts to the crop (15), and (*b*) using increasing degrees of saturation on decreasing amounts of clay to offer constant amounts of calcium to the crop (14). In both studies the calcium was associated with (*a*) decreasing hydrogen and thereby decreasing degree of acidity, and (*b*) decreasing barium and thereby with all soils nearly neutral.

When the decreasing hydrogen was associated with the increasing saturation of the clay by calcium in both of these cases, the exchangeable calcium moved into the soybean crop with a higher efficiency than when barium was the accompanying ion as is shown in Table 1. Here is the suggestion that as the hydrogen is adsorbed on the colloid and comes into the suite of ions held there, it may serve to push off or make more active, the other cations on the clay. Thus, the presence of hydrogen of no nutritional service itself, and too long considered a detriment, becomes a benefit in that it mobilizes the other cations of fertility value into the plant more efficiently.

That the active hydrogen ion on the colloidal clay serves to move larger shares of the other cations (nutrient ions) from the colloidal complex into the plant root was clearly demonstrated by growing spinach on two five-pot series of similar soils, one of which series was acid at pH 5·2, and the other was nearly neutral at pH 6·8 (6). The amounts of the separate nutrient ions put on the clay as chlorides to make the acid series and as oxides and hydroxides to make the neutral one, were duplicates throughout the series except for the calcium. This was put on as increasing amounts from 0 to 12 milligram equivalents by increments of three.

The spinach crop grown on the acid series showed a general yield increase with more calcium applied. More significant, however, were the much higher totals and higher concentrations of the soil-borne, inorganic nutrient elements, namely, calcium, magnesium, strontium and manganese, for this crop on the acid series than for that on the initially neutral soil. Also, as a result of both the increasing amounts of calcium added and the increasingly higher degree of saturation by calcium of the colloidal clay, there were increasing totals, and increasing concentrations of these elements in this vegetable crop, which was not the case for it when growing on the soil initially neutral. On all soils, the amounts of phosphorus and potassium did not show such clear correlations. They followed more nearly the crop yields.

TABLE I

Degree of saturation by			In plants %		Total mgms.		Efficiency	
Calcium	Hydrogen (acid)	Barium (neutral)	(acid)	(neutral)	(acid)	(neutral)	(acid)	(neutral)
Increasing saturation with amount of clay constant								
40	60	60	·507	·386	25·2	23·9	12·6	11·9
60	40	40	·651	·594	44·8	38·0	22·4	19·0
75	25	25	·702	·672	50·9	47·0	25·4	23·5
87·5	12·5	12·5	·764	·707	57·1	56·2	28·5	28·1
Increasing saturation with amount of exchangeable calcium constant.								
25	75	75	·27	·29	40·27	1·20	40·2	31·2
50	50	50	·55	·31	85·54	45·54	40·7	22·7
75	25	25	·71	·66	122·40	104·84	40·8	34·9

TABLE I. The increasing degree of saturation of the soil colloid by calcium was more efficient in moving calcium into the soybean plants when hydrogen (acid) rather than barium (neutral) was the reciprocal of the calcium.

The oxalate contents of the spinach, by combination with which calcium and magnesium become highly insoluble, and thereby indigestible, as a synthetic product of the plant's processes were even more interesting than the uptake of the six inorganic elements contributed from the soil (17). The oxalate contents of the plants from the acid soil were higher than of those from the neutral soil. Also, they increased with the increments of calcium on the former, but not on the latter soil. However, when matched against the equivalents of the crop's contents of calcium and magnesium combined, the oxalate there in case of the acid soils was less than required to make both of these alkaline earths insoluble. On the neutral soil it was more than enough. Here was evidence that the acidity of the soil is a help, and not a hindrance, not only in the transportation of the inorganic elements from the soil into the crop plants, but also in the plants' synthetic creations through which the soil fertility serves first in plant nutrition and then later in the nutrition of animals and man.

Soil acidity serves to process the applied minerals as well as those natural in the silt and thereby to restock the clay with active fertility

In our mechanical analyses of soils, the three separates, namely, sand, silt, and clay have not been emphasized for their differing potential contributions to fertility according to the humid or arid climates they represent. When the clay is the colloidal, dynamic separate which takes up, and gives off, nutrient cations but offers none of significance by its own chemical decompositions (5); and when the exchangeable supply of fertility in the soils of low exchange capacity is exhausted so quickly by a few successive crops (10); we must look to the silt and sand separates as the source from which the fertility store on the colloidal clay is regularly renewed.

For that renewal, the sand separate can offer little because of its large particle size and limited total surface for acid-clay contact. Its insolubility and hardness, by virtue of which it naturally remained as large particles, testify to its high potential in quartz as its mineral component and thereby little or no fertility value. The silt separate may well be expected to offer more to the clay because of smaller particle size or more surface for contact. Silt is of the size sufficiently smaller to be windblown. It is brought to the humid regions from the dry, unweathered areas by that means. By virtue of such origin it is more apt to be an extensive collection of minerals other-than-quartz containing more nearly all the elements of fertility. It is the silt loam soils in the semi-humid areas, or under moderate degrees of soil development, which have grown the legumes naturally and have given us the protein food supplies most abundantly (9).

By mixing specially prepared silt minerals with a colloidal clay suspension of controlled degree of acidity (11, 12), or by putting the moist silts into a collodion tube and immersing this into the acid colloidal clay, it has been demonstrated that the acidity of the clay serves like any other acid to decompose the silt minerals. The active hydrogen from the clay passed through the membrane. It decomposed the minerals, while the cations so released passed in the opposite direction, were adsorbed on the clay, and from there were taken up by the plant roots with plant growth according to the differing degrees of development the silts had undergone.

Thus, the acid clay is offering its active hydrogen as an agency decomposing the silt minerals, releasing cations from these reserve supplies, and developing more clay thereby. It suggests that our productive soils have been those with the proper mineral mixtures in their silts as reserves of fertility rather than silts as merely fortunate physical makeup for easy tillage. It suggests also more significance in windblown soils of the semi-humid areas for the fertility value of their origin in arid regions than we have been wont to believe.

That soil acidity should serve for decomposition of the soil's reserve minerals and for making their fertility contents available for plant use, should be no new concept, when we realize that liming the soil is that very same process. Particle sizes, of ten-mesh and smaller, of limestone applied on the soil are calcareous minerals being processed there by means of soil acidity. They are being so processed in order to make their calcium or magnesium contents available as fertility at various focal points throughout the soil rather than to change degree of acidity of the entire soil volume. The former, as a kind of heterogeneity (8) and not the latter as a distinct homogeneity, appears as the more logical concept of the soil as continued source of plant nutrition. All too long, however,has liming the soil been viewed not in terms of the soil acid as a means of processing this application of a calcium (magnesium) fertilizer, but rather in terms of this carbonate carrier as a means of neutralizing the soil acid. Liming is merely an illustration of how agriculture is an industrial chemical industry using mainly soil acids to provide the raw, starting materials for its creative business.

SUMMARY

In summary, then, it now seems evident that our research efforts on soil acidity for these many years would have been more fruitful and earlier for agricultural production if that research had been guided by the concept that the increasing degree of soil acidity is disturbing to our protein-producing crops because this soil condition represents not a disturbance by the increasing hydrogen, but by the decreasing fertility within the suite of ions adsorbed on the clay among which suite, in a productive soil, calcium occupies the major part. This concept visualizes the hydrogen ion, originating around the soil microbe and around the plant root because of their respirations excreting carbon dioxide, as the cation which they offer to the clay colloid through contact exchange for its stock of nutrient cations. A high degree of hydrogen saturation of the clay, then, is the result of the high concentration of this ion being built up around the microbial or root hair cells as well, when it can no longer be exchanged for other cations in the environment. A high degree of hydrogen saturation of the clay, then, is simply a high degree of fertility deficiency both there and in its immediate environment, including the silt and sand separates. That there is an increasing degree of hydrogen concentration built up around the root as the fertility in its environment decreases has been demonstrated by the research of Dr. E. R. GRAHAM and W. L. BAKER (13).

It is simple to conceive, then, that the higher hydrogen concentrations built up on the clay by plant root activities of plant growth serve as the acid reagent for reserve mineral breakdown and nutrient

cation exchange from there to the clay for the hydrogen from it. In this concept, the plant root is merely treating the soil with the acid generated by the root's own respiration; this acid then flows from the root to the clay; and, under higher concentrations resulting there, flows on to the mineral reserves (present naturally or applied as limestone, rock phosphate, etc). As a result of this acid treatment of the soil by the growing plant roots and the microbes, the fertility reserves are "made available" or they are moved out from their mineral crystalline forms into the active ionic conditions to make their way, under their own power of ionic activity and ionic exchanges in the opposite direction going from the mineral reserves to the clay, and to the plant roots for plant nutrition.

Thus, since the forms of life finding their nourishment in the soil do so by trading the hydrogen for it, it should be no other disturbance to our thinking when a soil is highly loaded with acidity than to tell us that when this occurs the soil has given up its fertility to microbial and plant crops for it. Soil acidity, then, is the regular natural result of crop production, and its accumulation is merely the result of our failure to restock the mineral reserves (of which limestone is only one) by which that acidity would neutralize itself in keeping more fertility flowing out from these restored resources and along the assembly lines of agricultural production.

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SESSION 5

MAGNESIUM AND THE MICRO-NUTRIENTS

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The recognition of the importance of the part played by micro-nutrients in plant and animal nutrition is a comparatively recent development in agricultural science. Already the literature is voluminous and in introducing the subject one must avoid a presentation so detailed as to be wearisome. Rather I propose to try to give you an outline of the story more particularly as it affects soil fertility and the health of crops and animals. In doing so I have concerned myself more with the field aspect of micro-nutrients, both in deficiency and excess, than with the equally important fundamental side. I have also paid rather more attention to crops than to animals, not that the latter are in any way less important but because they fall more particularly into the veterinary field.

For illustrations I have drawn largely on conditions as they exist in Britain, not that they can be considered widely representative but because they are those which are best known to me.

There is, of course, no sharp line of demarcation between those elements required in quantity and usually called the macro-nutrients, and those required in smaller quantities and referred to as micro-nutrients. All, from the point of nutrition, are equally important. Since neither the terms " minor element " nor " trace element " quite convey the right meaning they have been avoided.

The importance of micro-nutrients in nutrition has led to their study in all parts of the world but the emphasis on first one and then another varies from country to country and from crop to crop.

Although deficiency conditions in crops are usually attended by well marked symptoms there is also some reason for believing that, in certain areas, improvement in crop can be obtained by the application of one or more micro-nutrients where no marked symptoms exist.

Deficiencies may be due to a low total level of an element or to low " availability " in supply such as may occur under some specific soil conditions. For instance, it is true to say that whilst manganese is a constituent of soils, under certain conditions low availability leading to a deficiency can arise where relatively minute quantities of the element applied as a foliar spray will produce large yield increases. As indeed so often happens field recognition of symptoms and development of methods of treatment are in advance of fundamental knowledge of the mode of occurrence in the soil and the role in the plant.

The history of the development of the study of micro-nutrients has been, firstly, recognition of field conditions in crops or animals and the search for a remedy: secondly, a more detailed and controlled study of the deficiency (or excess) in culture solution, sand culture or in groups of animals; thirdly, an examination by the physiologist and biochemist of the role of a particular element in the plant or in the animal.

Thus the advisory officer is almost invariably provided with a remedy before the essential part played by the missing nutrient is explained.

Deficiencies and Excesses of Micro-Nutrients

Under British conditions, in addition to magnesium, iron, manganese, boron, zinc, copper, molybdenum and cobalt cover the range of elements so far concerned. Visual diagnosis has received much attention by WALLACE, HEWITT and PLANT at Long Ashton and by Soil Chemists of the Advisory Services. The Long Ashton pot cultures have placed knowledge of the part played by micro-nutrients in plant nutrition on a sounder basis and much that was suspected hitherto has been made plain. From the point of view of assistance to the Advisory Service this work has been of great importance. In the field, suspected conditions of deficiency can be detected by the correct choice of indicator plants especially if differential treatment is also carried out. This aspect of field detection has been exhaustively dealt with by WALLACE in his paper to the Congress of Amsterdam in 1950 (1) and is described in detail in " Mineral Deficiencies in Plants " recently published by H.M.S.O. 1951 (2).

Field diagnosis on agricultural and horticultural crops is now largely a matter of practice and is facilitated by the adoption of systematic methods of approach. Many of the symptoms are immediately recognisable by the eye, others after use of the watering-can, but in some instances special treatments such as ROACH'S (3) injection method or tissue and plant analysis may be needed. Doubtless investigators in other countries have evolved their own diagnostic methods adapted to their special needs.

Multiple deficiencies present greater difficulties, especially as some of the elements have very pronounced interaction effects sometimes accentuating or sometimes suppressing the symptoms produced by others. Not infrequently the strongly marked deficiency symptoms of one element can mask the feebler symptoms of another. At somewhat higher levels of cropping where marked deficiency symptoms are no longer seen, a response to an application of a micro-nutrient can sometimes still be obtained. The work of W. A. ROACH (4) and others on the effects of zinc on crop yields in the Romney Marsh points strongly to this conclusion. The question arises as to how far the conditions peculiar to that area may likewise occur in the rest of the country. At the moment informed opinion would probably not support the general case although more evidence is certainly needed. Field work in the Marsh further showed that the deficiency effects of trace elements did not always exist singly and that the combined influences of manganese and zinc on yield far outweighed their individual effects.

Mode of Occurrence in the Soil

Gaps exist in our knowledge of the form in which most of the trace elements occur in the soil. The bridging of the gaps will entail a very great amount of work in fundamental soil research. Meanwhile the quest continues for chemical methods which will distinguish between the total reserves and those " available " fractions which it

is presumed the plant can immediately utilise. That is probably putting the problem in its simplest terms and it is hardly likely always to follow that pattern. Often only a narrow margin exists between a sufficiency of an element required to maintain vigour and an excess acting directly as a plant poison; for instance, a dressing of 14 lb. borax per acre will usually provide sufficient boron to produce a healthy sugar beet crop while the same amount may prove to be harmful to a potato crop.

The most important factors entering into the story of availability are "soil reaction" (i.e. pH), organic matter, soil organisms, water, oxygen and carbon dioxide. Under conditions of acidity, iron, manganese, zinc and boron are available for crop nutrition while above a pH of 6·5 they are no longer readily mobile and their deficiency symptoms can occur. On the other hand molybdenum increases in availability with increasing pH values. It is, of course, almost impossible to distinguish in the field between the destructive effects of an excess of hydrogen ions and the co-related harmful effects of excessive amounts of such elements as manganese or aluminium. Studies by means of sand cultures made under controlled conditions by WALLACE and HEWITT (5) have gone far to unravel many of these problems.

Magnesium

Although hardly to be regarded as a micro-nutrient, magnesium is not one of those elements applied to crops in normal fertiliser treatment. It is essential in quantity and most soils in Britain are sufficiently well stocked to supply the plants' needs. In spite of that it is true to say that the frequency of cases where a shortage is manifest is increasing. This is for several reasons. Firstly, as is also the case with calcium, sandy soils are gradually losing their supply through leaching and removal by crops. Secondly, many acid soils brought into cultivation in recent years have been given dressings of calcium limestones devoid of magnesium. Thirdly, potash fertilisers have tended to be of the purer forms and not the double salts of K and Mg. formerly used. Fourthly, very little magnesium limestone has been used except in the vicinity of the supply areas. Fifthly, less organic matter has been used on many farms. Lastly, heavy dressings of other elements (potassium) tend to aggravate the symptoms. It may eventually be necessary to incorporate magnesium in certain fertilizers for some soils and crops as is already done in other countries.

Magnesium deficiency symptoms are usually striking and occur throughout a wide range of crops. The element is a constituent of chlorophyll and if in short supply gives rise to a pale green or chlorotic foliage. Unlike calcium it seems to be highly mobile in the plant and the growing tip is the last to starve.

The soil analysis usually consists in leaching with a neutral salt or dilute acid and estimating the exchangeable magnesium. Reserves may be present as carbonates or as exchangeable magnesium.

The remedy for deficiencies is the occasional use of magnesian limestone or dressings of crude Epsom salts. Under glasshouse conditions foliar sprays of magnesium sulphate have proved very effective.

There is little evidence to support the contention that excessive

magnesium does harm under field conditions particularly if the calcium is properly in balance.

Iron

In Britain iron is found in all soils and it is unlikely that a genuine deficiency ever occurs. Nevertheless lime-induced chlorosis in plants is common on most calcareous soils such as the chalk and the softer limestones. It is not clear whether the chlorotic condition is due to a reduced intake of iron or to its immobility in the plant, probably both, although the latter is more easily proved by analysis of the tissues. A high pH is likely to lead to iron deficiency conditions as a result of reduced availability. The presence of a number of metals such as zinc, copper, chromium and nickel, such as may occur in soils of certain sewage farms and river valleys found in the vicinity of towns engaged on metallurgical processes (6), may indirectly cause symptoms of iron deficiency in crops. The occurrence of iron deficiency under acid conditions may be associated with the presence of an excessive amount of elements such as these mentioned. Numerous devices have been tried in order to overcome iron deficiency including treatment of the soil with sulphur, growing a grass cover in fruit orchards and of covering the soil with several inches of an acid peat. Applications of iron salts to the soil are almost invariably unsuccessful since under high pH conditions they become immobilized. Injections of iron salts e.g. ferrous sulphate by direct application to the plant, if woody and stout enough to bear the treatment, are on the whole remarkably successful. Foliar sprays of dilute ferrous sulphate can sometimes be used but may cause serious damage.

With the possible exception of induced phosphorous deficiency under acid conditions, as far as is known no damage to crops arises from excess quantities of mobile iron in well aerated soils.

Manganese

Most British soils contain sufficient reserves of manganese but its availability to the plant depends on several factors. Under acid conditions the supply of available manganese is adequate for all crops and excessive—leading to toxicity—for some. At a pH above 6·5 a change in the form of manganese takes place (probably from a divalent to a state of higher valency) thought by some workers to be associated with microbiological activity, (7) and (8). At the same time a decrease in availability takes place particularly if the soil contains high amounts of organic matter. In fact low availability of this element is almost invariably the consequence of both conditions occurring simultaneously. The three commonest soils to exhibit manganese deficiency in Britain are alkaline peats, alluvial silts containing excess organic matter and black sands derived from podsols where over-generous amounts of lime have been applied.

Crop deficiency symptoms are very definite. They can usually be diagnosed visually and confirmed by means of the watering-can containing dilute manganese salts, by tissue tests and field trials. Chlorosis is often a symptom of deficiency. In some ways it is reminiscent of iron chlorosis but tends to be rather more diffuse, although in beans and peas the symptom is a central brown mark in the seed and in potatoes a spotting of the leaves. Treatment by application

of manganese salts to the soil is generally only partially successful in producing a crop for the same reasons that iron salts are unsuccessful, viz.:—that they become unavailable due to immobilization at high pH values. Applications of other manganese bearing materials such as basic slag are also relatively unsuccessful. Applications of acidifying agents such as sulphur (when available) have been used very effectively under experimental field conditions.

For general agricultural and horticultural treatment, manganese sulphate incorporated in foliar sprays applied, if necessary, several times during the season are the most effective.

Chemical methods of soil analysis (9) are employed to forecast possible manganese deficiency but require careful interpretation both in relation to soil and crop.

Some of the hitherto unexplained harmful effects of acid soils on plant growth have recently been shown by WALLACE and HEWITT (10), LÖHNIS and others (11), to be due to excessive soluble manganese in the soil acting as a toxic agent. This work carried out under controlled conditions in sand cultures indicates that certain crops are much more sensitive than others. On brassicas, for instance, these effects consist in stunting of the plant, cupping of the leaf, chlorosis and necrosis of the margin.

Boron

Under acid conditions most British soils are well supplied with boron easily available to plants. Low availability, arising from a depression of the solubility, only arises under conditions of neutrality or alkalinity. Unlike manganese, boron deficiency is not necessarily associated with excessive organic matter in the soil for it often occurs in mineral soils, particularly in dry hot seasons. The occurrence of boron deficiency in crops is very widely spread and is reported from almost all parts of the world. It is known by many descriptive names for different crops such as "Raan" in swedes, "Heartrot" in beet, "Hollow Stem" in cauliflower, etc.

In Britain boron deficiency is of little economic importance except in root crops. As already stated its occurrence is seasonal but in dry seasons it can be very troublesome. An assessment on sugar beet made by the writer a few years ago in the vicinity of one sugar factory estimated damage to occur on about 400 acres. In the same year on one 20-acre field the crop had been reduced by 50-75%. The effect on horticultural crops often makes them unsaleable.

Little is known of the mode of occurrence of the more soluble boron compounds and methods of assessing the availability are being developed.

14 to 20 lb. of borax per acre applied to the soil before the crop is sown is an effective remedy for several years. Borax can be readily sprayed on to crops but is generally unnecessary since soils dressings generally are readily available. From time to time boronated fertilizers reach the market but their indiscriminate use should not be encouraged.

Boron deficiency is readily controlled by treatment of the seed bed but, as stated previously, care in amounts applied are necessary as the margin between a sufficiency for a full crop and a toxic excess is narrow.

No natural excesses of boron seem to occur in British soils—the condition only arises if dressings have been too lavish.

Copper

Copper deficiency has received much attention in many parts of the world, especially on newly reclaimed land where it is called "Reclamation Disease" (12). In Britain its occurrence has only recently been observed, but it may be more widespread than was hitherto suspected.

The normal copper content of soils is low and some, notably those high in organic matter, appear to be able to fix copper in a form unavailable to crops. PIZER has found it occurring in wheat and barley in East Anglian Fens (13) where treatment with copper sulphate has produced spectacular results. Others have observed it on sands in Surrey (14) and Devon affecting fruit trees.

Deficiency of copper results in distortion of the heads of cereals and produces chlorosis and dying of the tips of shoots and heads.

Liming also seems to aggravate the situation; hence the soil pH is an important factor.

Chemical examination of the soil is being carried out at a number of centres but the methods employed need to be developed. Copper toxicity occurs spasmodically often in conjunction with other metals in old mining districts and in areas where streams containing metallurgical effluents have overflowed into the fields.

Zinc

Although zinc deficiency is widely distributed in many parts of the world (15), and particularly important in Citrus-growing countries, it is probably not of any great importance in Britain except in localized areas. Apples have been shown to be affected by this deficiency on the sands at Wisley (16) in Surrey and it probably occurs in other areas on similar geological formations. ROACH in the Romney Marsh, has obtained increases in potato crops by additions of zinc salts alone, but even more markedly with the addition of manganese. Whether such considerations are applicable outside these special areas is uncertain. Methods of soil analysis for zinc are in use at a number of the centres. In the Midlands zinc toxicity in black sands at pH 5·0 resulted in complete grass crop failure. This was corrected by liming to raise the pH to 6·5.

Molybdenum

Recent investigations in Britain have led to the conclusion that a number of crop conditions such as "Whiptail" in cauliflower (17) are due to a molybdenum deficiency although it is by no means certain that the story is a simple one.

Molybdenum deficiency in plants occurs in a number of parts of the world as well but, contrary to experience with zinc, iron and manganese, the availability of molybdenum increases with rising pH values and "Whiptail" would be expected more frequently therefore on soils with an acid reaction.

Its significance in the physiological processes of the plant are not

fully worked out, although it seems to have some connection with nitrogen changes.

Normally it occurs in very minute quantities in soils. It is an impurity in many of the materials used in pot experiments and more than usual care is necessary in purification of chemicals and protection of the young plant. Chemical soil tests for molybdenum are being developed.

Equally interesting in Britain is the "teart" problem of the Somerset pastures (18) where the effect of excessive molybdenum in the herbage on soils derived from beds of the "Lower Lias Clay," has catastrophic effects on grazing cattle. This is referred to later.

Chemical Determination of Micro-Nutrients in the Soil

It is the ideal of the Soil Chemist to devise rapid and accurate chemical methods for determining the soil nutrients. Over the last 100 years a great deal of attention has been paid to the chemical estimation of macro-nutrients but only within the last few years has similar attention been given to micro-nutrients. There is usually no difficulty in estimating the "total" amount of a nutrient; the difficulties begin when attention is turned to finding a suitable solvent for distinguishing the "available" fraction. Occasionally the chemical estimation of an element such as molybdenum is difficult as the amounts present in the soil may be below the sensitivity level of the methods employed for its detection, or below the impurity level in the reagents used.

A reasonably accurate chemical assessment presupposes knowledge of the chemical form of the material which it is intended to extract. Unfortunately that knowledge is more often than not missing and, without it, development of methods for estimating "available" nutrients are empirical.

Assuming that reasonably good laboratory methods of extraction become available there still remains the need to relate the results to soil type. On the field side accurate determination and delineation of the soil series are essential if chemical methods are to have other than localized application. In the final stage innumerable and well-conducted field trials are necessary to establish criteria. In Britain, all three stages are only slowly developing. I can only suggest that the need for development of the fundamental side is paramount. The field experimental side can more easily be conducted. Chemical extraction methods for soil micro-nutrients are slowly being developed, and those so far in use, which might be regarded as tentative, are given in Appendix I. (Britain, England and Wales).

In advisory work analytical methods must be rapid, accurate, economical in materials and labour and should be capable of being adapted wholly or in part to physical methods of measurement. Cumbersome methods usually tend to inaccuracy, slow down work and weary the operator.

As much uniformity as is reasonably possible is desirable between centres having regard to the different soil types. This is particularly necessary when comparing the analytical results from similar but widely scattered field experiments.

Bioassay of Magnesium, Zinc, Copper and Molybdenum by means of Aspergillus niger

It may seem that the more logical method of approach to the problem of the estimation of available nutrients in soils should be made by biological means. In other words, it would seem more reasonable to ask the question of the growing plant itself. Such is the basis underlying the well-tried MITSCHERLICH and NEUBAUER methods for the estimation of macro-nutrients. Similar methods for the determination of nutrients by the use of the moulds and bacteria have been used in a number of countries including Great Britain. In Britain methods for the determination of magnesium and a number of micro-nutrients using Aspergillus niger have been developed successfully by D. J. D. NICHOLAS and A. H. FIELDING (19) at Long Ashton, using E. G. MULDER'S strain. At present these methods, demanding a high degree of purity in the chemicals used and much care in avoiding contamination, are not well suited to routine work where a large number of soil samples and relatively unskilled labour are involved. For other types of investigation such, for instance, as the study of the distribution of nutrient elements in soil series, they may be invaluable.

The extent of sporulation and the dry weights of fungus produced are both used as criteria in determining the level of the nutrients in the soil.

It would be thought that the bioassay method ought certainly to be a logical way for determining the availability of nutrients to crops and further its sensitivity is strongly in its favour. Its value in detecting copper deficiency in fen soils, zinc and copper deficiencies in the Wisley soils and molybdenum deficiency in " Whiptail " soils has been demonstrated by NICHOLAS and others.

Aspergillus is considered by some workers to be the best method for all trace elements except boron.

Plant Analysis

Early hopes that the mineral make-up of the plant would be a guide to manuring were shattered when, for example, LAWES showed that the higher phosphatic requirements of turnips were not reflected in their composition.

As recently as 1920, however, WALLACE re-examined the position and established that the uptake of potassium in leaves and buds of fruit trees was directly correlated with the supply at the disposal of the plant. Since then much valuable work has been carried out in Britain, France, U.S.A., Sweden and elsewhere and established the usefulness of this method of attack. It is in effect another phase of the biological approach by extending it to analysis of plants growing under natural conditions and using as standards criteria derived from similar plants grown under controlled conditions.

This method finds considerable favour in the Advisory Service in diagnosing crop failures, but until its limitations are determined it is, perhaps, rather early to make any accurate assessment of its ultimate usefulness. Meanwhile, large amounts of data are being accumulated and gradually standards for minimum levels of nutrients are being established.

For healthy growth of apple trees WALLACE recommends as minima

CaO .... 1·10 MgO .... 0·40 K_2O .... 1·5

expressed as percentages of the dry matter of leaves taken from terminal shoots of apples collected in late July. Extensions of this method to cover the micro-nutrients are now being made.

Actively growing organs such as leaves and tips must be chosen and it is essential to ensure that they are at the same stage of growth.

Extraction methods in use are given in Appendix II.

Tissue Testing

Although they are growing in favour the methods just described are at present rather slow. During the last decade quicker ways of tissue testing based on rapid chemical tests of extracted juices of leaves or petioles have been developed.

Long Ashton and the Advisory Services have given much attention to developing tissue tests. They seem to be most useful when employed for examining extracts from plant organs growing under conditions of health and comparing them with those growing under deficiency or toxic conditions. Under fairly strictly controlled conditions it has been found possible to establish certain standards but much more work is still required before the extent of usefulness of the method is established. In spite of limitations it is still another weapon of value in determining the causes of crop behaviour.

Details are given in "Mineral Deficiencies in Plants," by T. WALLACE (20).

Plant Injection

In addition to curative treatment already mentioned under "iron," similar techniques have been developed by W. A. ROACH (3) at East Malling for "diagnosing deficiencies" by liquid injections into leaves and other growing parts. Considerable experience is needed in their use and they have not been widely adopted in advisory work. Foliar sprays are easier and for that reason have been used more widely instead.

Micro-Nutrients—Animals

The field of work concerning the effects of micro-nutrients in animals is jointly covered by Biochemists, the Advisory Chemists and investigators in the veterinary field. For that reason work in Britain has been approached mainly from the two angles, the animal and the plant, doubtless with advantage. The mineral micro-nutrient problems in animals are partly those arising directly from some shortage, or maybe excess, in the herbage or fodders on which the animal feeds and partly conditioned deficiencies or metabolic disturbances brought about by disfunctions within the animal. From the point of view of treatment both conditions may often be cured by the same remedy.

Magnesium

It is improbable that magnesium deficiency in the grazing animal, in the true nutritional sense, exists. Most disorders associated with this element are due to physiological disfunctions. Low blood magnesium occurs in cattle and sheep irrespective of the magnesium

content of the pastures they graze; in fact, the animal can often suffer even on grass which is relatively high in magnesium.

GREEN (21) postulates several kinds of hypomagnesaemia.

(1) Acute, when the fall in blood content happens suddenly, often resulting in colvulsive tetany and death. This has been called "grass tetany" in Holland. The condition "lactative tetany", cured by injecting magnesium, occurs frequently in milking cows, but can also occur in males. Practically nothing is known of the physiological mechanism responsible for maintenance of magnesium levels in the animal nor of the reasons for its being thrown out of gear.

(2) A slowly developing hypomagnesaemia not attended by severe symptoms. Occurs over months.

(3) An intermediate type occurring less rapidly than (1) but more quickly than (2). This condition often causes the practitioner considerable trouble.

No treatments of grassland are possible, since the relationship with the disease is not known.

It is probable that feeding with large quantities of easily soluble magnesium is sometimes helpful in overcoming disfunction in the animal body. Injection of magnesium salts have under certain circumstances proved beneficial.

Cobalt

Cobalt deficiency in animals is widely distributed in Britain (22) and extends spasmodically from Cornwall in the south to the north of Scotland. While certain areas such as Bodmin Moor and Dartmoor seem well defined others such as the Old Red Sandstones of Herefordshire and Brecon are much less so. If the close correlation such as exists between "pine" and geological beds in Devon and Cornwall could be established everywhere else, the problem of taking proper remedial measures would be greatly simplified.

In a recent report on trials with sheep to establish the prevalence of "pine" in the Old Red Sandstone of the English Midlands, only three cases out of seventeen gave a positive confirmation of its presence.

In Northern England cobalt deficiency occurs round the slopes of the Cheviots, along the Tyne gap and in South-West Northumberland (23). In these areas pining is sporadic and may be severe on particular farms about four years out of nine but virtually non-existent in the other five. Treatment with cobalt salts has become a regular practice and the farmers are satisfied that it is worth while. Both soils and pasture analyses can be used to indicate areas sufficiently low in cobalt to cause pining

Copper

Copper deficiency is rather more widely distributed in Britain than pine. It affects sheep and is called "swayback," with a number of local names. More recently it has been investigated in cattle by Dr. ALLCROFT (24), and others, and found to be much more prevalent than was formerly supposed. Some farms have long histories of

losses of sheep and this fact, no doubt, has had some influence on farmers in giving up their flocks. Although prenatal damage cannot later be cured it can be prevented by feeding copper sulphate to the ewes early in pregnancy.

There is evidence to show that low copper content of the blood often occurs when that in the herbage eaten is normal. Although informed opinion tends, at present, to place most of the cases occurring in Britain in the "condition deficiency" category, that is not the case in some other parts of the world. Both real and conditioned deficiency of copper have been observed in diluvial and alluvial parts of the Netherlands.

Sheep are susceptible to copper poisoning and treatment must not, therefore, be excessive.

For a long time farmers in some areas had associated swayback with lead poisoning, but recent work now shows this not to be the case.

Molybdenum

A serious disorder has long been known in cattle grazing on the so-called "teart" pastures of Somerset but until recently the cause remained unknown. In Britain it seems usually to be associated with certain beds of the Lower Lias Clay and although the same geological formation is well developed in other counties, too, the condition is seldom met with except in Somerset. Within the writer's experience one authentic case has occurred in Warwickshire. One or two cases of suspected similar conditions have cropped up recently on calcareous soils other than Lower Lias Clay. The discovery of the causal factor behind this age-long complaint in cattle was a triumph for scientific investigation and was due to FERGUSON, LEWIS and WATSON using spectrographic methods at Jealott's Hill (18). The teart condition can be induced in pastures by dressing them with sodium molybdate when the molybdenum passes into the herbage. The condition is prevented by administering copper sulphate in small doses to the cattle and cattle cakes for this purpose are manufactured. Dressing the pastures with copper sulphate is not regarded as satisfactory as most of the copper remains ineffective in the soil.

Fluorine

Fluorosis in animals—cattle particularly—is invariably caused in this country by the ingestion of fluorine containing compounds emitted by industrial processes often but not invariably where fluorspar is used. In excess it severely affects grazing animals and with long continued ingestion causes lameness, brittleness of bones and softening of the teeth. Feeding becomes difficult and starvation ensues and there appears to be no cure. Elimination of the effluent fluorine products at the source is the ideal but often difficult to achieve. The farmer so unfortunate as to have his holding severely affected is forced to turn entirely to crop husbandry or to keep animals so short a time on the holding that he is able to dispose of them before severe symptoms appear.

Manganese

There is considerable doubt whether any disorders in animals (other than poultry) are really caused by manganese deficiency. At

one time it was thought to be a causal factor in sterility in dairy cows but recent work would not confirm earlier suspicions. It is probable that manganese requirements of sheep, cattle and horses are very small and normally satisfied by ordinary feeding stuffs. Porosis or slipped tendon in poultry has long been considered to be due to a deficiency of manganese in the diet.

Iodine

Goitre and other conditions in the animal, caused by iodine deficiency, are world wide. Little trouble, however, occurs in Britain except in a few well defined districts.

In concluding this short introductory paper I am conscious of many omissions. Subsequent speakers will fill in the gaps and give us the benefit of first-hand knowledge of various phases of the subject. It may be thought that I have taken rather an insular view in so far as I have discussed conditions mainly from the British angle. I have done this advisedly and for the reason I have already stated and must leave the task of developing the story in other countries in the hands of those with first-hand knowledge and who are best able to do it. It is gratifying that studies in plant and animal nutrients are now proceeding vigorously in most parts of the world for we need every bit of useful information in the vital work of feeding livestock and humans. Unfortunately as in other fields of agriculture, the speed of accumulation of knowledge is outstripping the rate of its application. If it were possible to put into practice much that is now known, as in fact it is by the better farmers, it would result in vast increases of vegetable and animal food.

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APPENDIX I

MAGNESIUM AND MICRO-NUTRIENTS.

Extraction Agents — *Soils* — T—*Total* A—*Available*

Province	Magnesium	Iron	Boron	Manganese	Copper	Zinc	Molybdenum	Cobalt
South Eastern ... (Reading)	T. Acid Extract A. Amm. acetate or Acetic Acid	—	A. Aqueous	A. Amm. acetate followed by Sod. Acetate (·2% hydroquinone)	T. H_2SO_4 + HNO_3 + Perchloric Acid A. 2·5% Acetic Acid	T. H_2SO_4 + HNO_3 + Perchloric Acid A. 2·5% Acetic Acid	T. HF + Perchloric Acid or Acid Digestion	T. HCl. A. 2·5% Acetic Acid
South Eastern ... (Wye)	A. Morgan's Reagent	—	A. Aqueous	—	—	A. Morgan's Reagent (for XS)	—	—
South Western ...	A. Morgan's Reagent	—	A. Aqueous	A. Amm. acetate	T. Perchloric Acid + Nitric Acid	T. 10 N. HCl.	A. Aqueous	A. 2·5% Acetic Acid
Yorks and Lancs. ...	—	—	—	—	—	—	—	—
Northern	A. Morgan's Reagent	—	A. Aqueous	—	—	—	—	A. 2·5% Acetic Acid
Eastern	A. N. Amm. nitrate (soil : ext :: 1 : 6)	—	—	A. Morgan's Reagent (N/2 Acetic Acid) (1 : 6) (N/2 Na. Acetate)	—	A. Morgan's Reagent (1 : 6)	—	—
West Midland ...	A. N/2 Acetic Acid (non calc.) or N/5 Sod. chloride (calc.)	—	—	A. Aqueous and N. Amm. acetate	T. H_2SO_4 + HNO_3 A. N/2 Acetic Acid	—	T. Ash. HCl.	A. 2·5% Acetic Acid
East Midland ...	A. NaCl or N/2 Acetic Acid	—	A. Aqueous	A. N. Amm. acetate	T. HCl. conc.	T. HCl. conc.	T. HCl. conc. + HNO_3 conc.	A. 2·5% Acetic Acid
Wales	A. N. Acetic Acid	—	(pH test)	A. N. Amm. acetate	A. 2·5% Acetic Acid	A. 2·5% Acetic Acid	—	A. 2·5% Acetic Acid

APPENDIX II

MAGNESIUM AND MICRO-NUTRIENTS.

	Extraction Agents					*Plants*		
Province	Magnesium	Iron	Boron	Manganese	Copper	Zinc	Molybdenum	Cobalt
South Eastern ... (Reading)	Ash HCl	—	Ash H_2SO_4	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid	Ash HCl
South Eastern ... (Wye)	Wet Ashing	Ash HCl	Ash HCl	Morgan's Reagent (for XS)	Ash HCl	Morgan's Reagent (for XS)	—	—
South Western ...	Morgan's Reagent	*Digest* HNO_3 + Perchloric Acid	Ash HCl	*Digest* HNO_3 + Perchloric Acid	*Digest* HNO_3 + Perchloric Acid[1]	Ash 10N HCl	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid[1]
Yorks. and Lancs.	—	—	—	*Digest* HNO_3 + Perchloric Acid	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid	—	—	—
Northern ...	Ash HCl	Ash HCl + HNO_3	Ash H_2SO_4	Ash $H_2SO_4 + Na_2SO_3$	Ash Hcl + HNO_3	—	Ash HCl	Ash HCl (Aq. extr)
Eastern ...	Ash (500°C.) Ext. 0·05N HCl	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid (100°C.)	—	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid (100°C.)	—	—	—	—
West Midlands ...	Ash HCl	*Digest* $HNO_3 + H_2SO_4$ + Perchloric Acid	Ash H_2SO_4	*Digest* $H_2SO_4 + HNO_3$	*Digest* $H_2SO_4 + HNO_3$	Ash HCl	Ash HCl	*Digest* $H_2SO_4 + HNO_3$
East Midlands ...	Ash HCl	—	Ash H_2SO_4	*Digest* with $H_2SO_4 + HNO_3 + H_3PO_4$	Ash HCl	Ash HCl	Ash HNO_3	*Digest* HNO_3
Wales ...	Ash HCl (1 : 1)	—	—	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid	*Digest* $H_2SO_4 + HNO_3$ + Perchloric Acid	*Digest* $H_2SO_4 + HNO_3$ + Perchlore Acid	—	—

SESSION 5

SOME ASPECTS OF THE MICROBIOLOGICAL DETERMINATION OF MAGNESIUM, ZINC, COPPER AND BORON

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The principle of the microbiological determination of plant nutrients will be well known to most of you. A suitable microorganism, in most cases the mold Aspergillus niger, is cultivated in a nutrient solution which is complete except for the one element to be determined. This element is supplied by the material (soil, leaves, minerals, etc.) to be investigated. Four days after inoculation at 32°C and without special care for keeping the cultures sterile, the weight of the mycelium, or in the case of copper, the colour of the spores, is

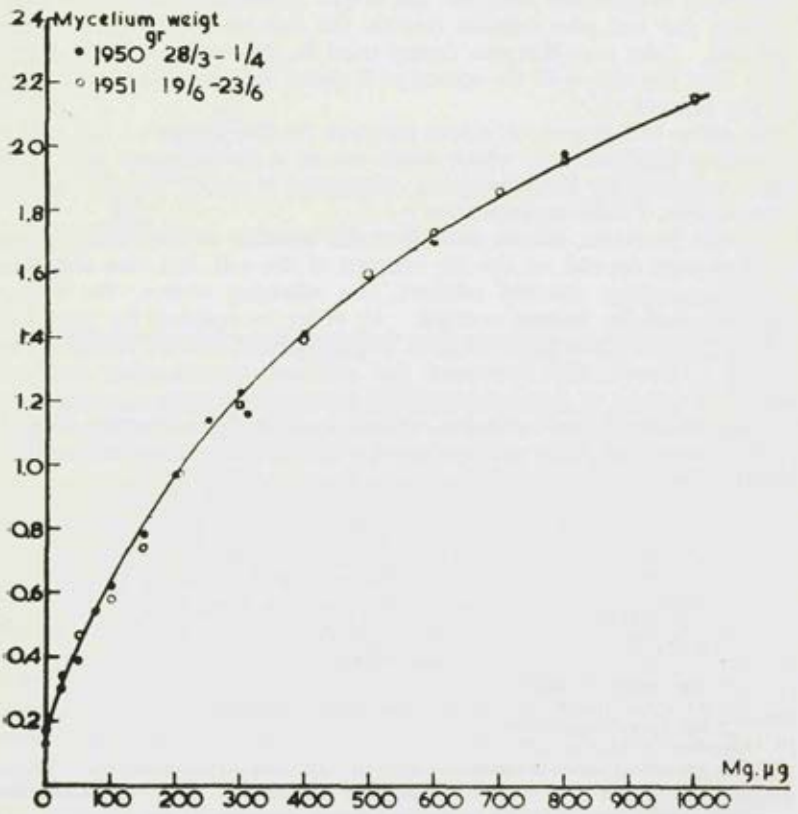


Fig. 1—The accuracy and especially the constancy of the Aspergillus niger strain is clearly shown by the fact that practically all the points of the determinations made in June, 1951, lay on the same curve as those made in May, 1950.

compared with that of a standard series with known quantities of the element to be determined. It is a great advantage that such widely divergent elements as potassium, magnesium, zinc, copper, molybdenum and phosphorus can be determined with a single and rather simple method and with an accuracy which in most cases equals or even surpasses that of the usual chemical methods. Even in the case of copper, zinc and molybdenum the chemical method is either inadequate or too laborious. Moreover, the way in which the plant nutrient is extracted from the soil by the mold shows a greater resemblance to that of the plant than the chemical method does. The Aspergillus constantly uses up the element as soon as it diffuses into the solution, and we have a progressive dynamic extraction as contrasted with the chemical extraction, which proceeds to a certain static equilibrium.

I want to make a few remarks on the determination of magnesium, zinc and copper and on our attempts to add boron to the list of elements, which in the future may be determined microbiologically.

NIKLAS and his assistant TRISCHLER (1930) were the first to determine magnesium with the aid of the Aspergillus niger, but their method did not give reliable results, the culture solution not being optimal. SMIT and MULDER (1940) tried to improve the method and they used the colour of the spores as a visual indicator for the amount of Mg present.

In order to have an objective measure for the colour of the spores I made a simple device which made use of a photoelectric cell. The light, reflected by the mycelium, originated a photo current, which was read on a milliampèremeter.

It was, however, shown soon that the number of the black spores did not only depend on the Mg content of the soil, but also on other factors, e.g. the calcium content, the nitrogen source, the buffer capacity and the humus content. In order to account for this, the culture solution was buffered with Ca citrate and sodium humate was added. Though this improved the accuracy considerably and enlarged the scope of the determination from 300 to 1000 γ, using 1 gr. of soil, finally it proved more reliable to determine the dry weight of the mycelium. One gram of air-dry soil is added to 75 ml. culture solution, which contains per l. :—

TABLE I*

100 g. glucose	15 mg. $(Fe_2)(SO_4)_3 . (NH_4)_2SO_4 . 24aq.$
10 g. citric acid	10 mg. $ZnSO_4 . 7aq.$
4 g. urea	5 mg. $MnSO_4 . 4aq.$
2·5 g. K_2HPO_4	1 mg. $CuSO_4 . 5aq.$
1 g. K_2SO_4	1 mg. $Na_2MoO_4 . 2aq.$
	1 mg. H_3BO_3
10 mg. sodium humate	}
1·25 g. Ca citrate	} per 75 ml. culture solution
1 ml. spore suspension	}

Incubate 4 days at 32°C.

The standard series contains 0—25—50—75—100—150—200—250—300—400—500—600—800—1,000 γ Mg. in 75 cc. solution. The determinations are made in NEUBAUER cylindrical dishes, diameter 11 cm.

*(More detailed information on the different soil tests with Aspergillus will be published shortly in *Plant and Soil*.)

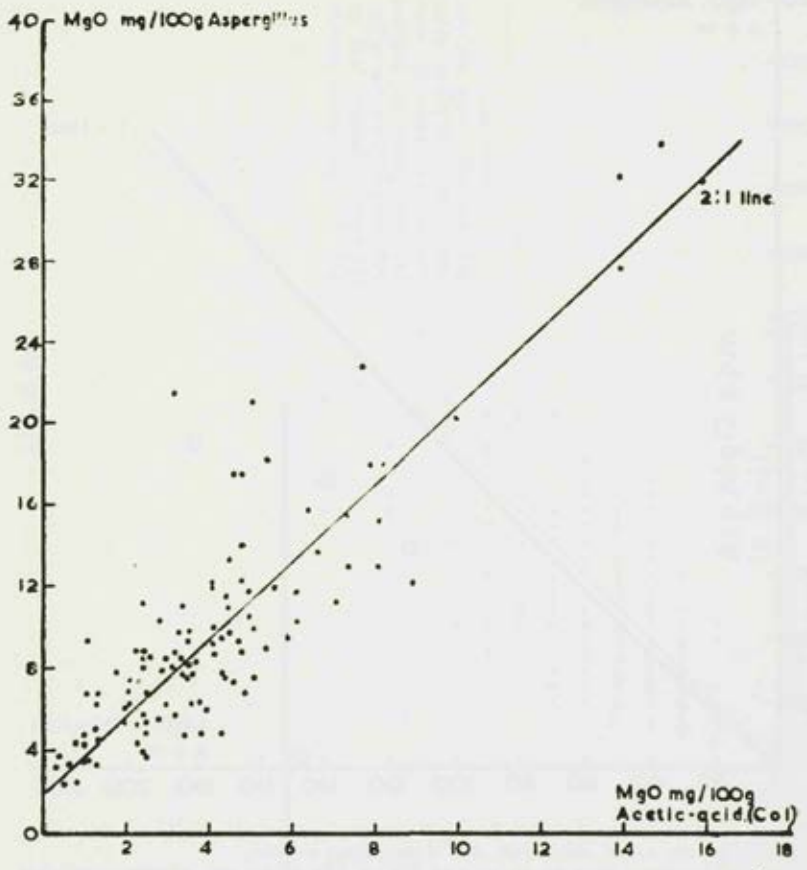


Fig. 2—A close correlation exists between MgO as determined with the Aspergillus method and MgO determined colorimetrically after extraction with diluted acetic acid. About twice as much Mg is extracted by the mold as in the latter case.

The opinion is sometimes expressed that the constancy of such a biological reaction tool will leave something to be desired, but from the next slide you will see that this is not the case (Fig. 1).

Here two standard curves are shown, one made in April 1950 and the other one in June 1951; both curves are identical, proving that the reactivity of the Aspergillus has remained absolutely constant during more than a year. When we compare the results obtained with the Aspergillus method with those of the colorimetric determination in diluted acetic acid soil extract with the aid of thiazol yellow, both made in the same soil samples, we may conclude that in general with the Aspergillus method about twice as much Mg is extracted as with the latter method (Fig. 2). When we compare the quantities of magnesium extracted with 0·1N hydrochloric acid with those extracted by the Aspergillus, it seems both methods give about the same results; though the correlation is fairly good, the spreading, however, is greater than in the former case (Fig. 3).

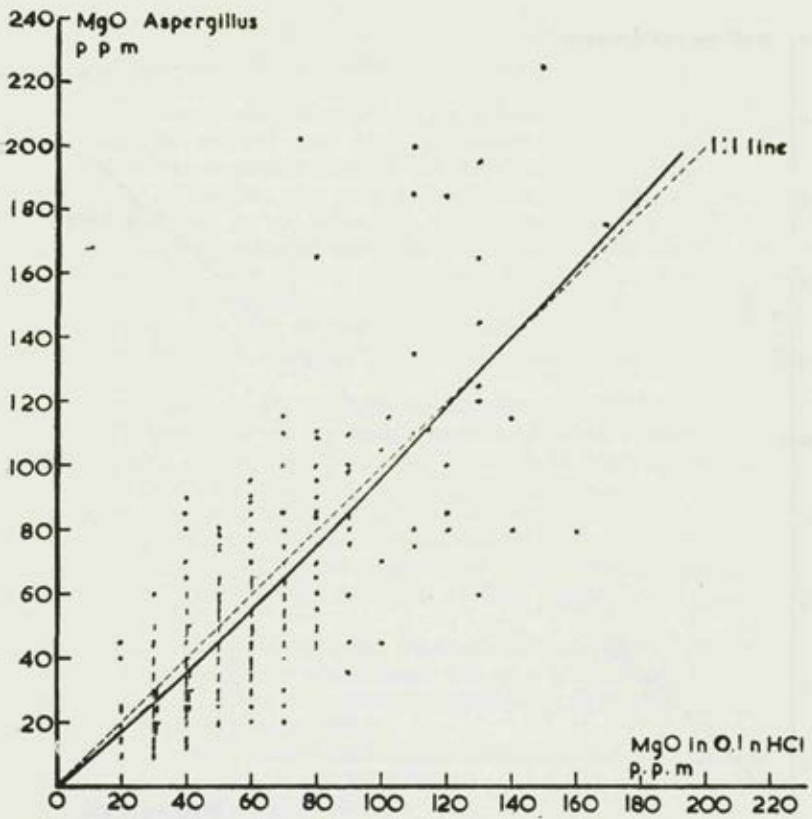


Fig. 3—The correlation between the MgO extracted with 0.1N HCl and the values obtained in the same soils with the Aspergillus method. Spreading is greater than in the case of Fig. 2 The points are equally distributed around the 1 : 1 line.

One might ask what is the advantage of the Aspergillus method when we possess chemical methods of equal accuracy. The difference is the simplicity. With the Aspergillus method a girl with elementary school education makes 300 determinations a week. When no special accuracy is wanted, as generally will be the case for advisory purposes and it suffices to know whether a soil is deficient in Mg or not, a classification in 4 or 5 degrees will do. In that case the growth of the mycelium mat may be compared visually with a standard series, which even allows a distinction of 8-10 degrees to be made. This makes washing, drying and weighing of the mycelia superfluous, so that in this way at least 450 determinations can be made by one girl in the same time.

The evaluation of the determinations with regard to their practical application and their correlation with the yield of different crops does not belong to my task, as this part of the work is carried out by other specialists at our Experiment Station. With their aid, however, I am able to show you a few graphs on this subject. In the following graph (Fig. 4) the correlation is shown between the MgO content

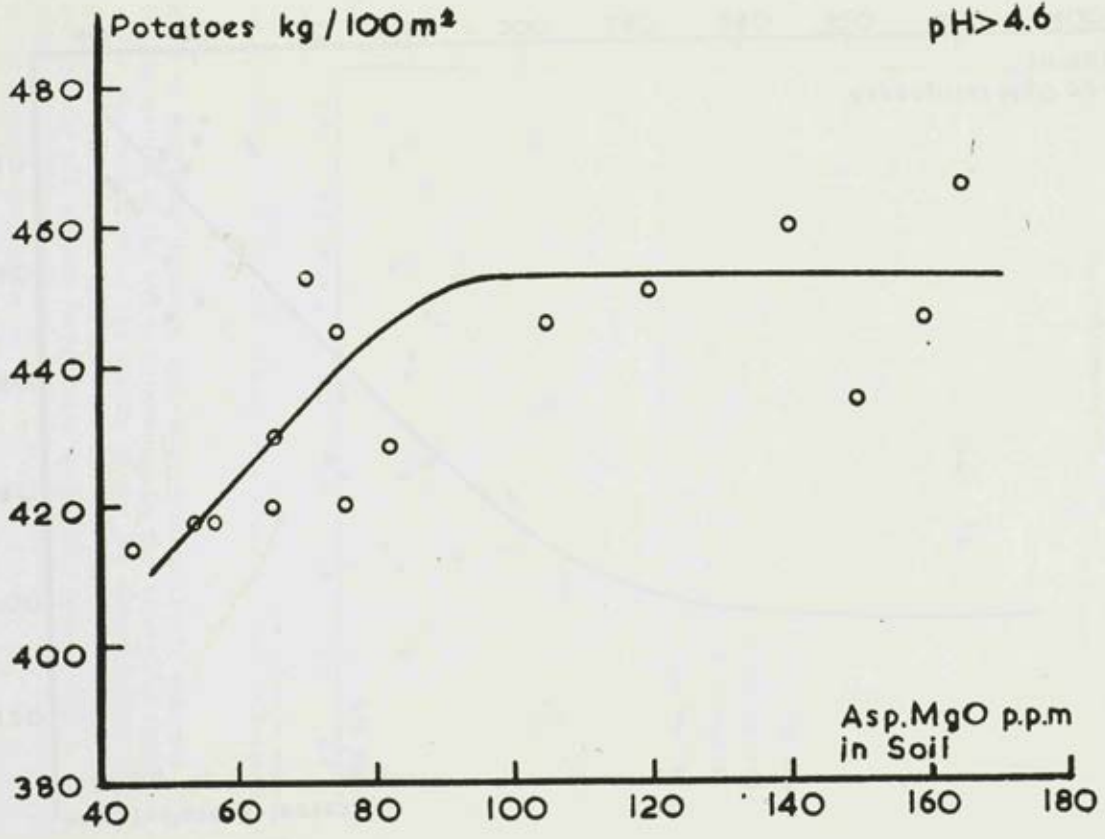


Fig. 4—The relation between the yield of potatoes and the MgO content of a dozen different soils seems to indicate that at a content of more than ± 100—120 p.p.m. MgO, Mg dressings will be unnecessary.

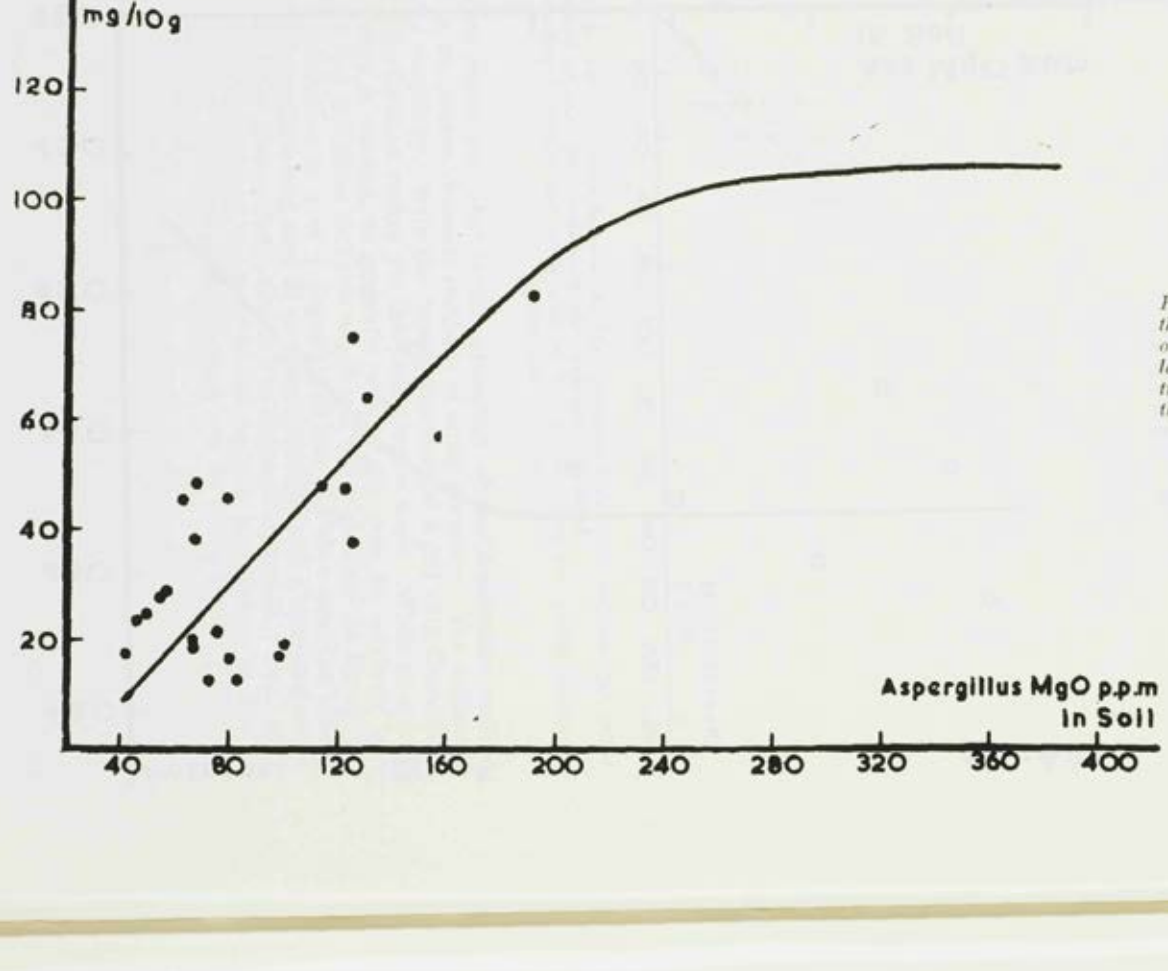


Fig. 5—The MgO content of the leaves of potatoes, grown on soils with different Mg levels, shows a distinct correlation with the MgO content of these soils as determined by the Aspergillus method.

of the soil, as determined by the Aspergillus method, and the yield of potatoes. It seems that above 100 p.p.m. these soils contain enough Mg to produce normal growth of the potatoes. A more convincing relation is seen in the following graph (Fig. 5), which shows the Mg content of the leaves as compared with the Mg content of the soil. Most convincing, however, is the next graph (Fig. 6), which shows very distinctly that on a dozen different soils of divergent pH's the

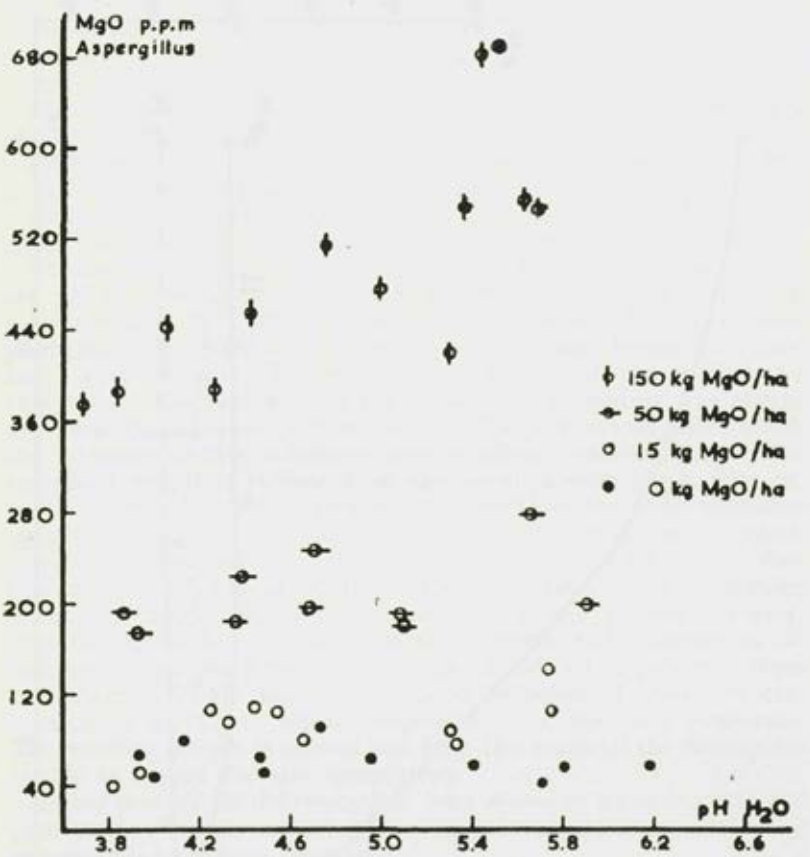


Fig. 6—The MgO values obtained with the Aspergillus method distinctly reflect the Mg status of a number of different soils, which received increasing Mg dressings.

effect of increasing dressings with Magnesium is clearly reflected in the Mg content of the soil as determined by the Aspergillus method.

For the evaluation of the results of the Mg determination it is generally advisable to take into account the humus content of the soil and the pH, as both factors may appreciably influence the availability of the Mg in the soil, according to numerous field tests made at our Experiment Station.

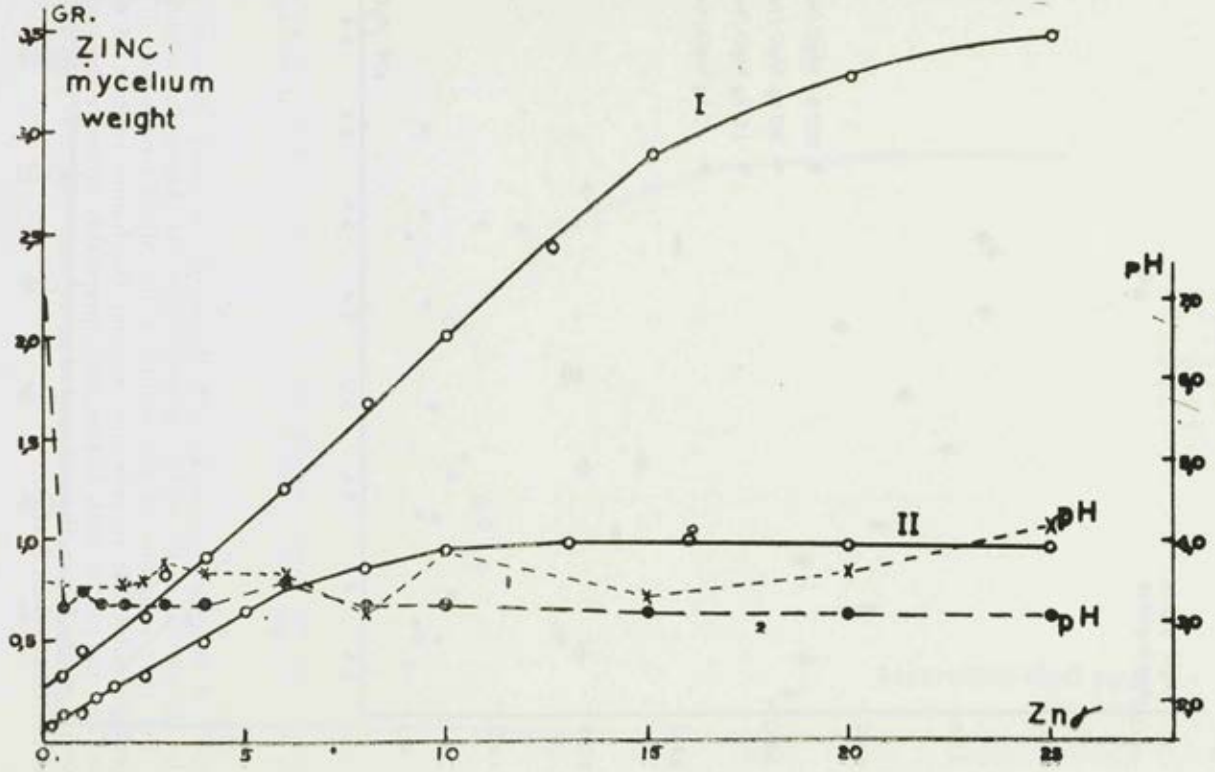


Fig. 7—Adding calcium - citrate to the culture medium has the effect of increasing the maximum mycelium weight threefold.

Zinc determination

Already in 1864 RAULIN showed that zinc stimulates the growth of Aspergillus niger, but it took more than half a century until the positive proof was brought by STEINBERG (1919) that zinc is an indispensable element for normal growth of this mold. Experiments on determination of Zn, have obviously been going on simultaneously and independently of each other at Long Ashton (NICHOLAS, 1947-1951) and at Groningen (GERRETSEN, 1948). The determination of zinc closely resembles that of magnesium. As the ordinary glassware often contains appreciable amounts of zinc, as well as some of the chemicals, it is necessary to use Zn-free glassware (SCHOTT, JENA, DURAN) and quartz distilled water. Purification of the culture solution is easily achieved by treating the solution (100 g. glucose, 2·5 g. K_2HPO_4, 1 g. $MgSO_4.7aq.$ in 1 l.H_2O) with norit. The other constituents, citric acid, urea and trace elements are practically free from Zn, when high grade brands are used.

The standard series contains: 0, 2, 4, 8, 12, 16, 20 and 25 γ Zn. After 4 days at 32°C the mycelia are washed, dried and weighed.

The necessity to have the culture solution well buffered and to keep the pH as constant as possible, is for the Zn determination even more essential than for the other determinations. The Aspergillus produces citric acid during its growth and it is well known that zinc has a very distinct influence on the production of organic acids by this mold. The best way to buffer the culture solution was also in this case by means of calcium citrate. The pronounced effect which the addition of this substance to the culture solution has on the mycelium weight is evident from the accompanying graph (Fig. 7). In the unbuffered culture solution the growth of the mold stagnates because of the presence of the undissociated organic acids, which simulates a constant pH. Another difficulty is caused by the fact that zinc is volatile at relatively low temperature and evaporates during the ashing of the plant material. It was proved, however, that the Aspergillus is able to extract directly and quantitively all zinc from dried plant material and that it sufficed to pulverize these substances. Woody materials, such as branches of trees, are carbonized at 250°C, at which temperature zinc does not evaporate. The resulting carbon is ground and from this material the Aspergillus is able to extract the zinc quantitively.

In our country Zn deficiency has been shown to occur in apple and pear yards, but as yet no systematical investigation or fertilizing experiments have been going on.

One of our experimental plots, which for a number of years, besides different fertilizer dressings, had received stable manure and town refuse, showed some interesting differences as is shown in the following Table:

TABLE 2

Mg and Zn content of soil from experimental plots

	Mg p.p.m.	Zn γ/gr.
Untreated	62·5	7·5
N,P,K.	62·5	12·5
Stable manure	142·5	26·5
Town refuse	201·5	212·0

The zinc content of the compost plot was forty times that of the undressed control plot, also in the stable manure plots a distinct increase in zinc was to be observed. It is also interesting to note that the magnesium content of the soils which had received stable manure had increased notably, whereas the compost plot even contained 3·5 times as much Mg as the control.

The Determination of Copper with Aspergillus niger

The Aspergillus test for determining copper was worked out first by MULDER (1938) and is founded on the fact that the colour of the spores of this mold depends on the presence of minute quantities of Cu, the colour varying from cream yellow, brown and blackbrown to black. Though this method stood up rather well, it was necessary to make a few improvements.

The culture solution was insufficiently buffered, which resulted in diverging final pH's depending on the quantity of Cu present. As ion availability is considerably influenced by soil reaction (ACOCK, 1941, PEACH, 1941) it is important that the pH of the culture solutions remains constant, independent of the Cu content of the soil. Neither the addition of $CaCO_3$, nor of calcium citrate gave satisfactory results; with ammonium citrate as a nitrogen source, however, the pH remained sufficiently constant for practical purposes and the mycelium developed into a homogeneous mat, whereas the blanks were whiter than was the case when the original culture solution was used.

TABLE 3

pH of substrate after growth of Aspergillus niger. (Cu determination)

Original culture solution (MULDER)		Culture solution for enlarged scope of determination		Revised culture solution with ammonium citrate as N source			
Cu content γ	pH after 4 days	Cu content γ	pH after 4 days	Cu content γ	pH after 4 days	Cu content γ	pH after 4 days
0	7·50	0	7·82	0	3·03	0	2·84
0·2	7·32	1·5	4·19	0·2	3·07	1·5	2·97
0·5	5·63	3	4·01	0·5	3·05	3	2·81
0·8	4·65	4	3·96	0·8	3·06	4	2·88
1·2	5·61	6	4·16	1·2	3·02	6	2·98
1·6	4·88	8	3·86	1·5	3·09	8	2·86
2·0	5·04	10	3·84	2·0	3·06	10	2·92
3·0	4·72	15	3·70	2·5	3·09	15	2·83

Another point which needed consideration was the fact that the scope of the determination was limited to the region between 0 and 2·5 γ per gram of soil. It had been observed that cattle sometimes suffer from copper deficiency on grassland, which according to our standards for arable land, contained sufficient copper. So it seemed desirable to enlarge the scope of the determination in order that quantities above 2·5 γ per gram of soil could be determined. This could simply be achieved by doubling the amounts of nutrients in

the culture solution either by increasing the concentration, or by doubling the total quantity of the solution. This results in a more vigorous growth of the mycelium and as the mycelium itself needs a certain quantity of copper for its normal development, less copper remains for the spores, i.e. the quantity of copper necessary for the blackening of the spores is increased. In this way we could determine 5 times as much Cu, as with the original culture solution, an amount corresponding to 12·5 γ Cu per gram of soil. The culture solution contains per l.: 50 g. glucose, 2·5 g. K_2HPO_4, 5 g. KNO_3, 1 g. $MgSO_4$ and trace elements.

In connection with the fact that the cattle sometimes showed copper deficiency when feeding on grass with a normal copper content, the question was raised as to the possibility of differences in availability of the organic copper compounds in the grass. Would it be possible to detect such differences by means of the Aspergillus method? In order to get informed on this point I started to investigate to what extent the Aspergillus could use a few definite chemical Cu compounds of widely divergent solubilities as a Cu source. I used copper sulphate, copper sulfide, copper glycinate and Ebesal, a very insoluble Cu preparation used in veterinary practice (Cu allylthioureum.sodium benzoate). Of these different compounds equal quantities of about 1 γ were suspended in 40 ml. culture solution and the result was that the Aspergillus promptly assimilated 1 γ Cu irrespectively of the solubility of the compounds. Undoubtedly this is caused by the ability of most microorganisms to extract the minutest traces of an element from their culture solution and though these substances have very low solubility and are dissociated to a very small extent, the ions are constantly delivered at a rate which is proportional to the rate at which they disappear from the solution.

By putting a suspension of the compound in a collodion sack and hanging this in pure distilled water it was expected that the number of Cu ions passing per unit of time through the membrane would bear a close relationship to the number of Cu ions which were inside the sack in equilibrium with the substance. At regular times samples were taken from the solution outside the collodion sack and the Cu content determined with the Aspergillus method. Now, the compounds convincingly show the expected differences in solubility. With this method a number of grass-samples from different localities were investigated and in it was shown that there existed indeed great differences in solubility of the copper compounds in the grass; the percentage of Cu dialysable under the circumstances of the experiment varied between 27% and 91% of the total Cu in the dry material.

Unfortunately, there was no correlation with the condition of the cows.

For practical purposes the results are evaluated according to the following scheme, which holds only for sandy soils and reclaimed peat soils:

> 2·5 mg. Cu/kg. soil	.... abundant Cu available.
2—2·5 mg. Cu/kg. soil	.... sufficient, generally no Cu dressings wanted.

1—2 mg. Cu/kg. soil	....	sufficient for potatoes and rye: oats, wheat and barley may show deficiency symptoms. Advice: 50 kg. $CuSO_4$ or 300 kg. copperslag meal/H.A.
0·4—1 mg. Cu/kg. soil	....	potatoes normal, rye slightly deficient, other cereals more or less pronouncedly deficient. Advice: 75 kg. $CuSO_4$ or 400 kg. copperslag meal/H.A.
< 0·4 mg. Cu/kg. soil	..	potatoes generally normal, all cereals diseased. Advice: 100 kg. $CuSO_4$ or 500 kg. copperslag meal.

The situation of clay soils is not yet sufficiently cleared up. Cu deficiency seems to occur only in rare cases. Experiments on grassland are not yet concluded. 1 mg. kg. soil seems to be the limit, below this amount application of Cu is necessary in most cases.

Attempts to determine Boron biologically

Though the investigations concerning this problem have not yet been concluded, it might perhaps be of interest to say a few words about our experiments on the biological determination of boron. Though it is a well established fact that higher plants want boron for normal growth, little is known about the need of micro-organisms for this element. Miss L. YAGESWARI (1948) obtained increased growth of different Fusaria on the addition of boron. JORDAN and ANDERSON (1950) conclude that " Boron seems to increase the nitrogen fixation of Azotobacter chroococcum in soils and in pure culture," but some of their results are rather conflicting.

In my first experiments the carbon dioxide evolution of the microbial population of a B deficient soil, to which mannitol and phosphate had been added, was compared with that of the same soil after the addition of 5 p.p.m. B. The latter produced 10—20% more CO_2 than the first. In a second experiment sterile sand with Ca gluconate and nutrient salts with and without boron in duplicate was inoculated with a suspension of Azotobacter chroococcum. In this case the effect of the addition of boron was still more pronounced, the sand cultures with boron produced 9·8 g. CO_2 in 120 hours, those without B only 5·8 g. CO_2 in the same time. As it might be possible that in the latter case a small amount of B was still present, an attempt was made to free sand and chemicals from the last traces of boron by mixing these materials with methyl alcohol and acetic acid, evaporating to dryness and repeating this treatment six times. (It must be emphasized that all the material for both experiments was treated in the same way and that finally the only difference between the two series was, that one had received boron and the other not).

The result of this experiment is shown in the following graph (Fig. 8), the quantity of CO_2 finally produced by the Azobacter in the sand culture with boron being 4·5 times that of the culture without boron. Fig. 9 shows the results of another experiment in which increasing quantities of boron had been used and which shows such a regular correlation between boron-content and CO_2 evolution that one gets

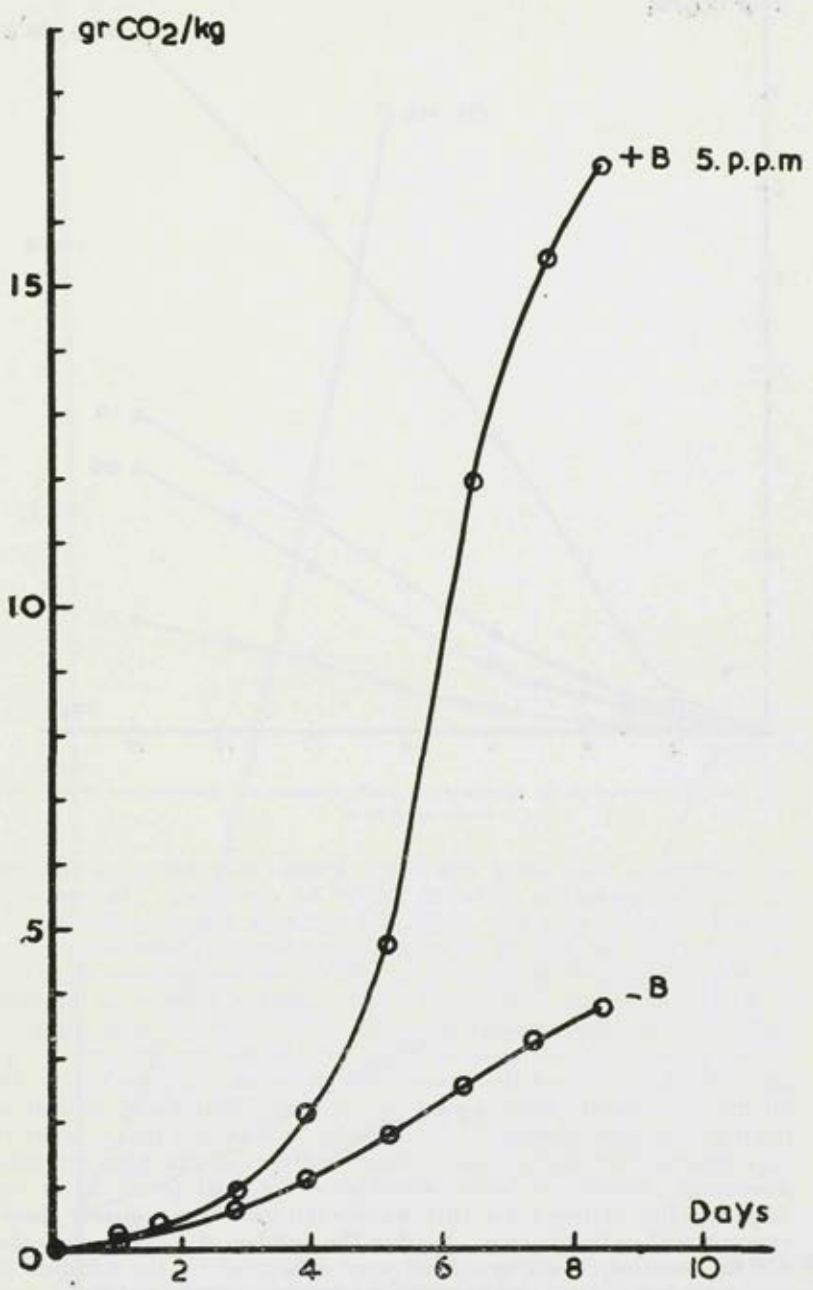


Fig. 8—CO_2 developed by a sterile sandculture containing mannitol and nutrient salts and infected with Azotobacter chroococcum without Boron and with 5 p.p.m. Boron.

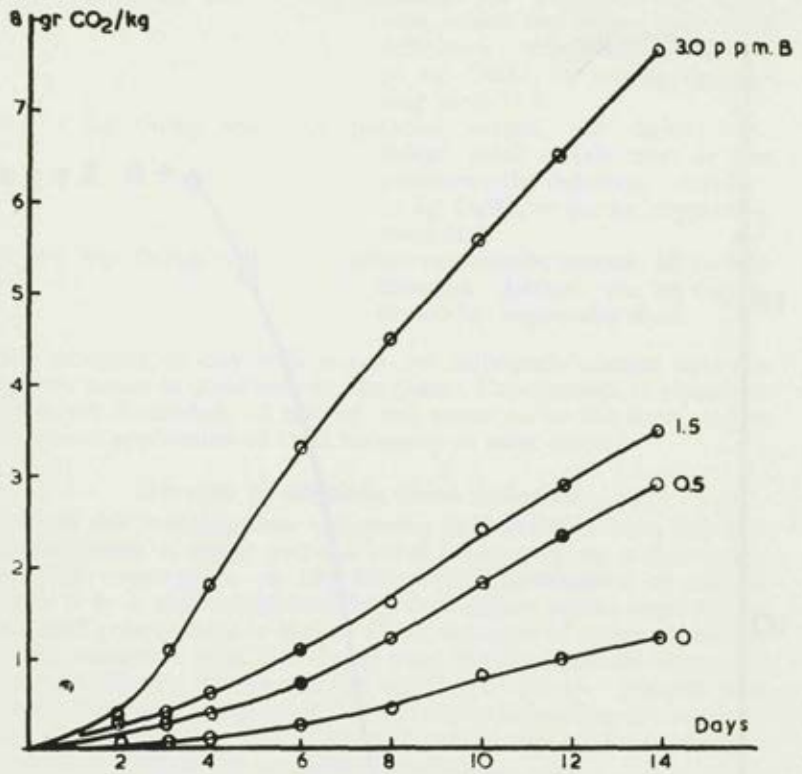


Fig. 9—CO_2 developed by sandcultures with Azotobacter chroococcum at different levels of Boron.

the impression that along this line a simple microbiological method for the determination of boron might be developed. Moreover it seemed very plausible that boron did not only stimulate the growth of Azobacter, but that it is an indispensable trace element for the normal development of the bacteria. In the following graph (Fig. 10), in which the influence of boron on the nitrogen fixation at different pH's is shown, this assumption seems to be affirmed: with 3 p.p.m. B the quantity of nitrogen fixed by the Azotobacter amounts to 45 mg., which is 30 times the amount of the culture without B. So far all the experiments were carried out in sand cultures and seemed to point in the same direction. So it might be expected that a series of experiments with liquid, well aerated cultures of Azotobacter with increasing amounts of boron would give the final proof of the indispensability of boron for this microorganism. The contrary, however, proved to be the case. Neither the number of Azotobacter cells, nor the amount of nitrogen fixed were influenced by the addition of boron to the culture solution. Only in one aspect they differed, viz. the final colour of the bacteria-suspension. Without boron it was a cream-white, fairly thick suspension, with boron the colour of the suspension was brown black. Though this opens the possibility of

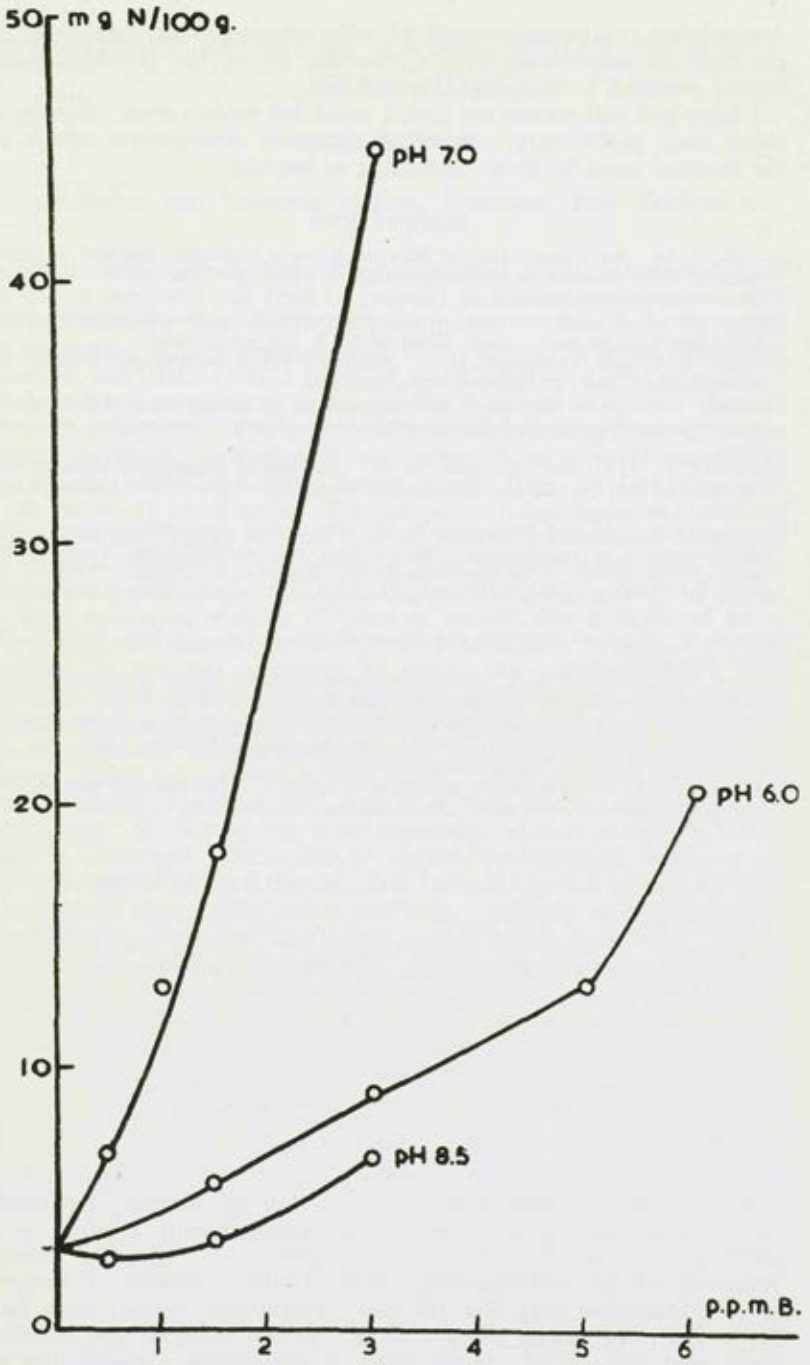


Fig. 10—The quantities of nitrogen fixed by Azotobacter chroococcum in sand-cultures increase many fold with increasing quantities of boron in the substrate at pH 7·0. At other pH levels nitrogen fixation though reduced, is favourably influenced as well.

determining the boron content of soils by comparing the colour of the bacteria suspensions with a standard series, the problem needs further research to elucidate the situation.

I hope you will excuse me that I could not refrain from telling you about these preliminary, somewhat immature experiments, which at the moment seem to be as conflicting as hopeful.

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SESSION 5

MINOR ELEMENT PROBLEMS IN NEW ZEALAND

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Plants and animals have their particular requirements for trace or minor elements and tend to respond to a shortage or excess with certain more or less well-defined symptoms. These may be useful in diagnosis. In New Zealand much of the country is under permanent pasture, and pasture has a habit of adapting itself to circumstances. Deficiencies are reflected rather in the balance of species than in obvious symptoms. The system of grassland farming is, on the other hand, singularly conducive to the reflection of mineral unbalances on animal health, for stock derive almost their total requirements from relatively small areas. The composition and activity of the soil microflora is of vital concern and undoubtedly influenced by supply of mineral nutrients. The effect of trace element deficiencies on the biological health of the soil itself is, nevertheless, the least obvious.

Once a disease, whether of plant or animal, has been found to be the result of a mineral deficiency or excess and a method of control devised, it becomes necessary to define the affected areas. Soil analysis, plant analysis and analysis of animal organs have all been used in conducting surveys to this end. Soil analysis may fail because of the difficulty in differentiating the fraction of the element concerned which is available to the plant. Plant analysis has proved very successful in some cases, e.g., in certain mineral deficiencies of fruit trees. With pastures, more especially when it is animal health that is concerned, effects due to season, management, variation in sward composition, and the fact that animals ingest a certain amount of soil with the pasture, come into play. Analysis of animal organs is applicable, of course, only when animal health is affected, and it involves the death of the animal. Incidences of iodine and cobalt deficiencies have been surveyed by this means. The most logical approach is through the soil.

The definition of soil types and their grouping into a genetic system has been of great assistance in fixing the extent of known deficiencies and in indicating likely soils, e.g., strongly leached podsols, for investigational work. A further approach by officers of the Soil Bureau has been the rearranging of soils into suites derived from similar parent materials and in order of their stage of development. Deficiencies inherited from the parent rock substances are distinguished from those acquired during the course of soil development. The former will affect all members of the suite, the latter only those beyond a certain threshold stage. Investigation of the youngest and most mature members respectively will give information as to whether any shortage will be common to the group, will exist at all, or will appear at some stage of development. In this last case it will be necessary to find the member of the series marking the threshold.

WRIGHT (1951) gives the following examples of inherited and

acquired deficiencies in the case of copper, the Aspergillus method of determination being used:

State of development of soil types	Available (copper p.p.m.)	
	Pinaki Suite (Inherited deficiency)	Omu Suite (Acquired deficiency)
Young	1·0	—
Immature	0·8	4·8
Semi-mature	—	2·2
Sub-mature	0·5	1·7
Mature	0·1	1·5

The above approach through the soil suite has been used by the Soil Bureau in a survey of the copper deficient soils of the North Island. Results have correlated well with the copper content of pasture in the case of inherited deficiencies, but less so in the intermediate members of suites showing an acquired deficiency. The Aspergillus method gives too high values for organic soils. WRIGHT (1950) states results on fresh material show better correlation than those on dried samples. A further example of an inherited deficiency lies in the low cobalt content of soils of the centre of the North Island derived from the Taupo and Kaharoa rhyolitic pumice showers. These ash showers had been mapped (GRANGE and TAYLOR 1932) and the occurrence of bush sickness associated with their distribution, before the disease was recognized as due to cobalt deficiency. The more strongly leached soils on the more basic Mairoa ash shower have acquired a cobalt deficiency, but bush sickness does not occur on less developed members of the suite.

"Induced" deficiencies also may be distinguished—ones brought about, for instance, by intensive farming, crop removal, or over-liming.

A further method envisaged by the Soil Bureau of prospecting for trace element or other deficiencies lies in spectrographic examination of specimens of one or more native plant species common to all localities. This follows on a project of BEESON (Private communication).

It is proposed to review briefly work which has been carried out with each of the recognized trace elements, with particular reference to methods of diagnosis.

Boron

Boron deficiency is widespread in New Zealand, as is evident from the incidence of "mottle-heart" of swedes, a crop that is grown in most parts of the country. In 1926 experiments conducted in Westland showed that the disease could be controlled by application of wood-ashes. Following reports of J. C. NEILL (1935) that the disease closely resembled "raan" in Ayrshire and "brownheart" in Canada, in which country control had been obtained by addition of boron compounds to the soil, widespread trials were carried out by the Department of Agriculture. Almost complete control was obtained by the application of 10 lb. of borax to the acre (WOODCOCK, 1936).

Meanwhile, in view of the earlier diagnosis of "corky-pit" of apples as a boron deficiency ailment, workers at the Cawthron Institute, Nelson, had laid down trials with turnips on an area where apples were severely affected. Fifty-six pounds of borax broadcast was found to reduce the incidence of mottle-heart from 93% to 24%. Chemical analysis of swedes and turnips from a number of localities showed a definite relationship between the incidence of mottle-heart and the boron content (RIGG, ASKEW and CHITTENDEN, 1937). In general, crops on older terraces and hill slopes were badly affected; those on more recent alluvial soils comparatively healthy.

A disease of apples known as corky-pit or internal cork had been noted in the Nelson district since 1912. In 1934 ATKINSON carried out injection experiments on trees severely affected the previous autumn, trying out some 16 different elements. Boracic acid practically eliminated corky-pit in the three trees injected (ATKINSON, 1935). Analyses by ASKEW (1935) showed fruit and leaves from affected trees to contain respectively one-third and one-half the boron in samples from healthy trees. Extensive trials by ATKINSON (1936) followed and borax, whether injected or applied to the soil, was found to control the disease.

A survey of the boron status of New Zealand fruit soils was carried out (ASKEW, THOMSON and KIDSON, 1937), samples being extracted with N/20 HCl. Separation of boron as methyl borate was followed by determination with turmeric paper. In the topsoils boron concentrations ranged from 0·05—0·68 parts per million. Over all, "healthy" districts had relatively high values, "unhealthy" relatively low. Within districts subject to internal cork, other factors were evidently involved, e.g., soil reaction in Otago and Southland where alkaline soils occur. In the Nelson district where the incidence of internal cork of apples was most severe, the correlation with boron content of the soil was not close. Healthy topsoils averaged 0·11 p.p.m., unhealthy 0·09 p.p.m. boron. The boron content dropped very rapidly with depth, particularly so in unhealthy orchards. The respective averages for 6–18 inch samples from healthy and unhealthy orchards were 0·05 and 0·03 p.p.m.B. Underlying gravelly layers seemed to be a predisposing factor towards internal cork.

Application of borax to the soil, injections and spray treatment were all found effective in control of internal cork by Cawthron Institute workers (ASKEW, CHITTENDEN and THOMSON, 1936). Soil applications were shown to penetrate fairly rapidly to a depth of 18". The lasting effects of borax applications (50 and 100 lb./acre), were studied over three seasons through soil and fruit analysis. Serious leaching losses were shown to occur in the first season, following which a fairly stable level was reached well above that of control plots. It was suggested that smaller annual applications might prove more economical (ASKEW, THOMSON and CHITTENDEN, 1938). CHITTENDEN and THOMSON (1938) showed that internal breakdown of fruit in the cool store increased with increasing soil applications of borax and concluded that a rate of ½ lb. per tree should not be exceeded. Spray treatments (1940) had no harmful effect.

Other crops in which symptoms have been traced to boron deficiency are tobacco (induced through over-liming a sandy soil) (ASKEW, 1946), grapes (ASKEW, 1944), celery (ATKINSON, 1948), hops (ASKEW

and MONK, 1951) and raspberries (ASKEW, CHITTENDEN and MONK, 1951).

A correlation between soil boron and deficiency symptoms has been attempted on a wide scale only with fruit trees. The boron content of the fruit (or leaves in the case of raspberries) has been found a better index of the boron supplying power of the soil. It is possible that a closer relationship between mottle-heart of swedes and turnips and soil boron would hold owing to a more defined depth of soil from which the element is drawn. Cawthron Institute workers first extracted the boron with N/20 HCl, later found the strength of acid was not critical (ASKEW, THOMSON and CHITTENDEN, 1938) and have latterly extracted the boron with boiling water. Figures derived by this last means did not correlate particularly well with incidence of die-back in raspberries. The effect of reaction, which is critical as regards boron uptake, does not seem to be reflected in the water soluble boron figures.

WRIGHT (1951) experimenting with claystone-derived soils in North Auckland (Omu suite) has studied the balance of mixed rye grass and white clover grown in pots, treatments including four levels of lime and two of borax. Liming greatly increased the growth of rye grass but suppressed that of clover. Borax application restored the clover balance. The optimum results were obtained with the soil limed to 75% saturation and borax applied at 20 lb./acre. Grass had a lower content of boron than the clover in the lime-only treatments, but was much more sensitive in boron uptake to applications. The uptake was increased 600% as against 30% in the case of clover. In other experimental work a 200% increase in growth of mustard above that in pots with a basal dressing was obtained with application of 20 lb. borax to the acre (WRIGHT and GRIDLEY, 1949).

Manganese

Very little work has been carried out on manganese. A lime-induced manganese deficiency of peach trees (*Prunus persica*) in Hawkes Bay has been remedied by annual spray treatment. Application of sulphur or manganese sulphate to the soil failed to increase the manganese content of the leaves (HEALY, 1952). ASKEW, CHITTENDEN and WATSON (1951), have demonstrated favourable effects of 1 oz. of manganese sulphate applied per bush to Red Antwerp raspberries at Motupiko and followed up with spray treatments.

GRIGG (1952) has associated whiptail-like symptoms of cauliflowers in soils seemingly well supplied with molybdenum, with levels of exchangeable plus readily reducible manganese higher than 250 p.p.m. Brown top (*Agrostis tenuis*) pastures on certain molybdenum responsive soils have been found at the Rukuhia Research Station to be extraordinarily high in manganese content, figures as high as 1635 p.p.m. being obtained. In one area where a sample of brown top contained 1418 p.p.m. manganese, the soil content was:—

	Mn (p.p.m.)	
	0"—3"	3"—6"
Water soluble	4·2	0·3
Exchangeable	10·8	4·2
Readily reducible	7·8	2·8

In a pot experiment comparing the effect of two limestones at

two rates of application and two finenesses of grinding on the growth of subterranean clover in Ngaio silt loam, yields were found to be inversely related to the manganese content of the herbage ($r = -0.77$), suggesting that the marked responses obtained may have been partly due to a reduction of the initially high level of active manganese.

Zinc

No determinations of the zinc content of soils have been recorded. Cawthron Institute workers have tried out the effect of spray treatments on fruit trees, but the only visible response has been in the case of cherry trees at Tasman affected with "die back." The zinc content of leaves was increased and the trees appeared to benefit considerably (*Annual Report, D.S.I.R.* 1949, p. 72). The Soil Bureau obtained responses of mixed white clover and rye grass in pot experiments with two of the older North Auckland coastal sands (*Annual Report, D.S.I.R.* 1950, p. 74). WRIGHT, GRIDLEY and CULLIFORD (1951) found mustard and rye-white clover to respond to zinc in pot experiments with Rangitoto sandy loam. Responses of apples to spraying with zinc sulphate have been noted at Auckland and at Tasman (VINEY, 1948). WATSON (1950) has carried out a large number of analyses studying the distribution of zinc in several varieties of apple trees.

Molybdenum

Molybdenum deficiency first came to notice in New Zealand through intensive investigation of the disease "whiptail" of cauliflowers which was seriously affecting crops grown under a Services Vegetable Production scheme. The disease was found to be controllable by application of 1 lb. sodium molybdate to the acre (MITCHELL, 1945). Seedlings grown in the glasshouse in soil from an area where whiptail was endemic, developed, in the absence of molybdenum, an intervenal chlorosis accompanied by an incurling of the leaf edges, and in some cases a marginal necrosis (DAVIES, 1945). Whiptail occurs in areas scattered throughout New Zealand.

In view of earlier reports from Australia of clovers responding to molybdenum applications (ANDERSON, 1942; FRICKE, 1943, 1944, 1945), a number of small observational trials on permanent pasture were laid down in the Waikato, but with negative results. On an ironstone soil in North Auckland a small but significant increase in pasture yield was obtained in a replicated trial (DAVIES and ARNOLD —unpublished data). This soil contained the highest concentration of total molybdenum yet found in New Zealand (5·0 p.p.m. in trial area). Means of determining available molybdenum were sought and eventually an oxalate extractant used by TAMM for separation of colloidal matter from mineral particles was selected (GRIGG, 1952). A range of soils of known molybdenum response was provided by Dr. PIPER from the Waite Institute for availability tests.

Meanwhile, attention had become directed to certain anomalous lime responses in Southland, on soils already heavily limed and with reactions about pH 6·5. The soils were low in "available" molybdenum and it seemed possible that heavy liming was having its favourable effect by increasing the availability of existing soil molybdenum. Southland limestones were found to be low in moly-

bdenum content with one exception. This stone, a very low-grade rock, contained 5·5 p.p.m. molybdenum and was regarded in the district as particularly effective. Field trials were set in train. Outstanding responses of the clover constituents of permanent pasture have been obtained in the initial yield trials and in a network of observational trials laid down by the Department of Agriculture (DAVIES, HOLMES and LYNCH, 1951).

A molybdenum survey of New Zealand soils using Tamm's extractant was commenced in Otago and has gradually been extended to other parts of the country, more particularly in the South Island. Levels have ranged from 0·02—1·42 p.p.m. At the present stage it seems that molybdenum deficiencies are widespread in the South Island. The main responses have been reported from Otago and Southland, but low soil figures have been obtained from other districts and field trials are under way. In the North Island two dramatic responses only have been obtained, one at Te Hana, North Auckland, the other in the Wairarapa. Comparatively few North Island trials have been run.

A comparison of field responses with analytical results shows that apart from a few doubtful cases no visible molybdenum responses have been obtained on areas with a pH above 6·2, even where the molybdenum level is low. Responses (with two exceptions) have been forthcoming when the pH is below 6·2 and the available molybdenum figure below 0·14 p.p.m. Liming at 3 tons per acre has produced results approaching those due to molybdenum alone in two yield trials and some observational trials. In North Otago a lucerne trial and a pasture trial have given markedly less growth with molybdenum plus lime than with molybdenum alone. It is thought that the liming has accentuated a boron deficiency, but the point awaits analytical and experimental confirmation.

The usual application in field experimental work has been 2½ oz. sodium molybdate to the acre. An application of ⅛ oz. per acre has given initial results equally good on one area and further trials with graded dressings are in progress. Evidence of responses due to traces of sodium molybdate spread by chance suggest that even smaller amounts might have an effect. In a property on the Taeri foothills a response to 2 and 4 cwt. of basic slag was apparent, but not to applications of up to one ton of superphosphate. A marked molybdenum response was obtained, but only when superphosphate also was applied. No sample of the particular slag was available for analysis, but other samples have been found to contain only 7·5 p.p.m. Mo, an amount equivalent to 1/15th oz. sodium molybdate in 2 cwt. Slag contains considerable vanadium, but no response has been obtained from ammonium vanadate dressings.

Soil tests for available molybdenum on progressive ½ inch samples drawn from a trial area show that the molybdenum has been retained largely in the surface inch.

Pasture samples from many molybdenum treated areas have been analysed. On normal soils the 2½ oz. sodium molybdate has never raised the molybdenum level to more than 2·5 p.p.m., and no untoward effect on animal health would be expected. The lowest level associated with " teartness " is 12 p.p.m. (FERGUSON, LEWIS and WATSON, 1943). CUNNINGHAM (1946) has shown that where copper

is deficient, molybdenum levels of the above order in pasture may be harmful. On leached sands molybdenum dressings might be inadvisable unless copper sulphate also were applied. Pastures on peat land are low in copper and relatively high in molybdenum, leading to seasonal trouble with "peat scours" (CUNNINGHAM, 1946). The molybdenum content of these pastures reaches a maximum value from June to September, when the trouble occurs (CUNNINGHAM, 1950). CUNNINGHAM (1950) has pointed out that as peat land consolidates and becomes mineralized through slow oxidation, problems of molybdenum toxicity may arise.

The responses observed in legumes—lucerne and red and white clover—are, no doubt, due to stimulation of nitrogen fixation by Rhizobia (ANDERSON and SPENCER, 1950). Molybdenum also plays a part in the reduction of nitrate as a step to protein synthesis (HEWITT, JONES and WILLIAMS, 1949). It is a check in this stage of nitrogen metabolism which accounts for the symptoms in cauliflowers and rape, both of which species have responded markedly to molybdenum applications when grown on soils deficient in that element. The visual symptoms of molybdenum deficiency in the two species, both in the seedling and more fully developed stages, are similar.

Grassland farming in New Zealand is dependent on balanced swards of grasses and clovers, for the latter through symbiotic Rhizobia provide essential nitrogen. It can readily be seen that supply of molybdenum to deficient areas may greatly stimulate production.

Copper

The effect of copper deficiency on crops or pasture has been reported in but a few instances. A pronounced response of onions to copper applications was obtained on a peat soil near Christchurch, spray and soil treatments both increasing the crop many fold, and also increasing the copper content of the leaves. Total soil copper was determined, values ranging from 7·5-9·2 p.p.m. The Aspergillus method indicated 5-6 p.p.m. (ADAMS, 1948, 1949). ASKEW, CHITTENDEN and WATSON (1951) have reported beneficial effects of soil and spray treatments on Red Antwerp raspberries, the bushes holding their leaves much better late in the season. Jonathan apple trees at Harakeke showed marked improvement in foliage and set of fruit (*Annual Report, D.S.I.R.* 1949, p. 72).

Copper deficiencies in New Zealand have become evident through their effect on animal rather than pasture health, though marked pasture improvement on peat land at Waitakaruru has been noted by CUNNINGHAM and PERRIN (1946). Pastures consisting almost entirely of Yorkshire fog (*Holcus lanatus*) and *Lotus major* were treated with 5 lb. copper sulphate in 2 cwt. of lime and 5.6 lb. copper sulphate in 2 cwt. of super respectively in successive years. At the end of two years they contained approximately 40% of *Poa pratensis* and white clover. The incidence of Scotch thistle (*Cirsium lanceolatum*) was favoured by copper sulphate applications. Regarding animal symptoms, CUNNINGHAM (1950) distinguishes simple copper deficiency, where copper content of pastures may be as low as 3 p.p.m., and complicated copper deficiency where the pasture copper is of the order of 7 p.p.m. and molybdenum moderately high ranging from

3 p.p.m. in summer to a peak of 16 p.p.m. in the spring. The symptoms in cattle are poor growth and bone fragility in the young, anaemia and loss of coat colour. In the complicated copper deficiency, as mentioned under molybdenum, a seasonal scouring coinciding with the peak in molybdenum uptake by pasture also occurs. This complicated copper deficiency is endemic on practically all peat country, hence the name " peat scours." There are some 400,000 acres of peat in New Zealand, 250,000 of which have been developed. The distinction between the two types of copper deficiency is not noted in sheep, the trouble being evident as acute osteoporosis or a permanent ataxia in young lambs. The simple copper deficiency occurs on leached consolidated coastal sands, leached sandy soils and gumland soils.

A low copper status in the soil may be detected by determination of copper in livers of sheep or cattle, of copper content of pasture, or of copper content of the soil, using the Aspergillus technique. Total soil copper is not a reliable indication. Deficient sands examined by the Aspergillus niger method give figures from 0·1 to 1·6 p.p.m. Normal mineral soils may contain as high as 22 p.p.m. The mapping of copper deficient soils has already been described.

Cobalt

Cobalt, on present evidence, does not appear to be essential to plant growth. In sheep and cattle an insufficient supply leads to a progressive wasting, ending in death. The disease is associated mainly with soils formed from the Taupo and Kaharoa pumice showers, and the more highly leached soils from the Mairoa shower, all in the central portion of the North Island. A further North Island occurrence is on older volcanic ash deposits in North Auckland. In the South Island the disease occurs on the Glenhope and Sherry Valley granitic soils in Nelson and in Morton Mains, Southland, where the soils are derived from loess. Published work in New Zealand has been ably summarized up to 1944 (F. C. RUSSELL) and comments will be limited to methods of defining " bush-sick " or cobalt deficient areas.

Soil Analysis : MCNAUGHT (1937) has determined the cobalt soluble in $\frac{N}{10}$ HCl in relatively few soils, finding the bush-sick ones to average 0·12 p.p.m.Co and healthy ones 0·61 p.p.m. Morton Mains disease, another manifestation of cobalt deficiency, occurred on soils with intermediate values averaging 0·39 p.p.m.Co. Healthy and unhealthy soils in this area were not differentiated.

KIDSON (1937) has determined cobalt in a very wide range of soils representing most parts of New Zealand. Soils were first ignited and then extracted with concentrated HCl. Cobalt contents ranged from 0·3 to 381 p.p.m., but figures above 20 p.p.m. were exceptional. On the whole, bush sickness was prevalent where soils contained less than 2 p.p.m. cobalt, and rarely occurred with concentrations from 6-20 p.p.m. Morton Mains soils contained 2·8 to 8·3 p.p.m.Co, and, as was the case in MCNAUGHT's work, healthy and unhealthy soils were not distinguished. It was concluded that the determination of cobalt in soils was not entirely satisfactory as a guide in the use of cobalt supplements for stock. STANTON and KIDSON (1939) carried out a further survey of the Tadmor, Sherry and Wangapeka districts in Nelson and found the critical 2 p.p.m. level of cobalt to apply.

Pasture content of cobalt did not always follow the soil level. There was a definite connection between the cobalt content of soils and the geological formation from which they were derived.

Pasture Analysis: Determinations of cobalt have been carried out by McNAUGHT (1938) of pasture samples representing most of the North Island of New Zealand. He sums up that pastures containing less than 0·07 p.p.m. Co are unhealthy for sheep, less than 0·04 p.p.m. Co unhealthy for sheep and cattle. McNAUGHT and PAUL (1939) followed up with a study of seasonal fluctuation in cobalt content and found that the cobalt content tended to increase in late autumn and winter and under drought conditions when growth was retarded. ASKEW and co-workers found similar fluctuations. McNAUGHT points out the possible effects of soil contamination of pasture as being considerable, for the ratio of cobalt in soil to cobalt in pasture (dried) may range from 10 : 1 up to as high as 250 : 1. Soil ingested with pasture may well benefit the animal, as is obvious from the early control of bush sickness by drenching with soil from healthy areas (RIGG and ASKEW, 1934; DIXON, 1936).

The general impression is that while pasture analyses can be of value as a guide in detection of cobalt deficient areas, the effects of seasonal fluctuation, pasture management and soil contamination need to be taken into account. ASKEW (1946) has pointed out that in a trial where 1 cwt. of cobalt chloride was applied, clovers took up almost twice as much cobalt as grasses. Balance of the constituents in a sward might therefore be of moment.

Cobalt content of livers: ASKEW and DIXON (1937) showed that drenching sheep with cobalt raised the cobalt content of sheep livers. McNAUGHT (1948) from an extensive series of analyses concludes that there is good correlation between the concentration of cobalt in the livers and the incidence of bush sickness in sheep and cattle. The correlation is rather better than that with cobalt content of pastures. Critical levels were as follows:

	p.p.m. cobalt in liver	
Sheep 3 months and older	<0·06	cobalt deficient.
	>0·10	cobalt adequate.
Yearling and mature cattle	<0·05	cobalt deficient.
	>0·12	cobalt adequate.

Effect of Liming on Cobalt Supply: A widespread unthriftiness of lambs in Southland, which may possibly be connected with sub-optimal supplies of cobalt, is at present under investigation (ANDREWS and ANDERSON, 1952). Heavy liming may have a bearing on the problem, for dressings have been shown to reduce cobalt uptake in the pasture (ASKEW and DIXON, 1937; ASKEW and MAUNSELL, 1937). McNAUGHT and PAUL (1940) report on an isolated instance of cobalt deficiency on a limestone-wash soil. R. L. MITCHELL (1948), at the Macaulay Institute, Aberdeen, showed a depression of uptake of natural and applied cobalt by liming. On the other hand certain limestones, in particular Southland limestones, have been shown to contain appreciable amounts of cobalt (MAUNSELL, 1945: STANTON, 1944). DIXON and KIDSON (1940) showed an increased

cobalt content of pastures and of livers of lambs grazing thereon brought about by 3-ton applications of a Southland limestone. ASKEW (1943) showed a similar increase in pasture content. In each case, however, the advantage of limed pasture did not persist more than 4 to 5 months. The heavy liming may prove advantageous to pasture growth in increasing molybdenum availability, but at the same time detrimental to animal health through depression of cobalt uptake. No conclusive evidence has yet been obtained.

Nickel

DIXON (1937) found that nickel plus cobalt drenches gave better results measured by liveweight increases in lambs at Morton Mains than did cobalt drenches alone.

Iodine

Iodine deficiency occurs in New Zealand, cattle, sheep and horses having been affected. Young may be born dead, hairless, and with enlarged thyroids, or may die within a few days. In some flocks up to 50% lambs have been lost from this cause (CUNNINGHAM, 1950). Both humans and domestic stock are subject to simple goitre, which is regarded as due, in part at least, to iodine deficiency.

HERCUS *et alia* (1926) carried out a wide survey of iodine content of soils in New Zealand. Figures for Auckland, Wellington, Canterbury and Otago districts averaged 5·3, 4·8, 0·9 and 1·3 parts per million iodine respectively. They state that an inverse relationship exists between the iodine content of the soil and incidence of animal goitre. SHORE and ANDREW (1929) studied the incidence of goitre in school-children and iodine content of the soil over the North Island and found a similar inverse relationship, but with certain anomalous cases. A more detailed investigation of these (SHORE and ANDREW, 1934) showed a connection between soil iodine and iodine content of milk, eggs, and sheeps' thyroids, but no connection with human goitre. Since then a wide iodine survey of New Zealand has been carried out through analysis of lambs' thyroids (MASON, 1933; SYKES, 1934; MASON and WATERS, 1936; WATERS, 1938; WATERS, 1939). Westland, Southland, Buller Valley and Grey Valley in the South Island, and the Manawatu-Wanganui Plain in the North Island are low in iodine.

HOPKIRK *et alia* (1930) investigated an acute outbreak of iodine deficiency in the Wanaka area, South Island, and reported low soil iodine values ranging from 0·2 to 1·5 p.p.m. Iodine deficiency is associated with river flats and alluvial soils.

CUNNINGHAM points out the possibility of positive goitrogenic factors such as have been found in cabbage and brassica seeds being involved. Low soil and pasture iodine may not be the only cause of simple goitre.

Magnesium

Magnesium has been included for discussion with the trace element group.

The main diseases that have been attributed to magnesium deficiency in New Zealand are a premature defoliation of apple trees (KID-

SON, ASKEW and CHITTENDEN, 1940) and a chlorosis of tomato leaves (JOHANNESSON, 1951; MCNAUGHT and GDANITZ, 1952). In both cases heavy potassic applications have probably brought about the condition. The leaf symptoms in the apple trees were a brown blotching, particularly between the veins, followed by defoliation. The older leaves on new leader growth were the ones affected, a tuft of leaves with higher magnesium content being left near the tip. The deficiency could be rectified by injection or applications of magnesium sulphate, magnesium carbonate, or dolomite, to the soil. Injections were not adapted for commercial practice. Of the soil applications the last two proved more effective (KIDSON, ASKEW and CHITTENDEN, 1943; ASKEW and KIDSON, 1947). There was good correlation between leaf blotching and low magnesium content of the leaves. The effect of age and position of leaves on magnesium content has been examined in detail and reported in a number of cases by Cawthron Institute workers. Leaf analysis was an effective means of detecting deficiencies.

In soil work in New Zealand the exchangeable magnesium is usually determined. KIDSON, ASKEW and CHITTENDEN (1940) point out that in an orchard examined the early defoliation was pronounced on the completely fertilized block, but slight where no fertilizer was applied. The respective ratios of K/Mg (milli-equivalents) in the two portions were: 0"–6" 2·7, 0·75; 6"–12" 2·8, 0·57; 12"–24" 2·4, 0·55. The authors conclude that the ratio K/Mg was excessive in the fertilized portion.

DIXON and TAYLOR (1942) have pointed out a loss of exchangeable potash and magnesia from Waikato soils following long-continued phosphate topdressing, a point also noticed in a Taranaki comparison (BURGESS and DAVIES, 1951). Magnesium deficiencies in pasture land are therefore likely to develop. The use of serpentine superphosphate in place of superphosphate might compensate for current magnesium losses, but would not make good existing deficiencies. MCNAUGHT reports a build up in soil magnesium in tomato houses following very heavy applications of serpentine superphosphate. Massive dressings of crushed serpentine have been successfully used in cases of magnesium deficiency in tomatoes.

Conclusion

Trace element surveys in New Zealand using chemical analyses of soils have been attempted only in the cases of boron, cobalt, iodine and molybdenum. The Aspergillus method has been used for copper. The method used for molybdenum is proving useful, but has not as yet had a wide trial. In the case of each of the other elements mentioned, analysis of the plant or selected organ of the animal concerned has been found to give a more reliable indication. The difficulty of determining the "available" fraction in the soil, the influence of soil reaction, and possibly the interaction of other elements on plant uptake, weigh against reliable soil assessment. The methods in use, though not infallible, can nevertheless prove useful. More effective methods may be contrived. Soil analysis, as a means of determining soil deficiencies, is more readily linked with soil survey work. Moreover, in opening up new country, likely deficiencies can be foretold rather than diagnosed after trouble is encountered.

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SESSION 6

SOIL FERTILITY, ION INTAKE, ION ACTIVITY AND ION EXCHANGE

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In the evaluation of the fertility of a soil and also for the development of the method to determine its fertility, there are two different possibilities. One method is based on the correlative relation between the figures of the laboratory experiment and the results of the experimental fields. The other method is based on a causal relation between the data of the laboratory and the reaction of the crop.

That the starting point of the correlative method is more or less a casual one is not essential. The lime requirement of a soil is, e.g., related to the pH–H_2O and also to the pH–KCl. The main reason that the first relation is rather poor is due to periodical fluctuations of the pH–H_2O. These fluctuations are much lower in the pH–KCl. Therefore the experimental error of this figure is smaller and the correlation with the lime requirement better. Although the meaning of the pH–KCl from a physico-chemical point of view is very difficult to describe, it is as a routine analysis preferred. For a correlative purpose it is a good figure, for a causal purpose it is a bad one. In the correlative research a soil analysis is correlated with the yield. This in itself is a very complex conception. For studying a causal relation we use another way of thinking. We try to find a relation between a figure of the laboratory and one of the properties of the plant, e.g., the ion intake. Now it is absolutely necessary to know the exact meaning of the determined data. Plant and soil are very complicated systems. Their properties are scarcely known. Therefore we try to use physico-chemical and other theories taken from the knowledge of dead nature for understanding some of the reactions between both. The analogy of different physiological processes with known processes from chemistry must give us some comprehensible relations between plant and soil.

This kind of research gives some satisfaction of understanding, but is otherwise, until now, very limited for direct practical use. In most cases the results of the theories and hypotheses will give us only a qualitative insight. The quantitative relations are for a concrete object too difficult. The calculation of soil fertility with the theory is a thing that will perhaps be a possibility in the future. Otherwise it has the great advantage of giving a general view over the entire problem. The conclusions are not restricted to a special case but are valid on a broad scale.

In this lecture I will summarize some of the qualitative aspects, which are the result of the application of some theories. I will limit my subject by speaking only about cations, as these ions are mostly related to the adsorption-complex of the soil. This application will give us some facts which are of great value in the interpreting of the soil tests. Putting the causal relations in the centre, it is necessary to start with some properties of the plant, because the intake of ions is a result of these properties. The reaction of the growth of the plant is a

consequence of the medium. The intake of ions is more especially the result of the conditions of the soil. Essentially the intake of ions is the reaction of the plant on the five biofactors of the soil (heat-activity, oxygen-activity, water-activity, anion-activity, and cation-activity). I wish to limit the lecture to the influence of the cation-activity. The intake of these ions is then a question of the supply or offer of the soil to the plant. In a general sense we can speak of the physiological activity of the ions of the soils. How can we measure these physiological activities? The oldest method is to use the concentrations of the ions in the soil or some kind of available concentrations to record this physiological activity.

However, it has been known for some time that the ions in physico-chemical processes do not react with their real concentration, but with a somewhat lower concentration, called the activity. This activity a is related to the real concentration c by the formula

$$a = f \times c$$

f being the activity coefficient. In very dilute solutions f is about one, in concentrated solutions f can be 0·2, and in suspensions of adsorbing materials f can range from 0·1 to 0·001. In these latter-mentioned systems there is a great difference between real and active concentration. Therefore it seems beneficial not to use the concentrations but the physico-chemical activity of the ions to describe the physiological activity of the ions in the soil. MARSHALL and independently, I, have given some arguments which are encouraging. It seems therefore, reasonable to work out these conceptions on a broader scale. We can find in literature several scientists (LUNDEGARDH, MATTSON, WIKLANDER, etc.) who are of the same opinion.

I can summarize the arguments as follows:

1. The very important and very efficient value pH is an activity.
2. The difference between the concentrations of ions in the soils and in the well-known culture solutions is not so great if we take the activity instead of the real concentrations.
3. The influence of the pH of the soil on the activity of the cations has the same tendency as the influence of the pH of the soil on the availability of the cations for the plant.
4. The selectivity coefficient

$$\frac{(\text{cation I})_{\text{plant}} : (\text{cation II})_{\text{plant}}}{(\text{activity cation I})_{\text{soil}} : (\text{activity cation II})_{\text{soil}}}$$

gives a fairly good value. This coefficient is comprehensible in comparison with the incomprehensibly very high coefficients calculated by means of the concentrations.

5. There is no real difference between the uptake of ions from a solution and from a suspension, if the activity is used to describe the cation status of the medium. There is found, on the contrary, a great difference in uptake by using the real concentrations as a measure for the cation status.

A proceeding study of the ion intake of the plants does assume that the intake may be described by the formula :

$$i = K \frac{b_o (a_i)_m e^{-\left(\frac{nF}{RT}E\right)}}{1 + b_o (a_i)_m e^{-\left(\frac{nF}{RT}E\right)}}$$

i=intake of ions, K and b_o are constants (K is dependent on active root surface, temperature, oxygen tension of the medium and sugar content of the root, b_o is dependent on the properties of the root surface and the ion), $(a_i)_m$ is the activity of the ion in the medium, E is the root potential (LUNDEGARDH), n, F, R, T are well known symbols. The general meaning of this formula is that the absorption of ions follows after an adsorption of the ions on the surface of the roots. The logical conclusion is now, that the intake of ions depends more on the ratio of the ions in the medium than on their concentration. The concentration of the ions on the root surface is, with a not too low concentration of the medium, constant, as a result of the absorption laws. The fact that E appears as an e-power and that E gets a high negative value in low concentrations of the medium, intensifies the influence of the adsorption.

Only in the case of very low concentrations will the concentration be of more importance. In practice this is realized by the low concentrations of the minor elements in the soils. By studying the methods for determining the availability of the minor elements one is led to expect that the influence of the concentration (activity) of these elements is not disturbed by other factors. It will give a pretty good correlation with the uptake.

For the elements with a higher concentration—the major elements —there will be a competition of the cations for a place on the surface of the root. The consequence of this competition is that the ratio of the ions in the medium decides the concentrations of the ions on the surface. In this case the value of the concentration of the ion in the medium must be adjusted to the influence of the other ions. Proceeding from this point of view, I have to discuss the soil fertility problem in relation to the activity and ratio of cations, together with the importance of the adsorption complex of the soil.

In general the application of the DONNAN-equilibrium to the soil gives us some facts about the distribution of the monovalent ions and divalent ions between the solutions and the soil complex. In fact there is no DONNAN-equilibrium between the soil particles and the soil solutions, because there is no membrane between both. But the thermodynamic background of this equilibrium holds also for the soil-solution system. Essentially the formulas and conclusions of the DONNAN-equilibrium are valid.

Starting with an example with monovalent (M^+) and divalent (M^{++}) cations, monovalent (A^-) and divalent ($A^=$) anions and an acidoid R^- (the soil complex), we can set up the following equations.

inside		*outside*	
R^-	M_i^+	A_o^-	M_o^+
A_i^-	M_i^{++}	$A_o^=$	M_o^{++}
$A_i^=$			

E

$$M_i^+ + 2\,M_i^{++} = A_i^- + 2A_i^= + R^-$$
$$M_o^+ + 2\,M_o^{++} = A_o^- + 2A_o^=$$
$$\frac{M_o^+}{M_i^+} = \frac{\sqrt{M_o^{++}}}{\sqrt{M_i^{++}}} = \frac{A_i^-}{A_o^-} = \frac{\sqrt{A_i^=}}{\sqrt{A_o^=}} = \frac{1}{K}$$

$$K = e^{-\left(\frac{nF}{RT}\,E\right)}$$

From these equations we can deduce:

$$\frac{M_i^+}{M_i^{++}} = \frac{1}{K} \times \frac{M_o^+}{M_o^{++}}$$

$$R^- = (K - \frac{1}{K})\,M_o^+ + 2\,(K^2 - \frac{1}{K})\,M_o^{++} + 2\left(\frac{1}{K} - \frac{1}{K^2}\right)A_o^=$$

By partly mathematical and partly graphical calculations we can set up Table 1. It appears that the influence of the term with $A_o^=$ in the last equation is slight. Only in special circumstances will there be an influence of the anions on the distribution of the cations between solution and complex. Table 1 is therefore, with a great degree of approximation also of value in cases where the anions are mixed or only divalent.

TABLE 1. The ratio between mono- and divalent ions (M_o^+/M_o^{++}) in solutions for different ratios in the complex and for different ratios of complex : solutions.

	$R^-/M_o^+ + M_o^{++}$					
inside M^+_i/M_i^{++}	2	5	20	50	100	500
99·0/1·0	99·5/0·5	99·6/0·4	99·7/0·3	99·8/0·2	99·9/0·1	99·9/0·1
95·0/5·0	97·5/2·5	99·0/1·0	99·5/0·5	99·7/0·3	99·8/0·2	99·9/0·1
90·0/10·0	95·0/5·0	97·5/2·5	99·0/1·0	99·5/0·5	99·7/0·3	99·8/0·2
80·0/20·0	88·5/11·5	93·5/6·5	97·5/2·5	99·0/1·0	99·5/0·5	99·7/0·3
70·0/30·0	80·0/20·0	88·3/11·7	96·0/4·0	98·0/2·0	99·0/1·0	99·5/0·5
60·0/40·0	71·8/20·2	81·2/18·8	93·0/7·0	96·4/3·6	98·0/2·0	99·3/0·7
50·0/50·0	62·1/37·9	72·0/28·0	87·8/12·2	94·5/5·5	96·3/3·7	99·0/1·0
40·0/60·0	50·0/50·0	61·0/39·0	80·5/19·5	90·2/9·8	94·2/5·8	98·5/1·5
30·0/70·0	38·5/62·5	47·5/51·5	68·4/31·6	82·5/17·5	89·0/11·0	96·5/3·5
20·0/80·0	26·0/74·0	33·2/66·8	52·5/47·5	67·0/33·0	77·5/22·5	93·5/6·5
10·0/90·0	13·0/87·0	17·5/72·5	29·5/70·5	41·5/58·5	52·5/47·5	79·0/21·0
5·0/95·0	6·5/93·5	9·0/91·0	15·0/85·0	23·0/77·0	30·0/70·0	55·0/45·0
1·0/99·0	1·3/98·7	1·8/98·2	3·0/97·0	4·5/95·5	5·5/94·5	12·5/87·5

In Table 1 is given the influence on the ion distribution of different cation ratios in the solution and of different ratios of $R-$ (a measure for the exchange capacity of the soil) to the concentrations of the solution $(R^-/M_o^+ + M_o^{++})$.

We see the great influence of the ratio $R^-/M_0^+ + M_0^{++}$ on the distributions of the monovalent and divalent cations between the solution and the complex. A dilution of the solution ($R^-M_0^+ + M_0^{++}$ gets higher) has the result that more monovalent ions go into solution. The ratio M_0^+/M_0^{++} is increased. Therefore, the offer of monovalent ions to the plant is increased by diluting the soil solution. In general a wet soil offers more monovalent ions to the plant than a dry soil with the same content of exchangeable ions. In a wet soil, therefore, the potassium supply will not be lowered so rapidly as in a dry region. The theory teaches us also, that the supply of ions to the plant is more conducive to an uptake of monovalent cations in a wet period and more conducive to the uptake of divalent ions in a dry period. Periodical fluctuations of the ion intake by the crop are a result not only of the physiological state of the plant, but also of changes of the water content of the soil during the season. After a period of rainfall the monovalent cations are in the foreground. The periodical fluctuations in the mineral content of grasscrops, which are very important in relation to the conditions of the animals, can partly be explained by these phenomena.

The DONNAN-equilibrium brings out second important facts. A soil with a high exchange capacity will have a high $R^-/M_0^+ + M_0^{++}$ ratio, a soil with a low exchange capacity a low ratio. Table 1 shows that in the first case the soil solution will be relatively poor in divalent ions and in the second case the solution will be relatively poor in monovalent ions. The soil fertility in regard to ion ratios and ion activities—the activity of ions in solutions is much higher than the activity of the adsorbed ions—depends on the exchange capacity of the soil.

The application of the DONNAN-equilibrium is especially used by MATTSON, WIKLANDER and co-workers. It gives us an explanation of some practical facts, which we observe in the reactions of the plant on different soils. It is also important in understanding the reactions of different plants in connection with their acidoid content.

However, it gives us only a general view. We had to simplify the problem, e.g., by taking all the activity coefficients as one. The theory of using activity-coefficients in the DONNAN system is not solved yet. But even the incomplete theory warns us of mistakes. The use of the water extract of the soil for determination of the cation-status of the soil has a very limited value. It gives only the status at one moment. In reality there is a fluctuation during the season. The interpretation of the estimated figures of the water-extract requires a thorough knowledge of all the conditions of the soil.

The theory also teaches us that the determination of the exchangeable ions does not give us the figure for the physiological activity of the cations or the ratio of the ions which are supplied to the plant root. In interpreting these figures we must take into account the exchange capacity of the soil, the fluctuations in the water content of the soil, and the concentrations of the soil solution.

There is another disadvantage in using the DONNAN-equilibrium.

It gives us no information about the distribution of the different monovalent or different divalent ions between soil solution and soil complex. This is a consequence of the neglect of the activity coefficients. The DONNAN-equilibrium in the given simple form does not take into account the specific binding power of the adsorbent. We have, as yet, no complete theory on this point. Therefore, I must leave the theoretical considerations and go over to some experimental facts. These facts have to teach us the influence of the specific adsorption power on the supply of the ions to the plant root. I think the first known experiments on this point were made by SCHACHTSCHABEL. He experimented by percolating different clay minerals with solutions with a fixed ion ratio and determined the ratio of the adsorbed ions in equilibrium with the solution. He found out that muscovite has a great attracting power for potassium, whilst kaolinite and montmorillonite prefer the adsorption of calcium.

The solution to these problems must be found in the measurement of ion activities in suspensions of clay minerals and soils. Two methods have been developed: The first one is the indirect method (SCHUFFELEN and LOOSJES, PEECH), the second method is the direct one using specific electrodes (MARSHALL, v. SCHUYLENBORGH and VERVELDE).

For the indirect method one uses the relation:

$$(pH)_{susp.}-(pH)_{sol.}=(pK)_{susp.}-(pK)_{sol.}=\frac{p(Ca)_{susp.}-p(Ca)_{sol.}}{2}$$

SCHUFFELEN and LOOSJES measure $(pH)_{sol.}$; $(pH)_{susp.}$; $(pK)_{sol.}$ or the other cations of the solution and calculate $(pK)_{susp.}$ and the other activities. PEECH measures the electrical potential difference (E) between the solution and the suspension with agar-KCl-bridges and calomel electrodes. This E is connected to the difference in activity of the solution and the suspension by the equation:

$$\frac{(a)_{susp.}}{(a)_{sol.}}=e^{-\left(\frac{nF}{RT}E\right)}$$

MARSHALL and co-workers use membrane electrodes of clay material, SCHUYLENBORGH and VERVELDE use a special glass electrode for measuring the ion activities. The measuring is in this case as easy as a *pH* determination. The disadvantage of this method is the fact that mostly the electrodes react not only to the metal which must be determined, but react also to the other metals and especially to hydrogen ion activity of the medium. Therefore a more or less complicated calculation is needed for the real value of the ion activity of the metal. Both methods have until now an unknown error. There is a diffusion potential at the place of contact of the salt bridge in the suspension. The value of this potential is not known. PEECH and MARSHALL argue that this extra potential is low and can be neglected. JENNY and co-workers are of the opinion that this diffusion potential is quantitatively the reason for the electrical potential difference between the suspension and the solution. This problem is as yet unsolved. It happens that this potential is not so high, so that in general we can use the results of the measurements for a qualitative purpose. For our use of the ion activity in a study of the

fertility of the soil, it is not necessary to know exactly the ion activity of suspensions. We need information about differences in properties of clay minerals and soil organic matter in respect to the different cations. An idea about variations in activities and ratios, is sufficient at the present time to enable us to make a first approximation.

Another method, which shows us the influence of the differences in binding-power of the clay minerals for the cations, is to measure the exchange of the ions by means of a limited amount of hydrogen ions (MEHLICH, ALLAWAY). In using this method one gets a kind of DONNAN-distribution between the solution and the soil complex. After the determination of the concentration of the ion in the solution, we can compare the exchangeability of the different cations. This exchangeability is as good a qualitative measure for the relative activity as the activity measurement itself.

Therefore the results of the above mentioned methods harmonize in a qualitative respect.

Table 2 gives some results for magnesium and calcium. One can see a preference for a magnesium adsorption on montmorillonite in respect to calcium and on the other hand a preference for calcium adsorption by the kaolinite.

TABLE 2. Ion ratios for Ca and Mg (MEHLICH and COLWELL, 1943)

Soil	Clay-mineral	Ca/Mg. soil	Ca/Mg. exchangeable
White store	montmorillonite (75%)	4·0	2·7
Creedmore	montm. + kaol. (±1 : 1)	4·0	3·2
Durham	kaolinite	4·0	5·0
Muck	—	4·0	4·2

Table 3 gives some results for potassium and calcium. Here one can also see a great difference in ion activities in respect to the clay mineral used.

TABLE 3. Ion ratios for K and Ca (MARSHALL and BARBER, 1949)

Clay-mineral	ratio K/Ca		ratio K/Ca	
	concentration	activity	concentration	activity
Arizone bentonite	1/9	13/1	1/4	21/1
Wyoming bentonite	1/9	5/1	1/4	9/1
Putnam clay (beidellite)	1/9	4/1	1/4	12/1
Halloysite	1/9	4/1	1/4	8·5/1
Grundite illite	1/9	2·6/1	1/4	7·3/1
Moquoketa illite	1/9	1·2/1	1/4	4/1
Attapulgite	1/9	1·2/1	1/4	5/1
Kaolinite	1/9	0·8/1	1/4	2·4/1

The bentonite preferentially adsorbs potassium, the kaolinite on the contrary has a strong adsorbing power for the calcium ion in respect to the potassium. The other clay minerals have a medium position.

TABLE 4. Active fractions of K and Ca (MARSHALL, 1950)

Saturation %			Montmorillonite		Kaolinite	
Ca	H	K	K	Ca	K	Ca
0	0	100	0·2	—	0·35	—
0	50	50	0·1	0·02	0·1	0·04
50	0	50	0·3	0·001	0·4	0·03
100	0	0	—	0·04	—	0·15

In fact the problem is more complicated, because there is an influence of all the exchangeable ions on the activity of one of them. Table 4 gives some results of MARSHALL. It is above all things, the hydrogen ion, that has a lowering influence on the activity of the cations. In the first place, therefore, the figure of an amount of exchangeable potassium, magnesium, sodium or calcium has to be evaluated in connection with the pH of the soil. The influence of the other cations is not so great, but in special circumstances it may be necessary to take this influence into account. As yet it is not possible to give detailed facts. We need many more determinations to set up general rules. Although much research has been conducted on the correlations between ion uptake by plants and ion activity in soil, we need more information for a general theory. Different kinds of plants have different properties, consequently the reaction to the soil is not always alike.

In summarizing we can state generally that the theory teaches us, in respect to the evaluation of the results of soil testing, two important points:

(1) As a consequence of the DONNAN-equilibrium a result for the soil test must be evaluated in respect to the exchange capacity of the soil. The calculation of an exchangeable ion with reference to the exchange capacity of the soil, will give us the ratio of this ion to the total exchangeable ions. In theory this is a better figure as the calculated amount related to the soil. The activity of a monovalent ion (e.g., potassium), with a constant ratio in the soil complex will be relatively higher in a soil with a great exchange capacity. A divalent ion (e.g., magnesium) will in this case be lower. Calculating on exchange capacity lowers more the figure for the percentage of an ion in the soil in the case of a high amount of soil complex, than with a lower amount. On the other hand, a high exchange capacity gives more monovalent ions in solutions. Both factors make it possible, to some extent, to use the figure for monovalent cations, expressed in percentages of soil, for correlative purposes. The use of this figure on the other hand will be limited to soils of the same origin.

(2) As a consequence of the differences in adsorption power of the different clay minerals and organic soil materials for the different ions, the result of the soil test is dependent on the nature of the soil complex. This is also a factor that limits the use of correlating figures to soils with the same origin.

I know these facts are not new, and are familiar in agricultural

practice. Possibly they are more appreciated in practice than in the soil testing laboratories. The theoretical background of the facts has the advantage that a theoretical and practical study makes it possible to find ways for quantitative corrections of the figures of the soil test in respect to the nature of the soil.

In my opinion it is necessary to know the ion activity as a basis for the determination of the physiological activity of the ion in the soil. Ion activity can be determined directly or indirectly. Another way is to interpret the figures of the determinations of the total amount of exchangeable ions in terms of activity. In my opinion it is not correct to speak about the availability of the available ions (BRAY), as a disparagement of the research in the field of the ion activity. I suggest to change this term by speaking about the determination of the physiologically available ions. The aim of our work is to find out the reactions of the living plant on the dynamical system which we call soil.

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SESSION 6

ON THE RELEASE OF PLANT NUTRIENTS

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The uptake of nutrients from soil is a process involving several factors. Some of these are intimately related to the physico-chemical properties of the soil. In most soils the major part of the plant nutrients is adsorbed by the soil colloids or present in slightly soluble compounds. The nutrient uptake by plants, therefore, implies a desorption and/or dissolution as the first step of the process resulting in transfer of ions from the soil into the plants. The main purpose of this paper is to discuss the release of plant nutrients as determined by the desorption from soil colloids and the rate of dissolution, as well as to connect the release with a new theory of ion exchange for natural systems.

In discussing the available nutrients it should be immediately stated that a distinction must be made between the *availability* of a nutrient and the *available amount*. While the former is an *intensity factor* (I) the latter is a *capacity factor* (C). The availability of a certain ion is assumed to be an expression of the ease of transfer of the ion from the soil to the root surface. It is, therefore, a function of the ease of desorption from the soil colloids as well as the specific rate of dissolution of difficultly soluble compounds containing the ion. However, the availability is determined not only by the properties of the soil (I, C) but also by the nature of the plant (Y). An additional factor of importance for the nutrient uptake is, of course, time. The rate of intake of a nutrient into the root can, therefore, be written (diffusion effects not considered):

$$dq = k \cdot I \cdot C \cdot Y \cdot dt \qquad (1)$$

where dq means the amount transferred from the soil and adsorbed by the roots in the time dt, k is a constant and Y a variable the magnitude of which depends on the nature of the plant, e.g. the capacity of the roots to produce replacing ions, size of the active root surface, speed of translocation within the roots, etc.

Integration of formula (1) is not feasible since we do not know how I and C vary with t. However, it is of interest to examine the meaning of I and C and their dependence on certain factors.

When an ion, A, occurs in adsorbed condition as well as in slightly soluble compounds we have the relation:

$$dq_A = dq_A^{\lambda} + dq_A^{s} \qquad (2)$$

dq_A^{λ} being the amount taken up from the adsorbed condition and dq_A^{s} that from the slightly soluble compound. The corresponding availabilities are called I_A^{λ} and I_A^{s}. Thermodynamically the availability of an adsorbed ion may be considered inversely proportional to the affinity of the ion for the soil colloids and directly proportional to the affinity for the root surface and *vice versa* with respect to the influence of H^+, the affinity being taken as a measure of the mean free bonding energy of a mole of the ion adsorbed under the conditions obtaining. Thus,

$$I_A^{\lambda} = k_1 \frac{\Delta G_{AR} \cdot \Delta G_{HZ}}{\Delta G_{AZ} \cdot \Delta G_{HR}} Y; \quad k_1 = \phi(\Delta G_{AR}, \Delta G_{AZ}, \Delta G_{HZ}, \Delta G_{HR}, Y) \qquad (3)$$

where ΔG_{AR} and ΔG_{AZ} designate the mean free bonding energy of A adsorbed by root and soil respectively, and ΔG_{AR} and ΔG_{HZ} the same with respect to H^+. The above relation holds true whether the ions migrate via the soil solution or the absorption is of the contact exchange type (1), ΔG in the former case being related to the activity coefficient (f) by $\Delta G_{AR}=RT\ ln\ f_{AS}:\ f_{AR}$ and $\Delta G_{AZ}=RT\ ln\ f_{AS}:\ f_{AZ}$ and in the latter by $-\Delta G_{AR}=RT\ ln\ f_{AR}$ and $-\Delta G_{AZ}=RT\ ln\ f_{AZ}$ and the same for H^+. f_{AS} means the activity coefficient in the soil solution. By such a treatment the influence of the soil solution will be accounted for. For ions present in the soil solution formula (3) reduces to

$$I'_A=k_1\frac{\Delta G_{AR}}{\Delta G_{HR}}\cdot Y$$

The capacity factor, C'_A, corresponding to I'_A may be expressed:

$$C'_A=\frac{f_A[A]}{f_A[A]+f_B[B]+f_D[D]+\cdots}\cdot f_A[A] \qquad (4)$$

A, B, and D being monovalent ions, f the activity coefficient and [ ] concentration. The available amount of A is also a variable affected, besides by nutrient uptake (*up*) and supply (*su*), by weathering processes (*we*), fixation (*fi*), leaching (*le*), microbial activity (*mi*), etc. This may be expressed

$$[A]_t=[A]_0(1-up+su+we-fi-le\pm mi)$$

The rate of ion desorption from the soil colloids, which is the same as the subsequent adsorption on the root surface if the concentration of the soil solution is assumed to be unchanged, is obtained from formulae (1), (3), and (4). Thus,

$$dq'_A=k_1\frac{\Delta G_{AR}\cdot\Delta G_{HZ}}{\Delta G_{AZ}\cdot\Delta G_{HR}}\cdot\frac{f^2_A[A]^2\cdot Y\cdot dt}{f_A[A]+f_B[B]+f_D[D]+\cdots} \qquad (5)$$

As a comment on (5) it should be mentioned that the strength of the acidoids of soil and root is an important factor since it largely determines the ΔG_{HZ} and ΔG_{HR}. Also the degree of base saturation of the soil may be of importance, the ΔG_{HZ}, especially, being more or less affected by the degree of neutralization. Here the liming problem with regard to the availability of adsorbed cations comes into the spotlight.

When the ion A is present also in a slightly soluble compound, AX, the corresponding expressions can be arrived at as follows. The amount of A brought into solution per unit time and, thus, made directly available to plants, can be assumed to be proportional to the two following variables, introduced for this purpose, namely the *specific rate of dissolution* (the availability factor I''_A and a *certain function of the total amount* of AX (the capacity factor $\phi(C''_A)$ The function $\phi(C''_A)$ depends on such physical properties of the compound as the size of the contact surface between solid and solution, uniformity of crystals as regards size, shape and purity, compactness, intermingling with other solids, etc.

Under the assumptions made the availability of A reads

$$I_A^{(1)} = -k_2 \frac{\delta n_{AX}}{\delta t} \qquad (6)$$

where ^nAX means a unit mass of AX. The specific rate of dissolution is more or less governed by such factors as temperature (v), specific surface of AX (δ), saturation deficit (d), ionic strength (μ), hydrogen ion activity (a_H), etc., expressed by

$$\frac{\delta n_{AX}}{\delta t} = \phi(w, s, d, \mu, a_H)$$

The rate of the dissolution then becomes

$$dq_A^{(1)} = -k_2 \frac{\delta n_{AX}}{\delta t} \phi(C_{AX}^{(1)}) \cdot dt \qquad (7)$$

Equation (7) may also be usable for description of weathering processes.

The general expression of the rate of transfer from the solid soil phases to the root surface under the conditions stated above will be the sum of (5) and (7). Thus,

$$dq_A = k_1 \frac{\triangle G_{AE} \cdot \triangle G_{HZ}}{\triangle G_{AZ} \cdot \triangle G_{HE}} \cdot \frac{f^2_A[A]^2 \cdot Y \cdot dt}{f_A[A] + f_B[B] + f_D[D] + \cdots} - k_2 \frac{\partial n_{AX}}{\partial t} \phi(C_{AX}^{(1)}) \cdot dt \qquad (8)$$

It is evident from this expression that, despite neglect of diffusion effects, the release of nutrients is an extremely complicated physico-chemical process. It would lead too far to discuss all the factors involved, but they will be grouped as follows:

(1) Soil properties influencing the availability: ion exchange capacity, strength of acidoids, degree of base saturation, concentration of soil solution, kind and proportions of all the ions present, physical state of the solid soil materials, temperature, etc.

(2) Soil properties influencing the available amounts: total and relative amounts of dissolved, exchangeable, and soluble ions, uptake, weathering, leaching, fixation, microbial activity, etc.

(3) Plant properties affecting the availability: exchange capacity and strength of root acidoids, production of replacing ions, size of active surface, translocation of adsorbed ions to other parts of the plant body, etc. A high adsorption affinity for the root surface and a rapid translocation mean low concentration of the respective ion in the soil solution and thereby a high potentiality of the desorption and dissolution processes.

As discussed above, the ion desorption involved in the nutrient uptake is best described by a differential equation. It is characteristic of this type of exchange that it proceeds slowly due to a very low capacity of the replacing hydrogen ion per unit time, and that the activity of the released ions in the soil solution is small due to a more or less complete removal of the replaced ions from the exchange system. This is caused by the adsorption onto the root acidoids and

the subsequent transport to other parts of the plant. To distinguish this kind of ion exchange from other types of exchange, such as the dynamic and the batch types of exchange (3), the writer has proposed the name *continuous infinitesimal ion exchange* (CIE) (3). It can be pictured as a repeated batch exchange[1] taking place in an infinite number of steps, the amount of ions exchanged in each step being infinitesimal. Full equilibrium is supposed to be attained within each step but, if the process continues unimpeded, theoretically, a final equilibrium state of the exchange will not be reached before the soil is hydrogen saturated. Virtually the process does not go so far since the weathering is an opposing factor and the plants themselves do not grow under such conditions.

The theory of CIE has been worked out for the release of two monovalent ions A and B adsorbed by an exchanger at any mole fractions (2, 3). The ion exchange can in such a case be described by the differential equation

$$dA_S = \frac{{}^{a}A,B \cdot A_Z}{B_Z + {}^{a}A,B \cdot A_Z} \, dR \qquad (9)$$

where $A_Z = A_T - A_S$, $B_Z = B_T - B_S$ and $A_S + B_S = R$.

In (9) the subscript S means solution, Z exchanger, and T total amount. R means replaced amount and $a_{A,B}$ the equilibrium quotient of the mass law. A, B and R are expressed in milliequivalents. The boundaries of R are: $0 < R < A_T + B_T$.

Integration of (9) yields:

$$\frac{A_T - A_S}{A_T} = \left(\frac{B_T + A_S - R}{B_T}\right)^{a} \qquad (10)$$

or the equivalent expression

$$\frac{A_Z}{A_T} = \left(\frac{B_Z}{B_T}\right)^{a} \qquad (11)$$

These formulae allow a calculation of the amount of A released by a continuous infinitesimal exchange at any value of R.

In Fig. 1 the calculated exchange isotherm is given for two cases, namely $a_{A,B} = 4$ and $a_{A,B} = 0{\cdot}25$. In the former A is more weakly adsorbed than B while in the latter A is more firmly adsorbed than B. For comparison similar isotherms for batch exchange are also given, formulae previously published being used.

(2). Theoretically it is found that the continuous infinitesimal exchange, if compared with batch exchange, favours the release of weakly adsorbed ions but tends to conserve the firmly adsorbed ions. This effect is the more marked the greater the difference between the adsorption affinity of the ions and the more dissimilar the mole

[1] Occurring in static systems, equilibrium rapidly attained.

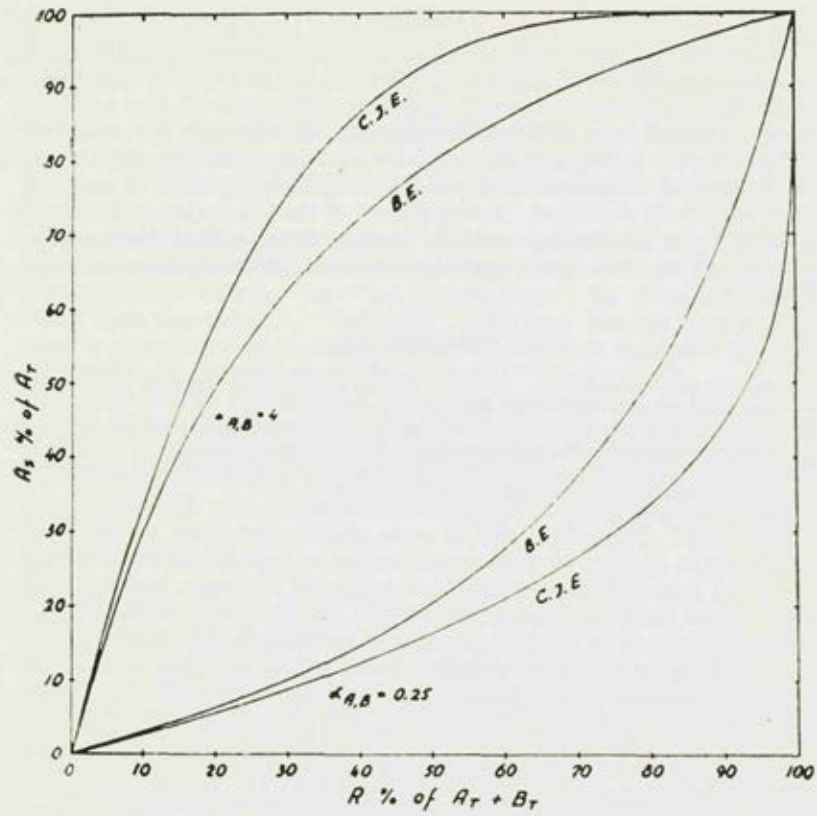


Fig. 1.—Influence of the type of exchange on the release of an ion A, combined with an ion B of the same valence, the equilibrium quotient ($\alpha_{A,B}$) assumed to be 0·25 and 4 and the replacement (R) of A + B to vary from 0 to 100% B.E and C.I.E signify batch exchange and continuous infinitesimal exchange respectively. AS means A in solution and AT total amount. Mole fraction of A—0.01.

fractions. The difference between the CIE and the batch exchange has its maximum at a certain magnitude of exchange and approaches zero at very low and very high exchange. Experiments conducted with resinous exchangers (3) proved to be in good agreement with the theory.

It is very likely that the ion exchange taking place in such natural systems as soil, plants, animals, etc., in general, is of the CIE type even though there may be other processes more or less overshadowing the ion exchange proper. In these systems the exchange processes are slowly proceeding, and time is, therefore, an important factor. The ion exchange connected with the nutrient uptake by plants and the leaching of nutrients belongs to this type and should, therefore, be treated according to the theory of the CIE. The logical inter-relationship of the nutrient release as a function of availability, available amount, and time, and the ion exchange involved in this process will thus be clear.

Summary

The transfer of nutrients from the soil to the root surface is discussed as a physico-chemical process determined by the three variables : availability, available amount, and time, the rate of the reaction being expressed by a differential equation. Availability is considered as the intensity factor, and the available amount as the capacity factor. Their physical meaning and dependence on the properties of soil and plant are briefly discussed. A new theory of the ion exchange involved in the nutrient release is presented. In accordance with its mechanism, this type of ion exchange is named *continuous infinitesimal ion exchange* (CIE).

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SESSION 6

NUTRIENT BALANCE AND INTERACTION EFFECTS ON SOIL FERTILITY

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The observed so-called "toxic effects" or reduced rate of plant growth in single salt solutions, as contrasted with better growth, "antagonistic effects" or "ion interactions" in solutions having more than one salt, i.e. "balanced" solutions, has led to the belief that a given ratio and concentration of different nutrients must be present in the external media for "normal" plant growth.

Similar results were found with clay suspensions, as the rate of growth in homoionic clays was less than in diionic clays within certain limits (17). Plants were found to grow equally well in soils of varying composition provided a given minimum of each nutrient was present (46). Although cation composition within the plant may vary within wide ranges, yield may still be more or less unchanged. It seems that plants have the ability to adjust themselves to a wide range of ion levels, a fact conceded by many workers in plant nutrition (3, 4, 47).

It has been observed that yield increase resulting from the addition of a nutrient that is limiting is related not only to the concentration of this ion but also to the levels of other nutrients as well (16, 42). These and other observations have focussed attention on the question of balance and interaction as they affect soil fertility and plant growth.

Concept of Balance

A "balanced" solution may be defined as that solution producing no toxic effects or deficiency symptoms due to mutual antagonism in plants growing in it. This implies that essential ions have to be present in certain proportions relative to each other in order to ensure "balanced" effects. No mention is made of its nutritional value as measured by the rate of growth or yield. A dilute solution may be "balanced," yet of little nutritional value to plants unless frequently renewed. On the other hand, solutions of high nutritional value, at least with respect to certain ions, may be "unbalanced" and plants growing on them may show deficiency or toxicity symptoms.

If one element is added in excess to a balanced solution, the balance within the plant may be disturbed and symptoms, either due to deficiency of one element or to accumulation of another, may show themselves. Therefore, it becomes rather difficult to distinguish between observed symptoms due to deficiency of one nutrient from those attributed to accumulation of another; as a deficiency of one element may actually be a toxicity of another that has accumulated in the plant at the expense of the element deficient. The point to be stressed here, is that symptoms of deficiency or toxicity could be looked upon as expressions of unbalanced nutrition which has persisted for some time.

The necessity for having a minimum quantity from each element to ensure balance among them can be easily visualized from the fact that each essential nutrient has a specific function in the plant which

cannot be performed interchangeably by others. The minimum concentration required from each element varies with the element, plant species, stages of growth and environmental conditions. Nutrient elements can be classified on the basis of plant requirements into macro-nutrients and micro-nutrients. As to the effect of plant species, it has been found that plants vary greatly among themselves in the minimum quantity of each nutrient required for healthy growth. Some plants, such as those belonging to the grass family, require relatively higher potassium levels, whereas legumes require relatively higher calcium levels (10). Nutritional requirements of the same plant also may vary with the stage of growth (9).

Total and Relative Cation Content of Plants as Related to the Composition of External Media

The data available at present seem to indicate that the total equivalent cation contents of many plants at comparable stages of growth are reasonably constant over a wide range of cation concentration in the medium (2, 48). In other words, the total cation content is a specific characteristic of the plant and is only very slightly modified by environmental conditions. On the other hand, the relative proportions of the cations in the plant are influenced to a certain degree by the composition of the external medium: changing the concentration of any one cation in the media is generally associated with a change in the internal composition of the leaves. The extent of the relative changes taking place in the composition of the plant is determined by both element and plant.

Some elements seem to have greater effect on changing plant composition than others. The order of effect may be related to the rate of absorption of the element by the plant, and the higher the rate the greater will be the effect. Accordingly, addition of potassium may have greater effect than magnesium and magnesium greater than calcium in changing the relative composition.

TYNER and WEBB (45) found that with corn plants the increase of nitrogen in the media increased the nitrogen content of the leaves while increasing the phosphate content was not accompanied by a significant change in their phosphorus content.

GREGORY (16) found that with barley plants, increasing the phosphorus level with nitrogen constant in the media, increased nitrogen content in the plants whereas phosphorus level did not change with increasing nitrogen in the media.

Relation between Nutrient Balance in the Soil and Plant

It has been shown that plant composition can be changed through fertilizer application (22, 41, 44) which may indicate that a relation seems to exist between nutrient balance in the soil and that in the plant. If such is the case, the ratios of the elements in the soil will bear certain relations to those in the plant. This has been claimed to be true for certain plants (7, 8). On the other hand, BEAR and TOTH (2a) found that the ratios of basic nutrient cations in alfalfa bear little resemblance to those on the exchange complex of the soil in which it was grown, calcium being the dominant cation on the clay whereas potassium is the frequently dominant cation in the plants. The dis-

crepancy between the balance in the two systems may be due to many factors, of which we mention :

(1) Selective absorption and exclusion of certain ions by plant reduces resemblance between those ions in the soil and those in the plant.

(2) Supplying power effect may upset balance in the soil. The concentration of a given ion in the soil solution may be low, yet it may be released at a rate sufficient to meet the requirement of the plant, or may even exceed these requirements and upset the balance.

(3) Activity of ions, for, if the balance in the soil is based on total concentration of exchangeable ions, then it may lead to erroneous conclusions owing to the fact that adsorbed ions vary in activity and fraction active from those ions in solution. Therefore, concentration bears little resemblance to fraction active. When we are in a better position to ascertain activity of different ions and supplying power of soil, and to explain selective absorption, a better relation may exist between the balance in the soil as computed on the ion activity and that in the plant (38,39).

Nutrient Balance as Related to Nutrient Level in Soils

The question of nutrient balance in soils is of great importance if the application of fertilizers is to be placed upon a scientific basis. If the content of a nutrient in the soil is originally low so that its concentration in the leaf is near the minimum required for normal growth, the addition of other nutrients to the soil in large amounts may cause the content in the leaves of the element originally present in small amounts to fall below the critical minimum and deficiency symptoms of this element may be induced as a result of unbalance, due to higher absorption of the nutrient added. This phenomenon is of common occurrence in soils where magnesium content is originally low and large doses of potassic fertilizers are added (49, 50). It is then stated that potassium induces magnesium deficiency. The depressive effects of certain fertilizers on yields is of common occurrence. This may be explained on the basis of unbalance resulting from too much absorption of the element added at the expense of others. Accordingly, addition of potassium to soils rich in available potassium may exert a pronounced depressing effect, and the method to correct such depressive effects is to increase the concentration of the elements that may become limiting.

When the mineral concentration within the plant is above the critical level throughout the entire period of growth, most likely plants will not respond to new additions of nutrients. If one of the nutrient elements reaches the critical level and becomes limiting, the addition of this element does not necessarily indicate that nutrient balance has been brought to the optimum for maximum growth. In considering the type of balance, we must, therefore, distinguish between normal appearance of plants and their maximum growth. Normal appearance requires merely a balance between nutrients whereas maximum growth requires a proper balance together with optimum concentration.

Interaction between Nutrients

Interaction effects between nutrient ions as generally understood, refer to differences in response to a given amount of a nutrient at different levels of other nutrients. This may imply that the efficiency of one element is influenced by the presence and levels of other elements. The composite effect of nutrients on plant growth is influenced by the nature of interactions between them. It is still rather difficult to explain why certain interactions occur but the fact that yield as well as physiological diseases are affected by the nature of such interaction is sufficient to make this factor an important consideration in fertilizer experiments.

If two elements are limiting growth in a soil, adding either of them will cause a slight increase in yield, whereas adding both of them together will increase yield considerably. Since the increase produced from adding them together is higher than the sum of increases obtained from each one separately, it is said to have positive interaction (36). The extent of interaction varies with the element and the plant. While nitrogen may have a depressive effect on potassium under certain conditions, it has little or no effect on phosphorus. In a similar way potash may intensify nitrogen deficiency and depress yield (16).

The response of crops to a given fertilizer element must be modified according to the internal concentration of other elements in the leaves, as yield increase is related to concentration of nutrients. LUNDEGARDH (23, 24) in his experiments with oats took account of the interaction among the principal nutrients. His estimates of response to potassium fertilizers were not based only on the potassium content of the leaves but also were modified according to their phosphorus content as well. This interaction effect between nutrients has been realized by many workers in this field and they prefer to compute certain ratios instead of simple ion concentration for use as diagnostic criteria. Some of the ratios suggested include N/P, K/P, K/N, and many others according to the element and plant studied.

Soil Fertility as Related to Nutrient Balance

Soil fertility refers to the nutrient status within the soil. It includes quantity, availability and ratios between different nutrients. A fertile soil can be defined as that soil having or capable of supplying a well-balanced and adequate supply of soil nutrients in available form to meet the requirement of the growing plant during different stages of growth.

In evaluating soil fertility or its nutrient status, consideration must be given to:

(1) Quantity of nutrients present in readily available form.
(2) Supplying power of the soil or its ability to release nutrients from different sources during different stages of growth.
(3) Balance between nutrients readily and potentially available as measured by activity.
(4) Exchange capacity as a measure of potential supply.
(5) Degree of clay saturation as a measure of relative supply of different nutrients.

The fertility status of the soil can be materially changed through the addition of a fertilizer material as it affects concentration, composition and balance between nutrients. This is particularly true in soils of low exchange capacity.

We must not confuse soil fertility with productivity as fertility is only one of the factors determining productivity. A soil may be fertile but not productive if any of the factors of productivity is limiting. Yield, which is the numerical index of the producing system, including climate, plant and soil is often taken as the measure of soil productivity or sometimes fertility. This is justifiable only when the factors of productivity other than the soil are kept constant. If the physical properties of the soil, together with other productivity factors, are kept constant, yield may be a function of fertility and soil productivity becomes synonomous with fertility (18).

Fertility of some Important World Soil Groups in the Light of Nutrient Balance

Desert soils, excluding sands, are well supplied with plant nutrients. Nitrogen and phosphorus are generally low. The problem of soil fertility is how to have the proper balance between nutrients.

Chernozems are highly fertile soils, because of well-balanced plant nutrients. This fact, together with good physical conditions, ensures high soil productivity.

Laterites and lateritic soils have low exchange capacity with low availability of phosphorus. The balance between nutrients can be easily disturbed through the addition of certain elements in excess. Podsol and podsolized soils are low in fertility because of lack in some macro-nutrients, especially calcium and magnesium. Liming and addition of complete fertilizers help to maintain the proper balance between nutrients.

Consideration of some Factors that Affect the Setting of Standards for Nutrient Balance in Soils

The application of the results of studies carried out on nutrient balance and interaction in water and sand cultures to the soil, is accompanied by discrepancies arising from differences in the properties of ions and methods of nutrition in both media.

In dilute nutrient solutions the activities of ions do not vary greatly from their molalities and it makes little difference whether we express absorption as a function of concentration or activity.

In soils, however, the activity of ions greatly deviates from concentration. If we agree with OVERSTREET's concept that the activity of an ion in the soil suspension or gel is the same as its activity in equilibrium filtrate, then, taking the activity in dilute equilibrium filtrate as equal to their molalities, and knowing the total concentration in both phases, we can calculate the activity coefficient of adsorbed cations and this was found to be much less than unity (35).

As to differences between nutrient solutions and soils as methods of nutrition, we now realize that the soil solution concept as viewed by BURD (6) cannot account for the absorption of different nutrients by plants. The adsorbed ions play an important rôle in nutrition either directly through contact mechanism as suggested by JENNY

(19, 21) or indirectly as a reservoir for some of the soil solution ions as suggested by BURD (5).

The point to be stressed here is that the concept of nutrient balance in soils will be more complicated, as many factors interfere in determining the ratio between different constituents. Of these factors we mention :—

1. *Type of clay mineral and its relation to ionic environment of plant roots*

Different clay mineral groups are characterized by certain properties which influence the ionic environment of plant roots. They include differences in exchange capacity, bonding energies of ions, ionization, activity and the fraction active. The effect of the type of clay mineral on ion uptake has been realized by many workers (1, 12, 33). ELGABALY, JENNY and OVERSTREET (12) observed that under comparable conditions, excised barley roots took up more potassium and zinc from montmorillonite clay suspensions than from kaolinite suspensions in spite of the fact that the release of these two ions by water, CO_2 and HCl is greater from kaolinite than from montmorillonite.

Recently, ELGABALY and WIKLANDER (13, 14) confirmed previous findings showing that barley and pea roots take up more calcium from montmorillonite suspensions than from kaolinite. The conclusions brought out from these experiments are :—

(*a*) Type of clay mineral affects ion uptake by plants.

(*b*) Carbon dioxide mechanism alone cannot account for absorption.

(*c*) Other mechanisms, such as contact or valence effect in a DONNAN system or activity concept, are involved in the uptake of ions from colloidal suspensions.

MARSHALL and associates (25, 26, 27, 28, 29, 34), using clay membranes to study cationic activities in homoionic and diionic clay suspensions, found that under comparable conditions, exchangeable cations adsorbed on kaolinite are more ionized than when adsorbed on montmorillonite and this may tend to compensate to a certain extent for the low exchange capacity of kaolinite. Calcium on kaolinite is 10 to 20 times as readily available to plants as compared to calcium on montmorillonite. The ratio of the activity of monovalent : divalent cations in all clays studied by them is higher than the ratio of adsorbed ions. These ratios vary with the type of clay mineral and degree of saturation. The ratios of the activity of monovalent : divalent cations is higher for montmorillonite than for kaolinite. Both activity and fraction active must be considered when dealing with nutrient absorption and balance because it is certain that different clay minerals hold the same exchangeable ions with varying degrees of bonding energies.

MATTSON and associates (30, 31, 32) hold the view that differential absorption of ions from different clays is governed by the valence effect rule in a DONNAN system. Relatively concentrated micellar solutions and relatively dilute outside solutions favour absorption of divalent cations.

COOPER *et al.* (7, 8) emphasized the relation between the energy properties of nutrients and intensity of absorption by plants. They

claim a correlation between the relative strength of ions, as determined by oxidation-reduction potential, and quantities found in plants. Selective absorption and selective exclusion of some ions by certain plants may be the cause of exceptions to this rule.

Whether the difference in the behaviour of ions adsorbed on different clay minerals as affecting their uptake by plants is explained on the basis of contact exchange as suggested by JENNY, or of difference in ion activity as suggested by MARSHALL, or of the valence effect in a DONNAN system as suggested by MATTSON, is beyond discussion here, as it still awaits further data and definite measurement and understanding of ion activity in colloidal systems. However, there seems to be a general agreement between workers in this line, that the nature of the clay mineral or the condition of adsorbing surfaces alters and determines the "ionic environment" of plant roots and as a result exerts an influence on ion uptake. Soils with different types of clay minerals are expected to show marked differences in availability of their ions to plant, a factor which must be considered when dealing with nutrient balance in soils.

2. Degree of saturation and complementary ion effects on uptake and balance

It has been realized that the relative degree of saturation of an adsorbed ion is more important in ion uptake by plants than the absolute amount present. The degree of saturation, with respect to a given nutrient ion, required for healthy growth, varies with the nature of colloid, the complementary ion and plant. This may be explained on the basis of activity and fraction active in different clay minerals. JENNY and AYERS (20) brought forward a concept of the effect of degree of saturation and nature of the complementary ions on ion uptake by plants.

Recently, EPSTEIN and STOUT (15) studied the absorption of certain micro-nutrients by tomato plants and found that at levels lower than 0·1% of the exchange capacity, the uptake was proportional or nearly so to the degree of saturation. The effect of the complementary ion varied with the original ion studied.

WIKLANDER and GIESEKING (51) studied the exchangeability of certain ions at extremely low degrees of saturation and found that, as the degree of saturation becomes lower, the more difficult is the replacement of the ion. The lower the activity coefficient of the ion relative to that of the complementary ion, the more difficult will be the replacement of the ion. The more the difference between the activity of adsorbed ions, the more their release will be influenced by the degree of saturation.

The exchangeability of a given ion at a given degree of saturation will be changed, increasing or decreasing, according to the nature of complementary ion as related to its energy of adsorption or activity. For example, ease of exchange of calcium, below a given degree of saturation, will be lower if the complementary ion is sodium than if it is potassium.

There seem to exist lower limits of degrees of saturation for different ions in different soils below which the quantity released to the plant will not be enough to meet plant requirements. Therefore, consideration of the effect of degree of saturation and nature of complementary

ion, as modified by the type of clay, on the availability of different nutrients to plants must be considered in evaluating the balance between the nutrients in different soils. This relation is complicated more by the fixation of certain ions in non-available form.

3. *Effect of plant species on nutrient balance and uptake*

The plant composition reflects all factors, including soil and climate, that influence its nutrition. Under similar environmental conditions, plants of different species or even different varieties were found to have different mineral composition (10, 40). This difference in composition may be due to different mineral requirements, different conditions of absorption or other reasons.

Information on the cation exchange capacity of roots may provide a fundamental basis for studying the differential absorption of ions by plants. MATTSON (30, 32) could explain differential absorption of monovalent and divalent cations on the basis of difference in exchange capacity of root or differences in concentration of micellar phase and outer phase. On the basis of valence effect in a DONNAN system, divalent cations displace monovalent better, the greater the relative activity of ions in internal or colloidal phase. Legumes with relatively high exchange capacity or relatively high concentration of colloidal phase will have preferential absorption to divalent cations over monovalent cations. The reverse is true for grasses, as they have a low exchange capacity. ELGABALY and WIKLANDER (13, 14) confirmed MATTSON's findings and showed that excised pea roots absorbed relatively more calcium and excised barley roots absorbed relatively more sodium from comparable concentrations of both Na, Ca-kaolinite and Na, Ca-bentonite systems.

DRAKE *et al.* (10) determined the exchange capacity of many plant species and came to the conclusion that roots of monocotyledons have generally lower exchange capacities than those of dicotyledons. Plants with low capacities were found to have relative preference for monovalent cations such as potassium and sodium, whereas dicotyledons have relative preference for divalent cations such as calcium and magnesium. The preference may be related more to the nature of plant colloids than to any specific high requirements.

It has been observed that grasses were able to take up relatively more potassium from a lower potassium concentration than legumes; a factor that needs to be considered in setting nutrient levels required for different crops.

The difficulties encountered in the use of plant composition as an index of optimum balance in the medium could be:

(*a*) Plants may vary greatly in internal composition without a corresponding change in yield.

(*b*) In case of "luxury consumption" plants may continue to accumulate more of certain nutrients than is required for maximum growth and yield.

(*c*) Nutrient uptake by plants is governed by all environmental factors.

In studying nutrient status of the soil and its relation to composition and yield, we must set up standards of reference for different crops and consider the deviation from these standards as resulting from less

satisfactory nutrient conditions. This requires data on yield at different levels of nutrients and internal composition. However, because of the great number of nutrients and possible interactions between them, it will be difficult to set up standards relating nutrient composition in the soil to the composition and yield of plants.

SUMMARY

1. Plants require for their normal growth a minimum amount of each of the essential nutrients. This amount varies with the element and the plant. Since plants take up the nutrients from the external medium, they have to be present in proportions sufficient to meet the amounts required.

2. The concept of nutrient balance in culture solutions will be different from that in soils, because of differences in the properties of ions and methods of ion uptake by plants in both systems.

3. In culture solutions, nutrients have almost the same degree of availability, and concentration differs but little from activity. Plants take up nutrients directly from the solution. Balance between nutrients can be easily adjusted according to plant requirements.

4. In soils, however, nutrient ions are present in varying degrees of availability (solution, adsorbed and precipitated) and therefore concentrations vary greatly from activities. Availability is influenced by, among other things, type of clay mineral, degree of saturation and nature of complementary ion. It seems that activity is influenced by the same factors. Until the activity of adsorbed ions is well defined and methods of measurement are perfected, it will remain difficult to determine the balance between nutrients in soils.

5. Plants seem to be able to adapt themselves to grow equally well over a wide range of soil composition provided a given minimum of nutrients is present, and yield may stay more or less constant in spite of variations in the relative cation content of soil and plant.

6. Changing the composition of the soil may change the relative cation content of the plant but the total content remains more or less constant and seems to be a characteristic of the particular plant.

7. Nutrient balance in the soil and plant may be changed through the addition of fertilizer material. The extent of response to the addition of a given limiting nutrient is determined not only by the level of that element but also by the level of other elements as well. This is due to the interaction between the different nutrients. Soils of low exchange capacity could easily suffer changes in their nutrient balance through the addition or removal of certain nutrients.

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Section B

SESSIONS 7 AND 8

SESSION 7

EVALUATION OF METHODS OF SOIL TESTING BY MEANS OF FIELD EXPERIMENTS

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All modern methods of soil testing are designed with a view to determining the nutrient available to the crop in agricultural practice. In so far as they are chemical methods, the chief aim is to determine the fractions which are easily soluble.

The reliability of a method should never be taken for granted *a priori*. This even applies to a method like the pot experiment according to MITSCHERLICH. To accept such a method as normative, as was formerly done in comparing methods carried out under the auspices of the International Society of Soil Science, really means the denial of the significance of interactions between the factors tested and all other factors determining the growth of the crop in farming practice. Such methods are only acceptable for a first orientation. It should be realized that a method of soil testing must be entirely based on actual agricultural practice.

It has been said that soil testing will never be able to ascertain the availability for a given crop, the more so as interactions between a particular factor and other practical factors in a specific case cannot be denied. However, the important point is whether the results of the soil test obtained are connected with the reaction of a crop in such a way that advice can be based upon them, which fulfils practical requirements in a given agricultural situation. Moreover, it is a misappreciation of the possibilities of research to deny that interactions with other factors can to some extent be distinguished and can be implicated in the evaluation.

The requirements a method should fulfil vary from case to case. The chief point is the aim and object in a specific agricultural situation. Wherever farming is extensive or may be considered as little developed, it may be sufficient to trace the more conspicuous defects. A close observation of the crop will in such a case possibly provide an adequate test for a method. In a form of progressive farming producing all but optimum yields, it is rather of importance to efficiently apply the available fertilizers and to improve the quality of the produce than to increase the yields. In this case accurate testing of a method will be essential before it can be recognized as efficient. In the various countries situations between these two extremes are numerous. The fact that in the Netherlands with its intensive and rationalized agriculture heavy demands are made on the usefulness of a method has no doubt been the reason that more attention is paid to the evaluation of soil testing than elsewhere. Therefore I venture to ask your attention, presently, for the discussion of a specific example of evaluation of soil testing in the Netherlands.

The chief requirement of a soil test lies in its effectiveness in indicating what fertilizer is needed and in what quantity it will have to be

applied to a particular crop, or to a complete crop rotation.[1] This standard demands a testing of a method against the reaction of the yield of one or more crops to the soil factor concerned and the quantities of fertilizers applied. Trials of one year's duration are very suitable for the purpose. To arrive at a more reliable average reaction, this research will have to be repeated in other years and on different trial-fields.

Though it is the agricultural aim to increase the yields, one cannot say that difference in yield is necessarily the most exact standard for measuring prevailing differences in the soil. All sorts of inaccuracies may be inherent in a considerable measure, which have little connection with the physiological reaction to the availability of a soil factor. Besides, the accurate determination of differences in yield requires field-trials that are fairly extensive. Moreover, difficulties may occur in the case of perennial crops or crops producing more than one yield a year, such as grass. Differences in vigour of the crop, in extent of tillering, or content of nutrient absorbed in a plant, etc., will sometimes more directly (and in a manner less influenced by secondary factors) mark the unequal availability of the soil factor. In this way more suitable data may often be obtained to disentangle the influences of various factors. Thus there are simpler methods than the performance of accurate field-trials. A great number of observations, often obtained without much elaboration, may render great accuracy less necessary. Adequate data are often obtained on simple trial plots or on observation spots.

Where particular methods are compared, the method showing the clearest relation to the reaction of the crop will be the best. However, this only applies to these special circumstances. It must never be concluded that some method is absolutely and exclusively the best. For example, in the Netherlands two methods for phosphate determination are employed. In one method the solubility is determined in warm water (50°C), in the second it is determined in 1% citric acid. It was proved that differences in availability of phosphate in a homogeneous soil is often much better indicated by the water method. Nevertheless the citric acid method is more satisfactory in comparing soils of a different nature. The water method is now only applied to one particular homogeneous type of soil.

It should be considered that the value of a method may greatly vary according to the kind of soil. This will be the result of the interactions of the particular single value with other factors on these soils. A phosphate value determined with citric acid must be, for example, 2½ times as high on peaty grassland than on loess grassland for an adequate nutrition of the grass. It is therefore extremely risky to apply methods which proved suitable in a certain area to a different region without further investigation.

However, if the investigation is confined to a comparatively homogeneous soil, it will often be possible to determine the remaining

[1] Besides, it is of importance to find the best fertilizing systems in order to maintain an existing manuring status for a long duration, or to raise it to a more economical level. This problem is mentioned only parenthetically. It may necessitate a further research, e.g., the development of methods for the determination of the fixation of phosphate and potash and the testing of these methods on long-term field-trials.

interactions with accuracy and to incorporate them in the evaluation of the particular single value. This has opened up the possibility of refining the interpretation of soil testing to a remarkable extent.

It is difficult to say what limitations should be observed in respect to the soil area in which a method can be tested. It seems advisable not to start with too extensive and too heterogeneous areas. Soils that do not show very much variation, could be chosen as objects of an investigation. The results of different regional investigations could be compared and combined afterwards. But in due course all the important agricultural soils will have to be tested.

Investigation was often begun by an attempt to find out whether differences prevailing on trial-fields can be demonstrated according to a method and the number of "strikes" was taken as a measure for its practical usefulness. This procedure is rather crude, however. The chief point is to determine whether a certain figure in one field represents an equal or a different value compared with the same figure on another field where the soil conditions are not the same (allowing for interactions and their effects eliminated). The method can only be employed if the results are applicable to an area of some extent. The certainty should exist that the method also holds good for extreme situations in this region.

What has been said will remain vague unless it is elucidated by an example. Therefore I will discuss one of the series of field-trials which have been laid out to test the K-value on marine clay soil. Corresponding investigations have, with interruptions, been carried out since 1936, both relating to arable land and grassland, especially as far as phosphate and potash are concerned. The example chosen is illustrative, because in evaluating the K-value (K-content in 0·1 N HCl in the case of 1 part of soil to 10 parts of liquid) it is mostly necessary to consider some factors simultaneously.

In designing such an investigation the data obtained in another way will often be a great help. It is well known that in many crops the effect of potash is physiologically determined by the lime status of the soil. Furthermore the base-exchange capacity of the soil, which depends on the clay and humus contents, determines the availability. Care should therefore be taken that at any rate these factors are correctly implicated in the investigation.

The trial-fields must be selected in such a way that a considerable variation occurs in the potash value together with the other factors mentioned. The selection therefore requires preliminary soil testing. If in the region intended for experimentation, large-scale soil testing for farming practice was previously carried on, the resulting data may be a great aid in making a decision on what fields are to be selected.

The number of trial-fields required for a successful treatment, depends on the number of factors which are expected to be influential, the extent of the correlations between these factors and the extent of their effects and their interactions. Experience has taught us that at least some tens of trial-fields are necessary for a limited district.

Care is taken that the distribution of the trial-fields is relatively even, i.e. as much as possible in equal measure fields should be selected which are poor, moderate or rich in potash (and also poor or rich in lime, clay or humus), even if these categories are rare in the particular region. Moreover it is tried to avoid correlations between the principal

factors to be studied. If, for example, there is an evident correlation between potash content and clay content, yet an attempt is made to select the trial-fields in such a way that both at a high and at a lower potash content sufficient variation in the other factor occurs and *vice versa*. Another aim is to acquire a regular distribution from a geographical point of view.

Fig. 1 shows an example in which the fields intended for experimentation have been selected from results of soil testing. The choice was made by plotting the potash value both against the lime content and the clay content (particles less than 16 μ) and also the latter

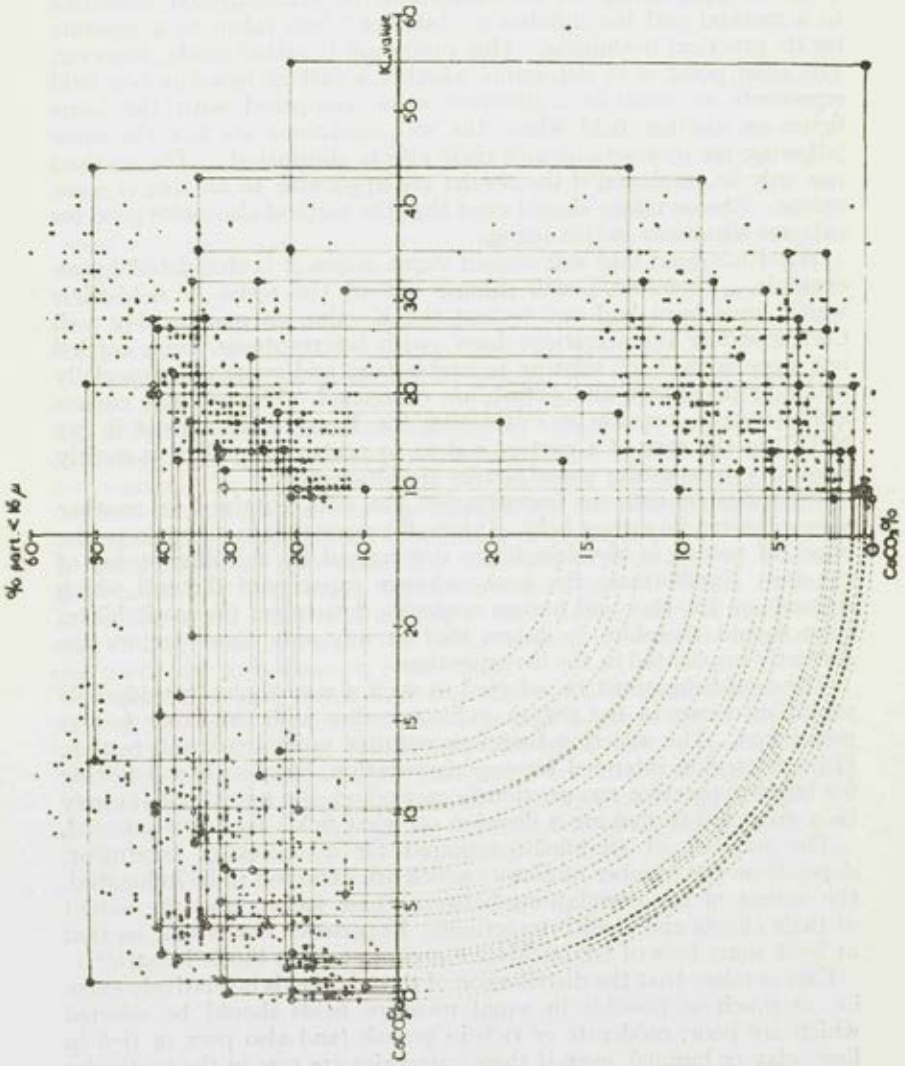


Fig. 1.—Selection of trial-fields after regional soil testing eliminating correlations of factors and aiming at a regular distribution. Dots represent results of soil tests. Large dots represent selected trial-fields.

against each other. If 3 factors are taken into account, the cases selected for the laying out of a trial-field, will, therefore, have to be evenly distributed over a cube.

The investigation in question was carried out in 1947 and 1948 in the largest polder (Haarlemmermeer) of the province of Noord-Holland with comparatively small series (18-20 experiments). In 1950 it was continued in other polders in Noord-Holland.[2] Our attention will chiefly be confined to this last year. Then there were 33 trial-fields under potatoes, variety: Bevelander (just as in 1947 and 1948), besides in one of the polders (Heer Hugo Waard) a series of 27 trial-fields carrying the variety of Eersteling. The two series of trials were studied independently.

The lay-out of the trial-fields was simple. Each field comprised 10 plots, of 25 square metres each. Four plots received no dressing of potash, the other plots, in pairs, 60, 150, 300 kgs/ha.K_2O as sulphuric potash.

The K-value was tested by:

(1) The increase in yield of tubers resulting from manurial treatment;
(2) The K_2O-content of the tops of fairly young plants;
(3) The K_2O-content of the tubers;
(4) The under-water weight of the tubers;
(5) The actual yields.

The increase in yield as a result of manurial treatment was indicated in the yield which is obtained without K-treatment, expressed in percentages of the yield that is obtained on the plot of the trial-field with the highest K-dressing. In employing this "relative yield" it is assumed that in applying a heavy K-treatment the need of potash on this soil is completely supplied. The first two experiment years were successful in this respect, but, as we shall see, not the experiment year 1950.

The K_2O-content of the potato tops gave the most evident indications, so that this tends to receive special attention. The easy method of determining the under-water weight also produced satisfactory results.

The relation between the K-value and the potash content of the potato tops from the Bevelander plots which received no potash dressing, is shown in fig. 2a.

Fig. 2b shows the same, after the effects of the factors clay content and lime content have been eliminated (the method of elimination will be discussed later). It appears that, allowing for these factors, a close relation exists.

The determination of the effects of the various factors is made successively, the strongest influences generally being analysed first.[3] After the influence of the K-value is provisionally determined by a free-hand curve (fig. 2a), the influence of a second factor is determined. This influence is also graphically determined after the influ-

[2] The investigations have been performed by the Agricultural Services in the Province of N. Holland.

[3] This method (called polyfactor analysis) is due to W. C. VISSER. It has been applied in even far more complicated cases. Much attention is now being paid to its mathematical foundation.

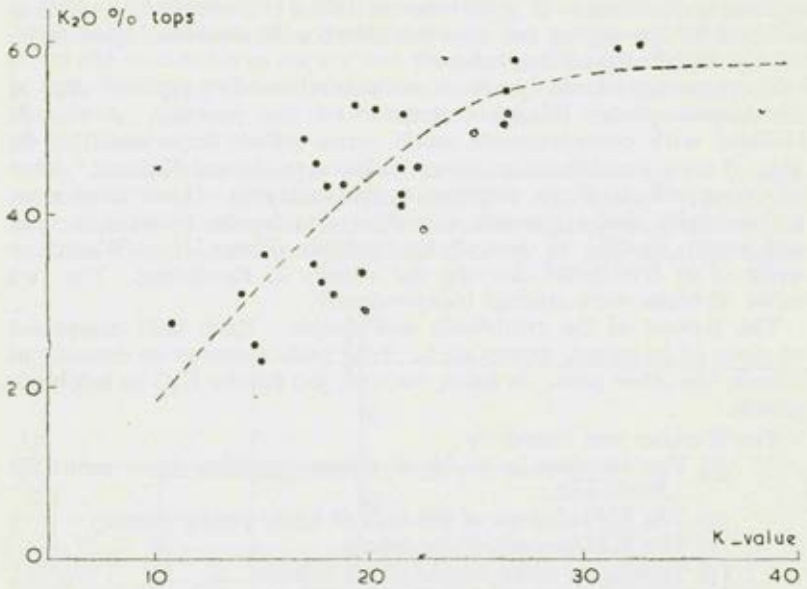


Fig. 2a

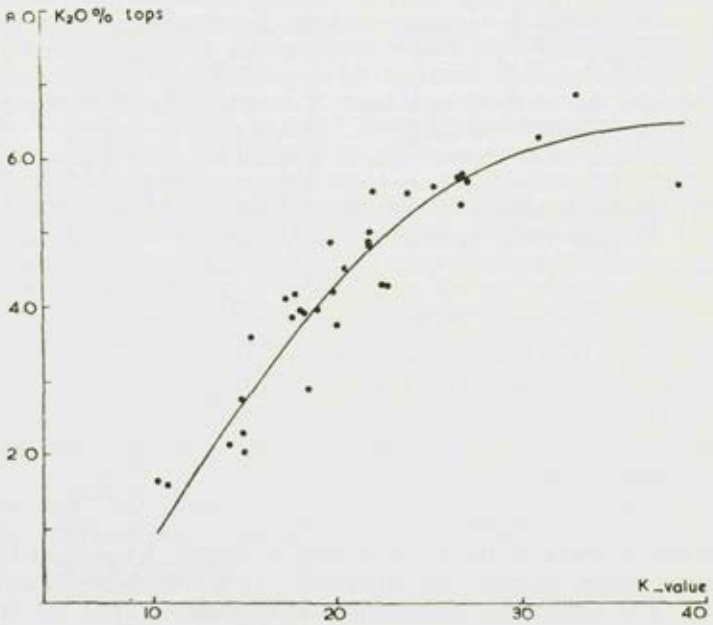


Fig. 2b

Fig. 2—Relation between K-value of the soil and the K_2O content of Bevelander tops : (a) before, (b) after elimination of the influences of lime status and content of particles $< 16\mu$.

ence of the K-value has been eliminated. In the instance in question this was done by plotting the distances of the dots of the curve in fig 2a, measured in a direction perpendicular to the absciss, against the second factor. A dot above the average curve indicates that the uptake was better than the average; a dot below it indicates the reverse.

Interactions between the factors are established as much as possible. If the extent of the material permits it, it is divided up into two or more groups of different K-values and this procedure is followed in these groups independently. In fact, it is very likely that the influence of the second factor on the K_2O-content of the potato tops (or something else) will be different according as the K-value of the soil itself is high or low.

If the influence of a second factor on the K_2O content of the tops is determined in this way, it can be eliminated. Then the influence of the third factor is determined in the same manner. If this has been found, corrections can be made again. The corrected K_2O contents are plotted against the K-value in fig. 2b. Moreover, it is possible to establish more accurately the influence of the second factor after elimination of the influence of the third factor, etc.

The relation between the lime status (here indicated as lrb-value[4]) and the deviations from the dots of the average curve (fig. 2a) has been separately demonstrated in figs. 3a and b for a low K-value (<20) and a high K-value (>20). In this case also the influence of the third factor (content of particles less than 16μ) has been eliminated.

The influence of the lime status is different in either case. At a low K-value the K_2O content appears to have been strongly affected by this. High K_2O contents have occurred on decalcified soils, low contents on moderately calcareous soils. At higher lrb-values there is a rise. Such a complex relation has frequently occurred in other series of potash experiments. There is little doubt that in case of an increasing lrb, decreasing K_2O contents are to be attributed to a lime-potash antagonism. It is less easy to give an explanation of a rise in case of a higher lrb.

In case of higher K-values, at which potash is to a less extent a minimum factor, only a slight indication of an influence of the lime status is found (fig. 3b).

The influence of the clay content appears from fig. 4. It was impossible to distinguish an interaction, so that all determinations have been used. In this figure the influences of the K-value and the lrb have been eliminated. Soils with a higher clay content have yielded lower K_2O contents of the tops than lighter soils.

[4] The pH is not a very suitable measure to indicate the differences in lime status of calcareous soils with some accuracy, because soils with varying contents of $CaCO_3$ are only slightly different in pH. On the other hand the $CaCO_3$ content is zero on decalcified soils. VISSER introduced the lrb-value (logarithm relative base content, lrb $= \log \frac{S + 20 \times CaCO_3\%}{T}$. The numerator is determined by measuring the neutralization of added 0·1 N HCl; T = sorption capacity in equilibrium with a surplus of $CaCO_3$) which can be determined in either case and connects the decalcified and calcareous soils in one scale. On soils in a neutral condition practically without $CaCO_3$, lrb = 0. Decalcified soils give negative values; those containing $CaCO_3$ give positive values. On a soil with 1% $CaCO_3$ lrb = ca. 0·2; the lrb = ca. 1·0 on a soil with 10% $CaCO_3$.

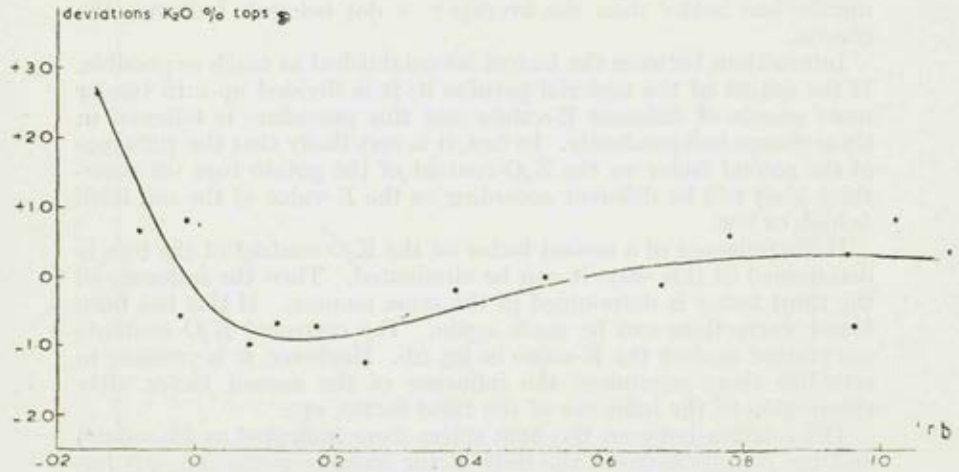


Fig. 3*a*

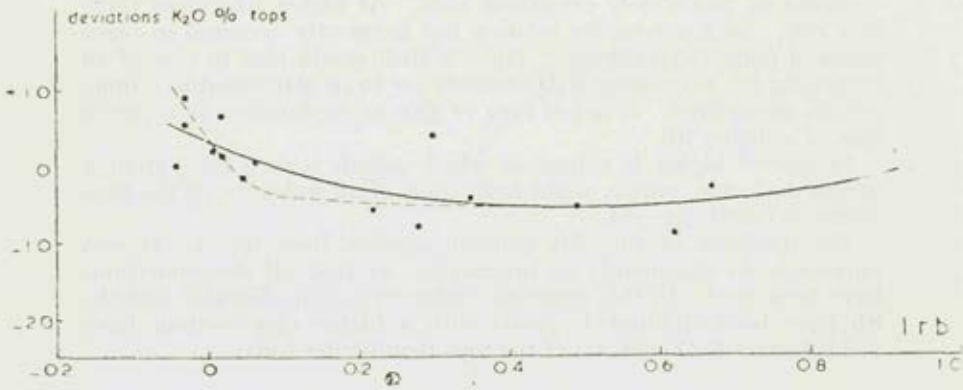


Fig. 3*b*

Fig. 3—Relation between lime status (lrb) and K_2O content of tops (measured as deviations from the average curve, fig. 2a) of Bevelander potatoes not dressed with potash after elimination of influence of content of particles $< 16\mu$ (average content $= 50\%$): (a) at K-value < 20, (b) ditto > 20

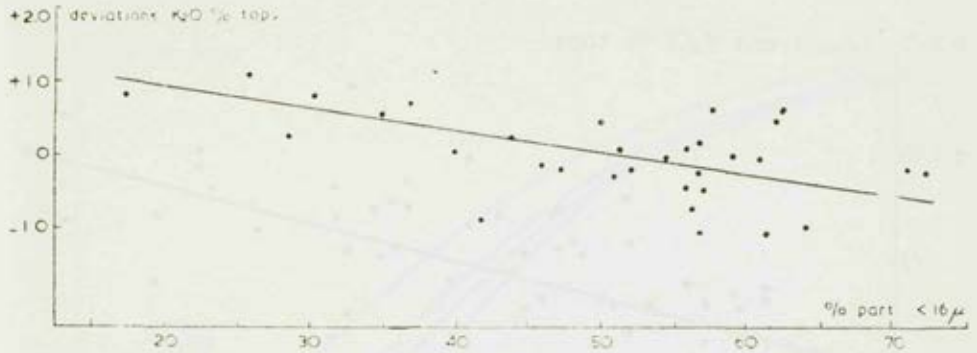


Fig. 4—Relation between content of particles < 16μ and K_2O content of potato tops.

The Eersteling variety, cultivated in the other trial-series, led in many respects to corresponding results. An important difference is, however, that this variety proves to be insensitive to a lime-potash antagonism, which is evident from fig. 5. The influence of the clay content was equal to that in the other experiment. In this case it appeared that tops with a higher nitrogen content also have a higher potash content (fig. 6). The explanation is probably that the crop was in different stages of development on the various fields and that a physiologically younger crop has both higher N and K_2O-content. By means of this relation the influence of the N-contents could be eliminated.

In interpreting the K-value, not only the corrected relation between the K-value and the K_2O content (as shown in fig. 2b), will be considered, but naturally also the influence of the clay content and, in the case of Bevelander, the influence of the lime status as well.

Fig. 4 shows that the K_2O content of the tops was higher by 0·3% when the clay content (at the same K-value) was lower by 10%. A difference of the same kind is also found on soils having the same

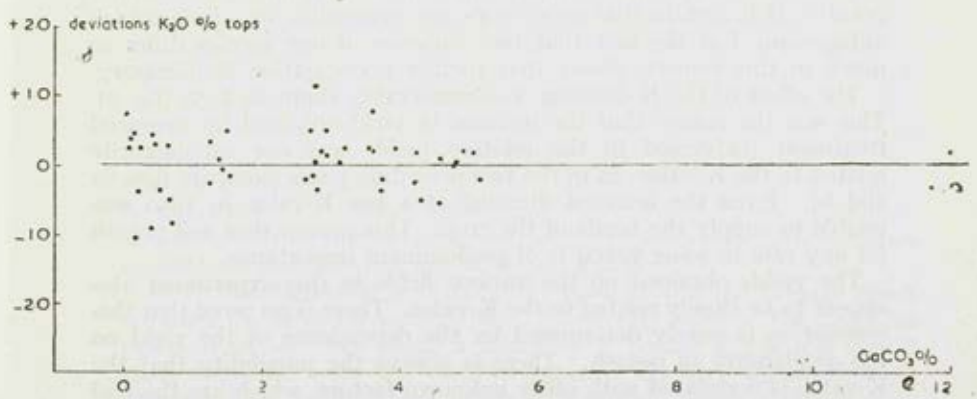


Fig. 5.—Relation between lime status ($CaCO_3$%) and K_2O content of tops of Eersteling potatoes not dressed with potash after elimination of influences of content of particles < 16μ and N-content of tops (average content of part. = 25%, average N content = 3·5%). Compare fig. 3a.

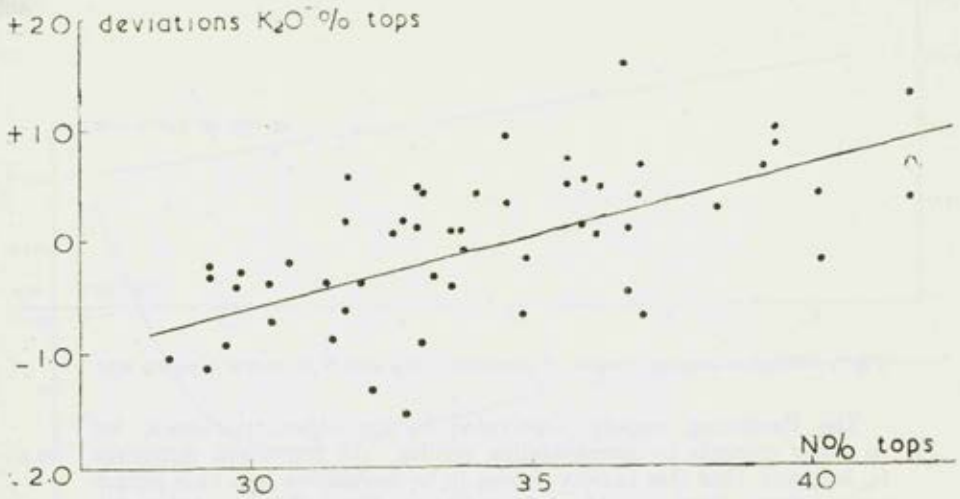


Fig. 6—Relation between N% and K_2O% of Eersteling tops.

clay content, but differing in the K-value by one unit (fig. 2b). So this means that a K-value on a lighter soil which is lower by one unit compared with a soil containing 10% more clay, must be evaluated equally.

It is more difficult to make allowance for the influence of the lime status. There is no great difference between calcareous soils. The greatest difference between lrb 0·1 and 1·0 expressed in the scale of the K-value definitely does not exceed 3 points. It is much more important to take the lime status into account with decalcified soils, where neglecting this factor would lead to an erroneous evaluation of the K-value.

A problem that has not yet been solved is whether the influence of the lime status on other crops is the same as that on the Bevelander potato. It is certain that most crops are susceptible to a lime-potash antagonism, but the fact that two varieties of one species differ so much in this respect, shows that further investigation is necessary.

The effect of the K-dressing was remarkably slight in 1950 (fig. 7). This was the reason that the increase in yield obtained by manurial treatment (expressed in the relative yield) was not satisfactorily related to the K-value, as in the two preceding years (compare figs. 8a and b). Even the heaviest dressing at a low K-value in 1950 was unable to supply the needs of the crop. This proves that soil potash (at any rate in some years) is of predominant importance.

The yields obtained on the various fields in this experiment also appear to be closely related to the K-value. There is no proof that this correlation is purely determined by the dependence of the yield on the availability of potash. There is always the possibility that the K-value is correlated with other unknown factors, which are the real causes of the differences in yield. However, in this instance in view of the reaction of the K_2O content of the tops, it is very likely that the differences in availability of potash are chiefly responsible for the differences in yield.

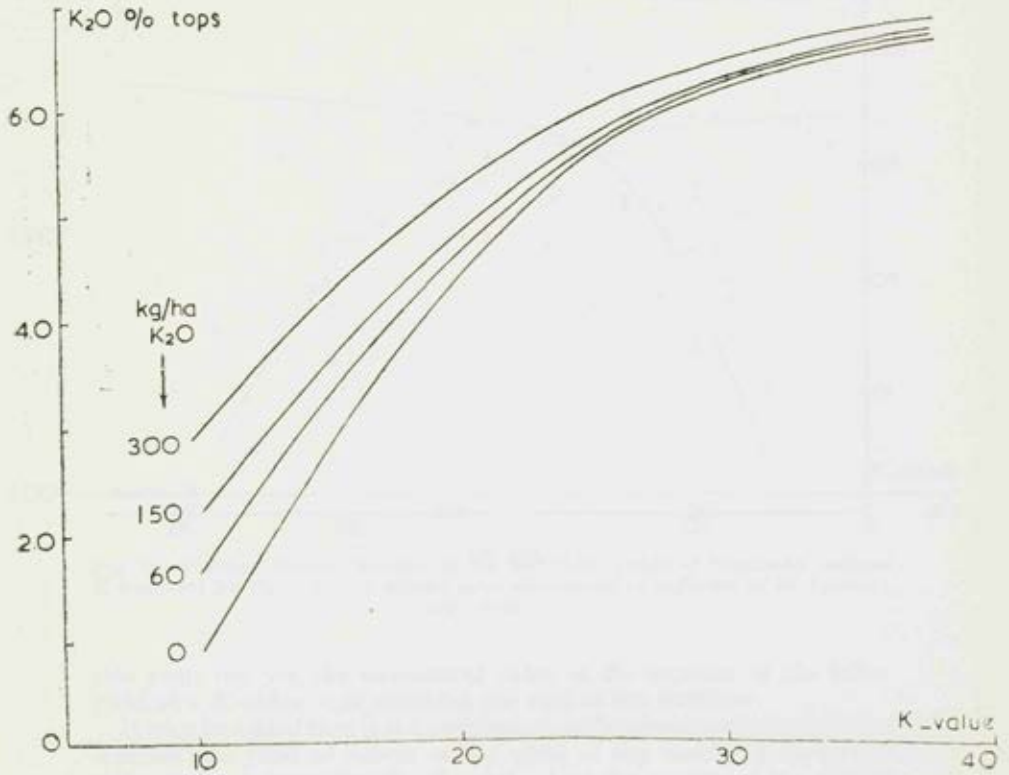


Fig. 7.—Relation between K-value of soil and K_2O% of Bevelander tops at differen K_2O dressings, after elimination of influences of lrb and content of particles < 16μ (average lrb = 0 and average content of part. = 50%).

Also this relation has been subjected to a further analysis. Fig. 10 shows the influence of the lime status. It is clearly evident (fig. 10a), that the Bevelander potato has produced the largest yield with an ample K-dressing on moderately calcareous soils. In case of potash deficiency (fig. 10b.) the effect of the lime status is less evident. We have seen that at the lrb-value showing the highest yield with an ample potash addition, the availability of potash is smallest (fig. 3a). It is clear, therefore, that an optimum lime status will only produce high yields, if ample availability of potash is ensured. It may, therefore, be concluded that in this fertile marine clay region appreciable increases in yield are possible (judging by Dutch standards!).

After this digression we finally like to show you the average result obtained in one of the polders (fig. 11) and this may be the basis for practical advice. An ample availability of potash in the soil was of great importance for the yield of tubers. The dry matter content (derived from under-water weights), however, shows a decrease at an increasing K-value. The result is that the extra amount of dry matter is much smaller and certainly does not justify an excessive increasing of the K-value. The effect of manurial treatment was slight

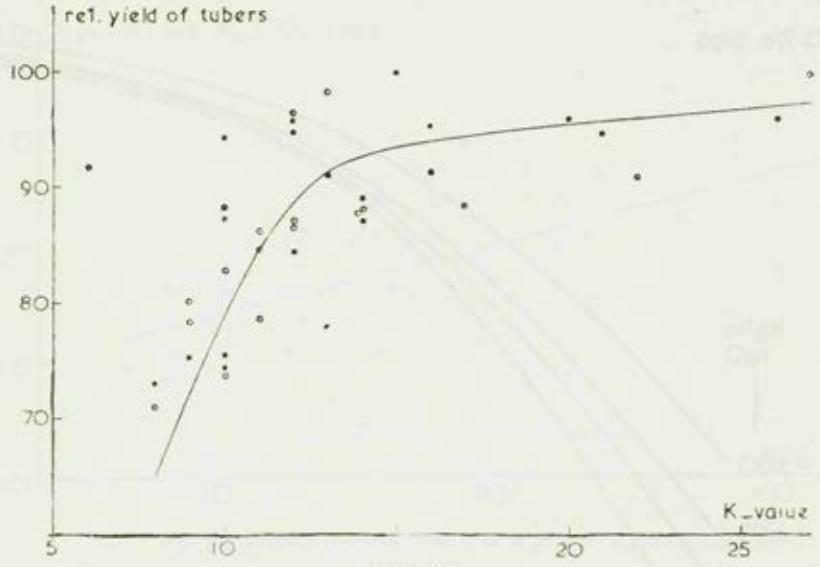


Fig. 8a

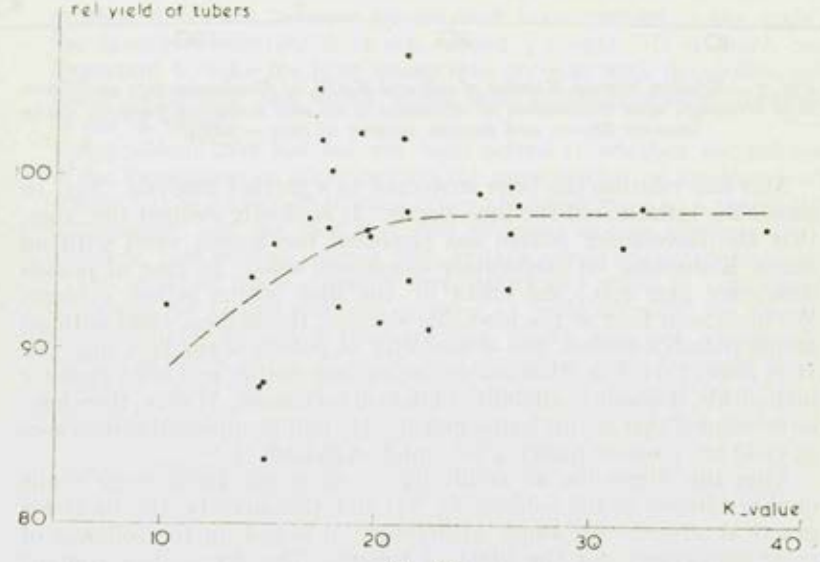


Fig. 8b

Fig. 8.—Relation between K-value of soil and relative yields of Bevelander tubers (a) in 1947 (dots) and 1949 (circlets), (b) in 1950.

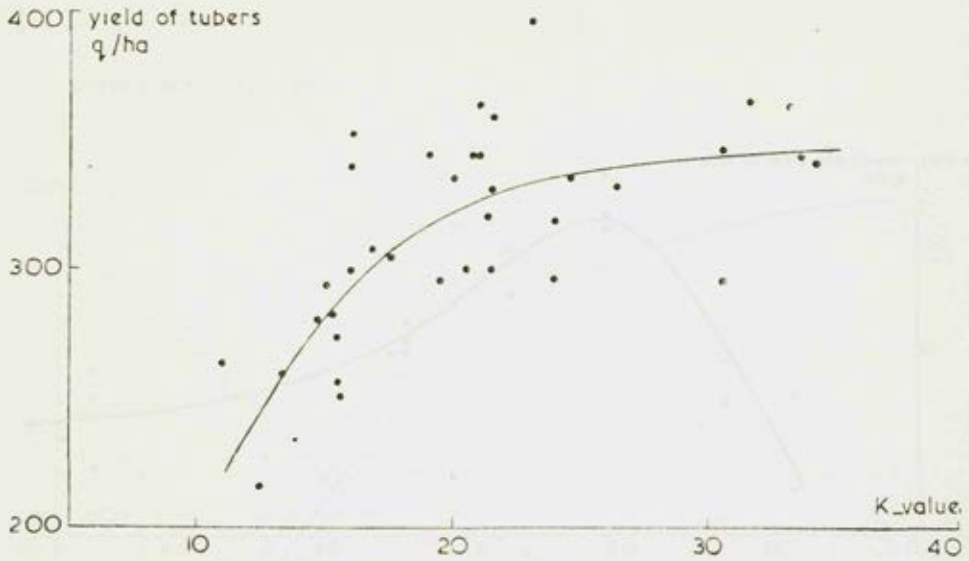


Fig. 9.—Relation between K-value of soil and tuber yields of Bevelander without K-treatment (in the Schermer polder) after elimination of influence of Irb (average Irb=0·08).

this year, but yet the economical value of the increase of the tuber yield at a K-value <20 exceeded the cost of the fertilizer.

It may be added that it is a problem of national economic significance whether the yield of tubers or the yield of dry matter is to be the criterion for determining the K-value. Also the quality of the tubers, which has not been discussed, must be considered. I just want to refer to this point to emphasize that although the evaluation of soil testing is essentially a scientific problem, economic and political considerations will ultimately be decisive for the evaluation of the figures.

It may not be superfluous to point out that this research, which describes the actual relation of facts but gives no causal explanation, is a great stimulus for the accomplishment of more fundamental investigations, which are thus closely connected to practical problems in farming. Also, the fact that these investigations tend to broaden our insight into the possibilities of manurial treatment, must be considered as important as the object proper, the evaluation of methods of soil testing.

This example may have shown that the possibilities of soil testing are numerous and that accurate calibration of the soil testing methods by means of field-trials is all the more justified according as practical farming has reached a higher level. I am convinced that the study and application of these possibilities in the various countries can lead to an appreciable increase in production and a more efficient use of fertilizers.

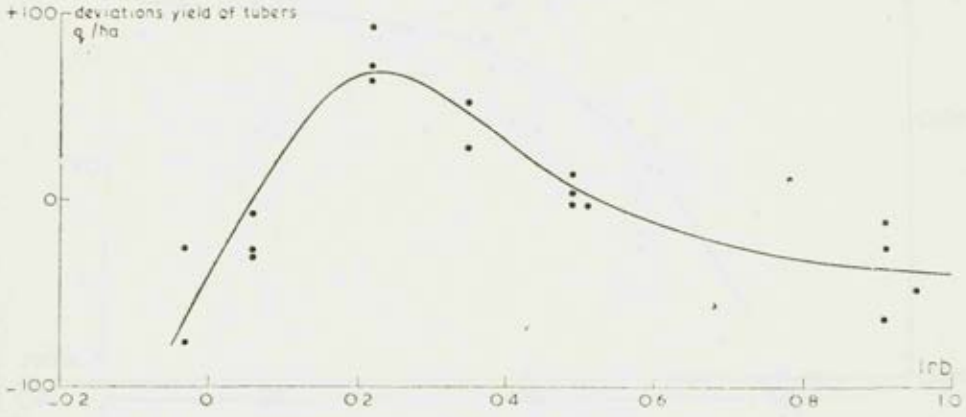


Fig. 10a



Fig. 10b

Fig. 10.—Influence of lime status (lrb) on tuber yield of Bevelander: (a) K-value > 20, *(b) ditto* < 20.

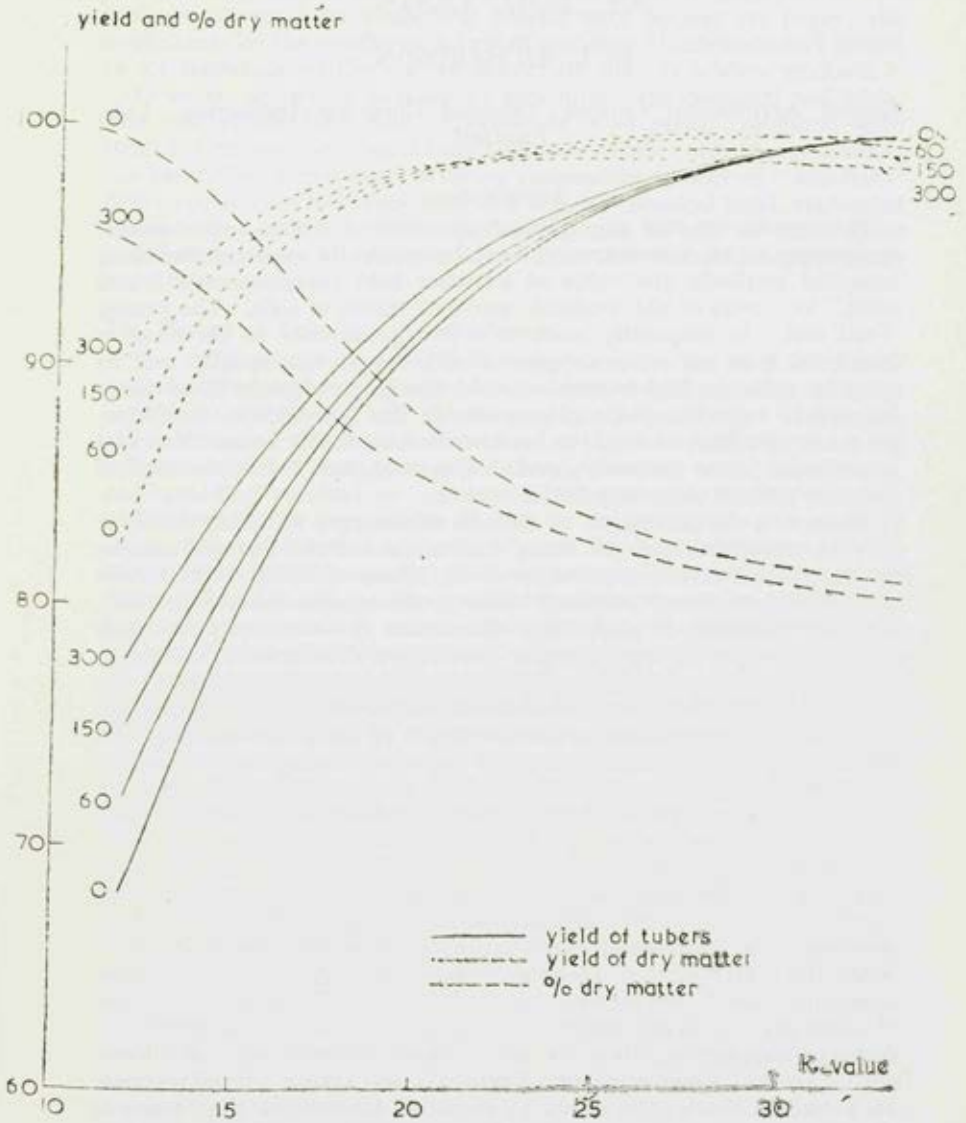


Fig. 11.—Final result, showing average relation between K-value of soil and tuber yield of Bevelander, dry matter, and dry matter content with different K treatments.

SESSION 7

THE USE OF FERTILIZER FIELD EXPERIMENTS AS "SOIL TESTS"

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Introduction

The purpose of this paper is not so much to discuss experimental techniques as to demonstrate, from the results of experiments using accepted methods, the value of fertilizer field experiments as "soil tests," i.e., tests of the available nutrient status of soils. The phrase "soil test" is frequently used as if it applied only to chemical or biological tests on small samples of soil, but it can equally well be used for suitable field experiments, in which chemical fertilizers may be said to take the place of reagents in the laboratory. In China, in the programme of work to be described later, the name "soil test experiment" was generally used in this way, and the application of the idea proved of great practical value.

There are disadvantages as well as advantages in using fertilizer field experiments as "soil tests." The chief disadvantages are the amount of labour and expense involved; the variability of the results both within an experiment and between one experiment and another; and the difficulty of expressing the results quantitatively in terms of the nutrient content of the soil. The chief, and indeed overwhelming, advantage of the method is its direct application to practice, in the form of reliable fertilizer recommendations. Despite the variability of individual experiments, the averages of sufficient numbers of well-designed field experiments give reliable information both about the relative nutrient status of the soils concerned and about their fertilizer needs, as well as about the crop increases that can be obtained by using fertilizers.

The broad assumption made in using field experiments as "soil tests" is that the response of a crop to a fertilizer supplying a certain nutrient is likely to vary inversely with the status of the soil in that nutrient. The relationship is not a simple, linear one, and interactions with other factors may complicate matters, but there is not time to go into this in the present paper. It is clear in a general way that if a soil gives a larger response to one nutrient than to another, in a factorial experiment, then the soil is more deficient, or has a lower status, in the former nutrient. Further, a soil giving a large response to a certain nutrient is likely to be more deficient in that nutrient than is another soil giving a smaller response, unless other environmental factors have limited the latter response. Where such a limitation occurs, it is likely to operate also in the general use of fertilizers, so that although the interpretation of the experimental result may be uncertain its practical value remains.

The plant-food status of a soil, estimated from its fertilizer responses, may be expressed only in qualitative or relative terms. This is less important than the fact that the yield or response data are directly applicable to practice, in the form of fertilizer recommendations and

quantitative estimates of the average effects of fertilizers. However skilfully a laboratory or pot-culture soil test may be carried out, and however accurate its numerical results may appear on paper, the application of the results in terms of fertilizer treatments and effects is an uncertain matter—more uncertain than is always realized.

There is, of course, a place in agriculture for chemical soil tests. The cost of fertilizer field experiments is so great, compared with that of chemical tests, that a fully adequate number of field experiments can rarely be carried out. Where a reasonable number of "soil-test" field experiments has been done in a region, chemical tests, calibrated against the results of these experiments, can be used to make more detailed fertilizer advice possible. But the chemical tests cannot stand alone.

The Design of "Soil-test" Experiments

The most suitable type of field experiment for use as a soil test is a factorial design, using soluble chemical fertilizers only, without organic manures, and laid out for a single season only. The object is to determine the fertilizer response of the soil itself, free from the influence of other manures applied during the year of the experiment, and avoiding residual or cumulative effects from earlier years of experiment. The programme should be continued for a number of years, but on different sites each year. Important crops of wide distribution should be preferred for such experiments, for the sake of comparison with other soils in other localities, and in order that the fertilizer responses will have wide application in practice.

In the first place, "soil-test" experiments will be carried out on the three major nutrients, and such experiments are often known as "NPK tests." Should it become evident that the local soils are rarely if ever deficient in one of the three nutrients, then two-factor experiments may be done; or if there is reason to suspect a deficiency of calcium, magnesium, or trace elements, these may be included as additional factors. In "NPK test" experiments, the writer prefers that all three nutrients—N, P_2O_5 and K_2O—should be present at the same level, or rate of application. Certainly nitrogen, which is generally the nutrient most important for increasing crop production, should not be applied at a lower level than the other two.

Much more could be said in a detailed discussion about the design of experiments, about the rates of application that should be used as standard, about the best size of plots, and other experimental details, but there is not time to go into these questions here. Plot size, in particular, must vary in different types of farming. The general object should be to standardize or unify the experimental designs and conditions as far as possible, in order to simplify the handling of the data when the experimental results are being worked up. The localities chosen for experiment should be representative of the chief soil groups, and of types of land which cover extensive tracts; as many experiments as possible should be laid out on ordinary farms rather than at experimental stations, where—especially in undeveloped countries—soil conditions may be very different from those common in the area.

The "soil-test" experiments are only one part of a comprehensive programme of manurial field experiments: continuous experiments, including those on the effects of bulky organic manures, and experi-

ments on such matters as the time and method of application of fertilizers, will also be needed, but these should as far as possible be kept distinct from the "soil-test" series. The latter series may usefully, however, include factorial experiments at more than one level, which give direct information about the best rates of application.

"Soil-Test" Experiments in China

In studying the nutrient status of soils in China, results from a wide range of fertilizer field experiments were used, as will be described later. The main body of the data, however, came from a "Soil Fertility Investigation" which was planned by the writer in 1938 for the National Agricultural Research Bureau of the Chinese Ministry of Agriculture. Details of this programme were given in "Soils and Agriculture of Szechwan," by H. L. RICHARDSON (Chungking, 1942), p. 132 *et seq.*

Very briefly, the programme was based on factorial NPK field experiments at 2 or 3 levels, the latter with confounding. The standard rate of application of N, P_2O_5 and K_2O was 8 *catties* per *mow*, equivalent to 60 kg./ha., or 54 lb./acre. (1 *catty*=0·5 kg.; 1 *mow*=0·0667 hectare). In 3-level experiments, the levels were 0, 4 and 8 *catties*/*mow*. Randomized block designs were generally used, with 27, 32 or 54 plots. Plots were usually about 1/20 *mow* (1/120 acre, or 1/300 hectare), a size which well suited Chinese agricultural conditions. The chief experimental crops were wheat, paddy rice, cotton, rapeseed, maize and millet; there were experiments also on barley, sugar-cane, Irish and sweet potatoes, and other crops.

Experiments in this series were carried out throughout central and western China during the war years. Before the war, considerable numbers of fertilizer field experiments had already been done in east China by Messrs. Imperial Chemical Industries (China) Ltd. as well as by the National Agricultural Research Bureau and co-operating institutions. Although few of these experiments were of the "NPK test" type, many of them fulfilled the essential conditions of "soil tests": i.e. they were single-year experiments, or the first year of continuous experiments; they employed soluble chemical fertilizers and organic manures were not used; if only one factor, such as nitrogen, was being tested, the others were present as a basal dressing. By combining all suitable experiments, practically the whole of agricultural China was included in the study.

In order to bring together the results from so wide a range of experiments the method of CROWTHER and YATES was employed (*Empire Journal of Experimental Agriculture*, 1941, **9**, 77-97). Constants and conversion factors were calculated for individual crops from the results of Chinese fertilizer field experiments at more than two levels, and these were used to convert the fertilizer responses, obtained in experiments at various rates of application, to responses at the standard rate already mentioned, namely, 8 *catties* per *mow* or 60 kg./ha. of nutrient.

It may be mentioned that this work was done as part of a still larger undertaking, namely, the conversion of the results of all Chinese fertilizer field experiments, whatever their type, to responses at standard rates. For the present study, the results of suitable experiments were grouped into a "soil tes " series. The work of

conversion was done by the Scientific Computing Service, and the further calculations were carried out by Messrs. Imperial Chemical Industries Ltd., with the help of Hollerith equipment. The results of the "soil-test" experiments with all crops, and the full results for paddy rice, have been written up in detail in typescript; only a few extracts are possible here. The total number of field experiments of all types was over 600, and the number of "soil-test" experiments on the six principal crops was over 300.

The Nutrient Status of Chinese Soils in General

The general means of all Chinese "soil-test" experiments, converted to the standard rates of application (60 kg./ha. of N. P_2O_5 or K_2O) were as follows (in kg./ha. of rough or paddy rice, other grain, or seed cotton):—

Crop	Response to			Mean Yield	No. of expts.
	Nitrogen	Phosphate	Potash		
Paddy rice ...	+620	+290	+ 40	2,805	81
Wheat	+370	+150	+ 15	1,575	108
Maize	+880	+130	+135	2,620	18
Millet	+555	0	- 10	2,265	12
Cotton	+195	+ 45	+ 15	1,410	56
Rapeseed	+250	+225	+ 45	600	42

(The mean yields and numbers of experiments refer to the nitrogen series; mean yields were very similar but numbers of experiments were rather fewer in the phosphate and potash series. Yield and response data are rounded off to the nearest 5 kg.)

Certain general trends are at once evident from these data. With all crops, the average response to nitrogen was larger than that to phosphate, and with all crops but maize (where the difference was negligible) the average response to phosphate was larger than that to potash. In consequence we can infer that Chinese soils in general tend to have a low nitrogen status, a moderate phosphate status, and a high potash status. This is a generalization that is very widely true, since it holds good for almost all crops and (as will be seen) over most of the great soil groups of China.

This result for the nutrient status of Chinese soils is clearly related to the traditional and long-continued use of local manures in China. These are mostly organic manures or fertilizers, such as animal dung, compost, night-soil, and oil-seed cakes, supplemented by plant ashes and (in some localities) pond mud. Practically all of the materials are much richer in potash than in phosphate, in consequence of which the available potash status of the soils has been maintained at a higher level than the phosphate status. As for nitrogen, this nutrient is readily lost both by volatilization during storage and by leaching from the soil. In consequence, the various natural sources of nitrogen "recuperation," such as free-living nitrogen-fixing organisms (including blue-green algae in paddy fields), leguminous green manures, and ammonia and nitrate from the atmosphere, have not sufficed to do more than maintain a relatively low status of available nitrogen in the soil.

The differences between different crops in their responses to fertilizers would repay further study, but these are complicated by regional differences in the distribution of crops: most of the maize, millet and cotton experiments were in central and north China; most of the rice and rapeseed in central and south China; wheat was the most widely distributed crop. The distribution of rapeseed was similar to that of rice, and from this table as well as the results at individual localities it was evident that rapeseed was more sensitive than rice (or other cereals) to phosphate deficiency. In this it resembles the other cruciferous crops such as turnips and swedes in western Europe.

Calcium Soils and Leached Soils

J. THORP ("Geography of the Soils of China," Nanking, 1936) has described the genetic soil groups in China, and has pointed out that these groups fall into the two main classes of pedocals and pedalfers, which he calls more simply, calcium and leached soils (THORP, in J. L. BUCK'S "Land Utilization in China," Shanghai, 1937). Calcium soils occur chiefly in the "Wheat Region" of north China, which has a relatively dry climate; leached soils occur chiefly in the "Rice Region" of central and south China, where the rainfall is higher.

The data from the Chinese "soil-test" experiments were classified according to the kind of soil on which they were done, the average results for the two main classes being shown below, in kg./ha.:—

Crop	Response to			Mean Yield	No. of expts.
	Nitrogen	Phosphate	Potash		
Calcium Soils					
Paddy rice ...	+1,095	+165	−140	3,180	8
Wheat	+ 255	+105	− 15	1,530	46
Maize	+ 970	+ 90	+ 60	3,240	8
Millet	+ 555	0	− 10	2,265	12
Cotton	+ 200	+ 40	− 15	1,580	45
Rapeseed	+ 135	+160	—	140	1
Leached Soils					
Paddy rice ...	+ 570	+300	+ 60	2,760	73
Wheat	+ 450	+165	+ 20	1,605	62
Maize	+ 800	+160	+180	2,120	10
Millet	—	—	—	—	0
Cotton	+ 170	+ 60	+ 75	690	11
Rapeseed ...	+ 255	+230	+ 45	610	41

(Mean yields and numbers of experiments are for the nitrogen series.)

There were certain consistent differences between the two soil classes. With every crop where a comparison was possible, leached soils gave a larger phosphate response and a larger potash response than did calcium soils. This clearly demonstrates the lower phosphate and potash status of the leached soils—a result that might be expected on theoretical grounds, although with regard to potash it has been found elsewhere that soils with a high calcium content sometimes tend to show potash deficiency. In China, on the other hand, the calcium soils are so well supplied with available potash that the use of potassic fertilizers tends, if anything, to depress crop yields.

The mean yields and the nitrogen responses of the two soil classes did not show such clear-cut effects as the phosphate and potash responses. With summer crops (rice, maize, millet and cotton), the mean yields and the nitrogen responses were both higher on calcium soils than on leached soils. This could be due in part to lower fertility of the leached soils, as a result of leaching having removed mineral plant nutrients, which limited both general crop growth and responses to nitrogen. With the winter crops (wheat and rapeseed), however, both yields and nitrogen responses were higher on leached than on calcium soils. Limitation of growth by lack of moisture was probably the cause of this difference: China has a monsoonal climate, but the winters are not so extremely dry in the south and centre as in the north, where most calcium soils occur.

Genetic Soil Groups

The distribution of the Chinese great soil groups, as described by THORP (*loc. cit.*), was revised in the "Generalized Soil Map of China," published by the Soils Division of the National Geological Survey of China in 1941. The location of "soil-test" fertilizer experiments on this map was used as a basis for classifying the experimental results under the chief soil groups. These groups were in general those described by THORP, with some slight "lumping" or "splitting" of certain groups where necessary for the present investigation. The long titles used on the 1941 Soil Map were abbreviated to those shown below.

With most crops, the numbers of experiments in different soil groups were too small to give a representative sample, and erratic results were obtained. Full particulars are given in the detailed study of the Chinese data, but in the present paper the results for only the two crops—rice and wheat—having the largest numbers of "soil-test" experiments are presented. These follow, the mean yields and responses being expressed as kg./ha.:—

Soil Group	Response to			Mean Yield	No. of expts.
	Nitrogen	Phosphate	Potash		
	Paddy Rice				
Light Chestnut Earth	—	—	—	—	0
Saline Alluvium ...	—	—	—	—	0
Calcareous Alluvial:					
Hwang Ho	+1,000	+170	−195	3,170	3
Yangtze	+1,150	+160	−105	3,190	5
Shantung Brown Soil ...	—	—	—	—	0
Purple Soil	+ 700	+240	− 15	3,225	7
Brown Earth	+ 670	(+ 45)	(+375)	3,420	2
Yellow Earth	+ 480	+165	+100	2,890	4
Red Earth	+ 540	+630	+190	2,180	15
Podzolized Red Earth	+ 620	+270	+ 75	2,595	7
Paddy Alluvial:					
Hwai and Yangtze	+ 600	+150	− 10	2,750	12
Chengtu Plain ...	+ 675	+200	+ 80	3,570	8
South of Yangtze ...	+ 470	+310	− 20	2,670	18

Soil Group	Response to			Mean Yield	No. of expts.
	Nitrogen	Phosphate	Potash		
	Wheat				
Light Chestnut Earth	+ 45	+ 50	− 30	1,100	8
Saline Alluvium ...	+ 330	+ 15	− 60	1,750	4
Calcareous Alluvial :					
Hwang Ho	+ 260	+135	0	1,575	28
Yangtze	+ 430	+ 60	− 20	1,770	6
Shantung Brown Soil ...	(+1,080)	(+220)	(+120)	(2,505)	1
Purple Soil	+ 510	+105	− 30	1,540	8
Brown Earth	+ 430	+ 45	(+ 90)	1,725	5
Yellow Earth	+ 375	+225	+ 75	1,590	14
Red Earth	+ 220	+180	+ 15	1,420	7
Podzolized Red Earth	—	—	—	—	0
Paddy Alluvial :					
Hwai and Yangtze ...	+ 800	+180	0	1,030	7
Changtu Plain ...	+ 380	+255	0	1,640	10
South of Yangtze ...	+ 460	+ 50	+ 20	1,425	10

(The mean yields and numbers of experiments are those for nitrogen. Brackets around a value indicate that it refers to only a single experiment.)

Time is lacking for a close study of these data, which must be left to readers of the paper. The first four soil groups belong to the class of calcium soils ; the remainder are leached soils ; the nutrient status of these classes was discussed in the previous section.

Even with rice and wheat the numbers of experiments available for most of the soil groups were far too small to be representative, yet certain general effects are fairly clear. In most of the groups, and with both crops, the nitrogen status was lower than the phosphate status and this in turn was lower than the potash status, as judged by the sizes of the respective nutrient responses. Thus the relationship observed with Chinese soils in general holds good also for the individual soil groups. The chief departures from the rule occurred with Shantung Brown Soil and Brown Earth, in instances that were represented by only one experiment.

There were some discrepancies between the two crops, when responses were examined as a guide to the nutrient status. The better water supply of paddy rice than of winter wheat was partly responsible for this. The very low nitrogen response for wheat on Light Chestnut Earth was almost certainly due to lack of moisture.

In general, taking both crops into consideration, the nitrogen response was rather variable as between the different soil groups, but it was usually large, and greater than the response to any other nutrient. Some of the largest nitrogen responses were given by alluvial soils, which may be attributed partly to a low nitrogen status and partly to the presence of sufficient moisture and mineral nutrients to allow nitrogen to exert its full effect. In any event, it is noteworthy that the reputedly fertile alluvial soils of China still give large responses to nitrogenous fertilizers.

Phosphate responses tended to be larger with soil groups belonging to the leached class than with those in the calcium soil class, although there were exceptions. The most strongly leached soil groups of China

—Yellow and Red Earths, and Podzolized Red Earths—were among those showing the lowest phosphate status, for one or both crops. Alluvial soils derived from these groups or from uncultivated mountains (Paddy Alluvial Soil, South of the Yangtze, and the Chengtu Plain) also gave evidence of low phosphate status. Red Earth, with paddy rice as test crop, was outstanding in its high average phosphate response; put in another way, we can say that with paddy soils on Red Earth the phosphate status is as low as the nitrogen status.

Potash responses were negative with both crops for all calcium soil groups. Clearly the potash status of all the Chinese calcium soil groups is very high. Among the leached soil groups, Shantung Brown Soil and Brown Earth (a single experiment with each crop), Yellow Earth and Red Earth gave the largest potash responses, indicating the lowest potash status. With all of these except Brown Earth, however, the potash status was still higher than the phosphate status. Most alluvial soil groups had a high potash status, but Paddy Alluvial Soil of the Chengtu Plain showed a rather lower potash status in the rice experiments. Chinese alluvial soils in general receive contributions towards their fertility from the erosion of cultivated soils higher up the river valleys, but the Chengtu Plain probably receives less than other alluvial soils from this source.

Although the results for only two crops are shown here, " soil-test " fertilizer experiments on the other crops mentioned earlier have given broadly similar results. The low phosphate, and sometimes rather low potash, status of Yellow and Red Earths was evidenced by the fertilizer responses with maize, rapeseed, potatoes and sugar-cane.

Fertilizer Recommendations for Chinese Soils

To go into this aspect of the results would require another paper, longer than the present one. The magnitudes of the average responses reported here indicate what chemical fertilizers can do to raise crop yields in China. Recommendations for the most efficient use of fertilizers in that country must take account of the plant nutrient status of the different soil groups, as shown in the present study. For example, on most Chinese soils nitrogenous fertilizers are the main requirement, supplemented by the occasional use of phosphate where needed; but on Red Earth, mixed fertilizers having an equal N :P_2O_5 ratio would be generally useful.

It is probable that Chinese farmers (like farmers in Japan) will continue to use compost and other bulky, local manures in addition to chemical fertilizers. The bulky organic manures and ashes will help to maintain the fertility of the soil, and to supply potash where potassic chemical fertilizers are not used. In the main series of Chinese experiments, the effect of such bulky organic manures on the responses to chemical fertilizers was studied. It was found that the nitrogen response was little affected, but the response to phosphate and potash was somewhat decreased by the presence of local manure. This agrees with experimental results in Britain (CROWTHER and YATES, *loc. cit.*).

Acknowledgments

The writer gladly pays a tribute to the work of his colleagues in China, who carried out the field experiments described here in spite

of many difficulties. He acknowledges also the kindness of the Chinese National Agricultural Research Bureau, and of Messrs. I. C. I. (China) Ltd., in making the results available for study. Thanks are likewise due to Messrs. Imperial Chemical Industries Ltd., for their assistance in the numerical work on the accumulated data, and for permission to publish this paper.

Summary

Suitable fertilizer field experiments can be used as "soil-tests," to indicate the relative status of soils in available nutrients. Such tests have great practical value.

The best design for "soil-test" experiments is a factorial one for N, P and K, at two or three levels, laid out in randomized blocks with confounding if necessary. Single-year experiments are used, a considerable number being laid out in representative localities over a period of years.

The results of such an investigation in China are summarized. The experiments gave clear-cut information about the nutrient status of Chinese soils, which generally have a low nitrogen status, a moderate phosphate status, and a high potash status.

The nutrient status of major soil classes and genetic soil groups in China is also discussed. Leached soils, particularly yellow and red earths, had a lower phosphate and potash status than calcium soils.

SESSION 8

PLANT DIAGNOSTIC METHODS

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Introduction

The final object in applying diagnostic methods to problems of crop nutrition is to enable the farmer to exercise control over the yields and quality of his crops. Maximum yields will usually be the chief aim of the farmer, though for many crops quality is of prime importance, for example in some specialized crops such as fruits and vegetables, whilst, in grass and fodder crops, feeding value, including the content (i.e. concentration) of mineral elements, may be a major consideration.

The methods adopted to provide guidance on these points fall into three groups :—

(*a*) Field trials with fertilizers and manures.

(*b*) Soil analysis, using chemical and biological methods, to assess the nutrient status of soils.

(*c*) Plant diagnostic methods, to determine the nutrient status of the crop plants.

Most investigators at the present time will use methods in all three groups, according to the nature of individual problems, and it is likely that such a practice will prove to be most effective in dealing with a wide range of problems. The present session is to be devoted to the discussion of methods under (*c*)—plant diagnostic methods—and, as one who has used these methods for the past thirty years, I am glad to be afforded this opportunity of opening the discussion. It is also opportune that plant methods should be considered at this meeting, since it is only during the past twenty or thirty years that they have gained in popularity and become widely used for advisory purposes.

Points relating to the mineral nutrition of crops that require consideration in discussing diagnostic methods

In discussing diagnostic methods it is desirable to keep before us some of the more important points of the problems that we seek to solve by the methods used, for, by doing so, we may be able, in particular, to discern some of the weaknesses of the various methods.

The following points are of fundamental importance in this connection :—

(1) Twelve mineral elements have been proved to be essential for the nutrition of higher plants and all have been shown to be of importance in crop production. The elements are nitrogen, phosphorus, calcium, magnesium, potassium, sulphur, iron, manganese, copper, zinc, boron and molybdenum. This list may not be a final one.

(2) A number of other elements, such as sodium, chlorine and silicon, may produce beneficial effects on the yields and quality of certain crops, though they are not essential

for the completion of the growth cycle. They are often designated as "beneficial" elements.

(3) Elements other than those above may occur in plants, even in large amounts, and may either not affect yields or quality, or they may be harmful.

(4) Mineral elements concerned in plant nutrition interact with one another both in the soil, affecting absorption, and in the plant, affecting translocation and metabolic processes. The interactions may be grouped as antagonisms and synergisms. Essential, beneficial and "other" elements may all be concerned in interactions.

(5) The ultimate nutrition of the crop, including yields and quality, depends both on the levels of the individual nutrients and their relative amounts in the plant tissues.

(6) Nitrogen, phosphorus, potassium and calcium are usually the most important nutrient elements concerned in problems of crop nutrition, though others are often important and for some crops and on particular soils must always be given special attention. Trace element problems are now recognized as being of widespread occurrence and of fundamental importance in the production of many crops.

Diagnostic methods must take account of these points and should be capable of providing information regarding all the elements that may influence yields and quality. They should also be based on principles in accord with the basic facts of soil science and the inherent characters of crop plants, and of the established principles of plant physiology.

It is common experience that the majority of nutritional problems are concerned with deficiencies of nutrients, occurring either as simple or multiple deficiencies; others relate to injurious excesses. The main point of practical interest is usually that of suboptimal yields, but where unsatisfactory nutritional conditions are severe, pathological conditions may develop as the result of improper functioning of the physiological processes—the so-called functional or physiological diseases or mineral disorders.

The Main Diagnostic Methods Using Plants

The main methods of diagnosis, based on the use of plants, are as follows:—

(1) The visual method.

(2) The application of nutrients to leaf surfaces by sprays or by painting treatment.

(3) The injection of nutrients into various plant organs, such as leaves, stems and trunks, by means of solutions or solid salts.

(4) Foliar diagnosis, comparing the chemical status of comparable leaves of high- and low-yielding plants.

(5) Leaf analysis method of LUNDEGARDH.

(6) Methods using plants as nutrient extractants from soils:

(*a*) MITSCHERLICH.

(*b*) NEUBAUER.

It is not proposed in the following discussion of these methods to refer to details of procedure, as these can be obtained by reference to the publications cited, but rather to discuss basic points underlying their use and to indicate their special points of value and their limitations.

1. *The visual method* (1, 2, 3)

This method was described in detail in my address to the 4th International Congress of Soil Science, Amsterdam (1950), and has also been discussed at length in my book on the subject. It will thus only be necessary for me to refer briefly to a few of the main features of the method.

The basis of the method is that plants suffering from deficiencies and excesses of mineral nutrients usually develop well-defined and characteristic signs of these disorders in various organs, particularly in the leaves, but also, in some instances, in other organs. The usefulness of the method can be extended by the use of special indicator plants and indicator plots which combine the use of indicator plants with fertilizer treatments.

The method can only be used when signs of disorders are present n the plants, and care and experience are needed in the recognition of symptoms. The method can be applied to detect both deficiency and excess effects, and can be used for all the essential elements. It is essentially qualitative, but where it can be applied it is extremely rapid and needs no special equipment. It is particularly useful in rapid survey work and as a preliminary to applying more tedious and exacting methods.

2. *Foliage spraying and painting methods* (2)

Like the visual method, these are essentially qualitative methods that are particularly useful in making preliminary diagnoses. Their efficiency depends on the fact that mineral nutrients are readily absorbed into actively growing leaves when solutions of them of appropriate strengths are applied to their surfaces. Action is rapid and often spectacular. The methods are often of particular value when used in confirmatory roles to visual diagnosis and for tests of trace elements. Unlike the visual method, their use is restricted to deficiencies.

The only precautions necessary in using them are to ensure that the strengths of the solutions are such as not to cause damage to the leaves whilst adding enough of the nutrients to be effective, and that the treatments are applied to relatively young leaves capable of responding to treatment.

3. *Leaf, stem and trunk injections* (2, 4, 5)

In these treatments nutrients, either in solution or as solid salts, are injected into the vascular tissues, where they are absorbed and translocated in the usual way. The methods are similar in many respects

to foliage spraying, for which they can be regarded as alternatives when their use is more convenient.

They are again essentially qualitative and of use only for indicating conditions of deficiency. Precautions regarding dosage and timing of operations are again needed to avoid damage and to ensure effective action.

4. *Foliar diagnosis* (6, 7, 8)

The concept of foliar diagnosis was introduced by LAGATU and MAUME after investigations extending from 1924, and since that time the method has been applied to a variety of problems involving comparative nutrient status.

The method has been the subject of much study by W. THOMAS and his colleagues in U.S.A., who have also applied it to a variety of problems, and by CRAIG and HALAIS in Mauritius as a basis for determining the manurial needs for N P and K of the sugarcane crop.

The method is essentially one of comparative nutrient status of crops, a fact that is emphasized time and again by THOMAS and MACK ; " But it needs to be emphasized again and again that the method has significance only in a comparative sense, and is, as are the data for entire plants, usable only with a key of interpretation." " No physiological significance is to be attributed to the foliar diagnosis of any one fertilizer treatment (plot) considered alone." (7, ps. 3 and 4). These workers also hold that all soil and plant tests are valid only when used in a comparative way. The method is based on the comparison of chemical data obtained from comparable leaves of plants (i.e. of similar physiological stage of development), one set of which is taken from high-yielding plants and the other from the plants under test. The leaves are taken from a definite point on the plants, e.g. the third leaf from the base of the terminal shoots of the vine.

Leaf samples are taken at the chosen points on three or more occasions during the growing season and determinations made of the mineral nutrients, usually three—say N P K —to determine their level at a given sampling time and the course of the levels of each over the period covered by the sampling dates. For each sample the sum of the three nutrients, on a millegram equivalent basis in dry matter, is calculated and also the percentages of the three individual nutrients forming the total. The sum is designated the " quantity " or " intensity " of the nutrition (e.g. N + P + K—in the leaf), and the percentages of each in the total, the " quality " of nutrition (e.g. ratios N : P : K).

The " quantity " data for each element are plotted on a graph against sampling dates, to show seasonal trends, and the " quality " data on a triangular diagram by a system of trilinear co-ordinates. Conclusions are drawn from comparison of the graphs for the two sets of plants.

It should be noted that in this method, leaves at a similar physiological stage of development are used to obtain comparative data ; seasonal cycles of the nutrients are recorded by periodic sampling ; data are computed on the basis of content of the nutrients in the dry matter of the leaf and account is taken of both the amount of each nutrient element in dry matter and the ratios between nutrients.

The method is strictly comparative and the nutritional diagnosis

is based on a comparison of data from test plants with other high-yielding plants grown simultaneously on adjacent plots. This latter condition obviates any difficulties that may be introduced by differences in climatic conditions that may arise when comparisons are made between plants grown at widely separated centres or in different seasons, but it limits the application of the method.

A major weakness of the method would seem to be that it serves rather to explain events that have happened than to provide information that can be used on the growing crop to effect improvement.

5. *Leaf analysis method of* LUNDEGARDH (9, 10*)

The principles on which this method is based have been established as a result of prolonged physiological investigations on the absorption of ions by roots, their interactions and movements, both in the soil and in the plant, their accumulation in plant tissues and the relations between ion concentrations in plant organs and growth. A basic conclusion from this work is that " For the rate of growth and for the final size and number of vegetative organs, the internal nutrient concentration is determinative : in particular, there is an obvious relationship between the internal nutrient concentration in the leaves and the growth of stems and leaves." The reason for this relationship is to be found in the functions of leaves, for they are the seat of carbohydrate formation and " carbohydrates control, both quantitatively and qualitatively, the yield of higher plants."

From the above-quoted conclusion it follows that only the nutrients absorbed by plants are significant for growth and hence their concentration in the soil has not a direct effect on growth.

LUNDEGARDH recognizes that the final concentration of nutrient elements in the leaf is affected by the antagonistic action of kations in absorption processes (true ion antagonism), which proceed in accordance with the Donnan equilibrium principle, and by various reactions of the ions within the plants, giving rise to apparent antagonistic effects which he terms " false antagonism " and " metabolic antagonism."

The leaf analysis method proposed relates to the four elements, nitrogen, phosphorus, potassium and calcium, for which " Index values " have been determined for cereal crops, grasses and potatoes. These values represent the concentrations of the elements, expressed as mgm.-atom/100 gm. dry matter in the leaf at a definite stage of growth—around flowering time for the above crops. The values in the first instance were determined in pot experiments in relation to the yields of stems and leaves (i.e., vegetative growth), at the time of sampling, and have later been correlated with crop yields in the field. The effects of factors, such as seasonal effects, drought, etc., have been examined and can be allowed for.

The curves relating nutrient concentration and yield usually approximate to the MITSCHERLICH type, though it is recognized that the form is not constant. Four rules are given with regard to index values :—

*A general discussion of chemical methods using plants, including the method of LUNDEGARDH.

(1) Index values are not absolute and may be altered by extreme conditions, such as a pronounced deficiency of a single factor or by extreme drought.

(2) The index values for the four elements are affected by their inter-relationships. If the index value of one of them is near a limiting concentration, raising the others by manuring will not raise yields.

(3) They are affected to some extent by rainfall and drought.

(4) Fluctuations in index values may introduce errors unless samples are taken at a definite stage of development of the crop, e.g., 8-10 days around the flowering period for cereals.

The method has been widely tested in Sweden and in comparative tests in that country with soil analysis, for potash and phosphate (EGNÉR method), it is claimed to have provided more accurate information on fertilizer effects. LUNDEGARDH holds that soil type would have little effect on yield increase produced by fertilizer applications on different soils where index values for the nutrients are similar.

Following considerable experience in field trials, the method should be capable of yielding valuable quantitative assessments of the effects of N P K fertilizers on the yield of particular crops. Its use for nutrients other than N P K and Ca remains to be tested, and in this connection the results of STEENBJERG (11), for copper are of interest, though not obtained by methods strictly comparable with the LUNDEGARDH technique. In particular, STEENBJERG has shown that the curves relating nutrient content and yields may, under some conditions, be S-shaped instead of the more usual MITSCHERLICH logarithmic curve.

6. *Methods using plants as nutrient extractants from soils*

These methods, which include as the best known examples those of MITSCHERLICH and NEUBAUER, have been discussed at length by STEWART (12), and it is only necessary here to refer very briefly to their main features and to the principles involved. They should be regarded as soil analysis methods rather than plant diagnostic methods, since they purport to measure the nutrient status of the soil, the MITSCHERLICH method by relating soil nutrient content to the growth (yield) of the crop, and the NEUBAUER method by determining "soluble nutrients" in the soil by their uptake by seedling plants. In contrast, the plant chemical methods, such as the method of foliar diagnosis and the LUNDEGARDH method, are concerned with relationships between the concentration of nutrients in plant organs (leaves) and growth (yield).

The methods are included to focus attention and promote discussion on these fundamental differences, the soil methods involving an approach to the problem from the angle of soil chemistry and the plant methods from principles of plant physiology.

(*a*) MITSCHERLICH *method* (13)

This method is based on relationships between "growth factors" and yield, the growth factors examined being nitrogen, phosphorus and potassium added to the soil as fertilizers. The relationship is

expressed as "The Law of Physiological Relationships" or "The Law of Diminishing Returns." It states "the increase in yield produced by a given increase of the growth factor is proportional to the decrement from the maximum yield which can be obtained by increasing that particular factor." The relationship is shown as a logarithmic (or parabolic) curve.

In carrying out tests on soils, oats are grown to maturity as the test plants in pots in the soils, mixed with definite proportions of sand—1 part soil : 2 parts sand by volume. Differential fertilizer treatments NPK, NP, NK and PK are given, the yields from the NPK treatment being regarded as the maximum possible, and the effects of the omission of N, P and K respectively in the other treatments on the yield determined. The manurial needs of crops are subsequently calculated from the data by means of the appropriate equation. The method has only been used for N, P and K.

(*b*) NEUBAUER *method* (14)

This method is restricted to the determination of phosphorus and potassium. The basis of the method is purely empirical and was developed by NEUBAUER and SCHNEIDER as the result of investigations on the absorption of nutrients from soils by plants in their early stages of growth. In particular, the quantities of phosphoric acid and potash absorbed by rye seedlings were found to be dependent on the soil used, and using a standard technique, constant values were obtained for any given soil.

A standard test technique was later devised in which seedlings were grown under standard conditions in glass dishes, the amounts of nutrients extracted by the seedlings in 17 days at a temperature of 20°C.being designated as the "root soluble" quantities in the soil. These were compared with so-called "limit values" for the two nutrients for various crops (i.e., corresponding with amounts extracted from soils giving high yields), and by suitable calculations the results were related to scales of fertilizer dressings necessary for maximum yields.

This method cannot claim to differ in principle from soil analysis methods in which acids are used as extractants of "available" nutrients.

Discussion

In considering the adequacy of diagnostic methods in crop nutrition problems, it is necessary to consider both the principles underlying the methods and their practicability in use from the viewpoints of the technical operations involved and the application of the results on the farm.

The underlying principles of the various plant methods concern basic physiological concepts of the processes of plant nutrition, particularly the processes of absorption and translocation of the nutrients from the soil to the leaf, their interactions and relative mobilities within the plant tissues and the fundamental relationships between the concentration of ions in the plant, particularly in actively functioning leaves, and the accumulation of organic products determining the yields and quality of the crops. The attempts to apply these concepts in full are most clearly evident in the discussions of LUNDEGARDH, but can also be easily recognized in the other methods described.

The test must also be applied as to the extent of the information which any method can supply and how far this information is of a qualitative or quantitative nature. So far as quantitative data are required, it would seem that any great degree of precision would only be needed for the elements nitrogen, phosphorus and potassium, since these are the only ones for which there are considerable ranges in the fertilizer dressings necessary in practice. Problems of calcium deficiency, which are dealt with by liming, may also need fairly precise data, but they do not arise on the farm so frequently as those of the above elements, though an accurate measure of calcium status may be needed, as is indicated by LUNDEGARDH, to give precise information on N, P and K requirements.

With regard to the other elements, particularly magnesium and the trace elements, there is relatively little latitude in the dressings that can be used to remedy deficiencies, and for many crops these are best applied as foliage sprays, when narrow limits to concentrations are set by the risk of damage on the one hand and effectiveness on the other.

It would seem advantageous also that there should be a choice of quick qualitative methods and more precise quantitative methods, the latter for use only where precision is needed.

On the purely technical side it is important that methods should not be too cumbersome and difficult in operation and not too expensive. This latter point may be largely overcome by the use of special apparatus, such as the spectrograph, operating on a large scale at centres specially equipped and staffed.

The plant methods, considered together, appear to meet these various requirements fairly well, perhaps the main point requiring further consideration being the accuracy of the quantitative data that can be obtained on a wide variety of crops and under different conditions by methods similar to those of LUNDEGARDH. In this work there may be scope for the introduction of tissue test techniques to replace the initially expensive and skilled spectrographic procedure, a point to which we have given some attention at Long Ashton (15).

Finally, in using plant diagnostic methods as a means of assessing fertilizer requirements, I should like to mention the value of certain soil characters in helping in the diagnostic procedures and in the interpretation of the data, namely pH and content of calcium carbonate soil depth and texture, organic matter and drainage. Consideration of these will often save much time in diagnosis and in indicating the probable major problems, and in enabling sound advice to be given on the effects of fertilizer dressings.

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PRELIMINARY DIAGNOSIS OF MINERAL DEFICIENCIES BY PLANT ANALYSIS AND PLANT INJECTION

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The mineral analysis of leaves of plants of good performance of a given species varies little, whereas there are commonly wide differences in composition between plants of good and poor composition, even when they are growing close together. There is no theoretically correct composition for a plant, as there is for a chemical compound, so we have to use the empirical method of comparing plants of poor performance with others of better performance that can usually be found growing nearby. If a series of three or four such plants are compared unimportant differences tend to be eliminated and the chances are increased of obtaining a clear relationship between improving performance and increase in a particular element.

The choice of leaf is an important matter. Vanstone has found wide differences in composition between different leaves on the same apple shoot and between leaves from similar positions on the shoot taken at different seasons; and there are large differences between leaves from extension and fruiting spurs. The leaf that has just attained its full size has the triple advantage that it is at an easily identifiable physiological stage; it is just at the end of a period of active growth and so should reflect the mineral status of the plant at the time of sampling and it has not long been exposed to contamination by soil dust, spray, etc. There is, as yet, no general agreement as to the best method for cleaning leaves. Brushing or wiping with a cloth may not be sufficiently drastic, but washing with dilute acid may well remove mineral of use to the plant. Attention is being paid to the fractional extraction of minerals by organic solvents in an attempt to separate the content of each element, not only into useful and useless portions, but also according to its state of combination, as a step towards determination of function.

Plant injection is based on the fact that plants, when cut, far from bleeding like animals, usually absorb aqueous solution bathing the cut. Solution so absorbed is distributed in the plant to form well defined and predictable patterns. Advantage may be taken of this fact to arrange for contiguous areas of the same leaf to be treated and untreated respectively, so that even small changes in colour or growth resulting from nutrient injection may be apparent, changes that might be unnoticed if the treatment were spread over a whole plot. Thus, if a cereal leaf is split along its median line and the two tips dipped in water and solution respectively, the liquids are drawn back about half the length of the leaf. If an incision, made between two main veins of an apple leaf near the midrib, is kept moist with solution with a suitable apparatus, the solution travels up to, but not beyond, the next main veins and the treated intervenal area is separated from the two untreated areas on either side by a vein only; and sharp comparisons can be made, almost as in an optical instrument.

In one experiment a green tinge was seen in an almost completely chlorotic leaf in only two days after injection; but usually two or three weeks elapse before a definite change in colour is seen. Increased growth is seen as a puckering of the surface of the treated intervenal area. Other methods allow of half leaves, single branches or whole trees to be treated. The small scale methods are used for the routine testing of five or ten nutrients each injected into four or more leaves or shoots.

Actively growing leaves should be chosen for diagnostic work because mature leaves rarely respond. Many failures have resulted from the use of mature leaves.

The injection method is based on the empirical observation that plants of good performance usually "look better" than those of poor performance, but this does not always hold good, especially when a good crop is compared with an even better one.

Both comparative leaf analysis and plant injection have been useful for diagnosing extreme deficiencies but only a comparison of indications given by them with the results of carefully carried out curative experiments will decide how far they can be used for guidance in attaining optimum crops.

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Section C

SESSIONS 9 TO 11

SESSION 9

THE BROAD UTILIZATION OF SOIL TEST INFORMATION THROUGH SUMMARIES[1]

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Soils vary greatly in fertility levels. These differences are due to past management practices and also to differences in soil types. Soil tests can be used to show the amounts of available major plant nutrients present, and a lime and fertilizer recommendation based on a reliable soil test is an important step towards profitable crop production.

The value of soil tests is being recognized more and more by farmers and agricultural leaders and the demand for soil testing has been increasing rapidly during the last few years. Of course, poor crop yields are not always due to plant nutrient deficiencies. Careful attention must be given to good varieties, proper cultural practices, correct seeding date, and control of weeds, insects and diseases if maximum benefits are to be realized from the lime and fertilizer applied.

It is recognized that the primary purpose of soil tests is to give the individual farmer dependable information as to the fertility status of each of his fields. However, a summary of soil testing data on a state, on a county, or on a type-of-farming basis shows general fertility levels. Such a summary is of value to local agricultural leaders and extension agronomists as a broad basis for estimating lime and fertilizer needs in a county or in a group of counties. Such a summary aids research workers in orienting certain of their research investigations. The summary is also useful to lime, fertilizer and allied indus-

TABLE I. Phosphorus level as related to crop to be grown (State average)

Crop to be grown	No. of samples tested	Percentage of samples testing*				
		VL	L	M	H	VH
Tobacco (Flue-cured)	11,868	3	8	7	18	64
Tobacco (Burley)	219	24	21	20	12	23
Cotton	2,165	8	12	9	17	54
Corn	7,351	18	22	11	16	33
Peanuts	1,660	1	7	11	22	59
Soybeans	133	8	21	19	19	33
Ladino-grass	4,274	32	32	12	12	12
Other pastures	648	45	31	8	8	8
Alfalfa	1,693	33	33	11	11	12
Irish potatoes	291	6	7	3	14	70
Sweet potatoes	83	5	12	10	14	59
Other truck crops	805	5	13	9	15	58

**See* page 246 for explanation of VL, L, M, H, and VH.

[1] Contribution from the Agronomy Department, North Carolina Agricultural Experiment Station, and the Soil Testing Division, North Carolina Department of Agriculture, Raleigh, North Carolina. Published with the approval of the Director of Research as Paper No. 424 of the Journal Series.

tries in determining the particular lime and fertilizer needs in respective areas of the state. If such data were obtained at appropriate intervals, they would also reflect trends in soil fertility.

TABLE II. Potassium level as related to crop to be grown (State average)

Crop to be grown	Percentage of samples testing				
	VL	L	M	H	VH
Tobacco (Flue-cured)	5	46	32	9	8
Tobacco (Burley)	1	11	19	14	55
Cotton	5	43	32	9	11
Corn	9	48	25	7	11
Peanuts	9	53	27	6	4
Soybeans	10	56	22	5	7
Ladino-grass	14	42	22	8	14
Other pastures	10	36	21	14	19
Alfalfa	4	26	23	17	30
Irish potatoes	1	15	18	18	48
Sweet potatoes	7	54	26	6	7
Other truck crops	11	43	17	9	20

A word of caution in using such a summary should be injected here. While the content of potassium or other nutrients in the soils in a given county might average medium, it should be kept in mind that the soils in individual fields in that county will test all the way from very low to very high. Hence, the average as shown in the summary might be very misleading as far as any given field or farm is concerned. It is very important then that individual fields be tested for specific lime and fertilizer recommendations.

Several summaries of soil test data have been made in states other than North Carolina (1, 2, 5, 6). In general, however, most of the summaries were only in mimeographed form and little attempt was made to give thorough interpretation of the information.

Three summaries have been made of North Carolina soil test data since 1945 (4, 7, 8, 10). This paper is based on the most recent North Carolina summary "Fertility Status of North Carolina Soils", published in July, 1951. The objectives of this paper are to show (*a*) the approach used in summarizing soil test data without going into detail as to specific information obtained, and (*b*) examples of the use of a soil test summary in agronomic programmes.

Procedure

The source of the information was the soil test data obtained on samples received during the period July 1, 1949 to June 30, 1950, by the Soil Testing Division, North Carolina Department of Agriculture. Approximately 32,000 samples were utilized in the summary.

In the soil testing programme in North Carolina, the soil test results for phosphorus and potassium are rated as VL (very low), L (low), M (medium), H (high) and VH (very high). A reading of L or VL means that the soil does not contain enough of a plant food element for maximum production with average fertilization. At the M or H levels, sufficient plant nutrients should be applied to equal the

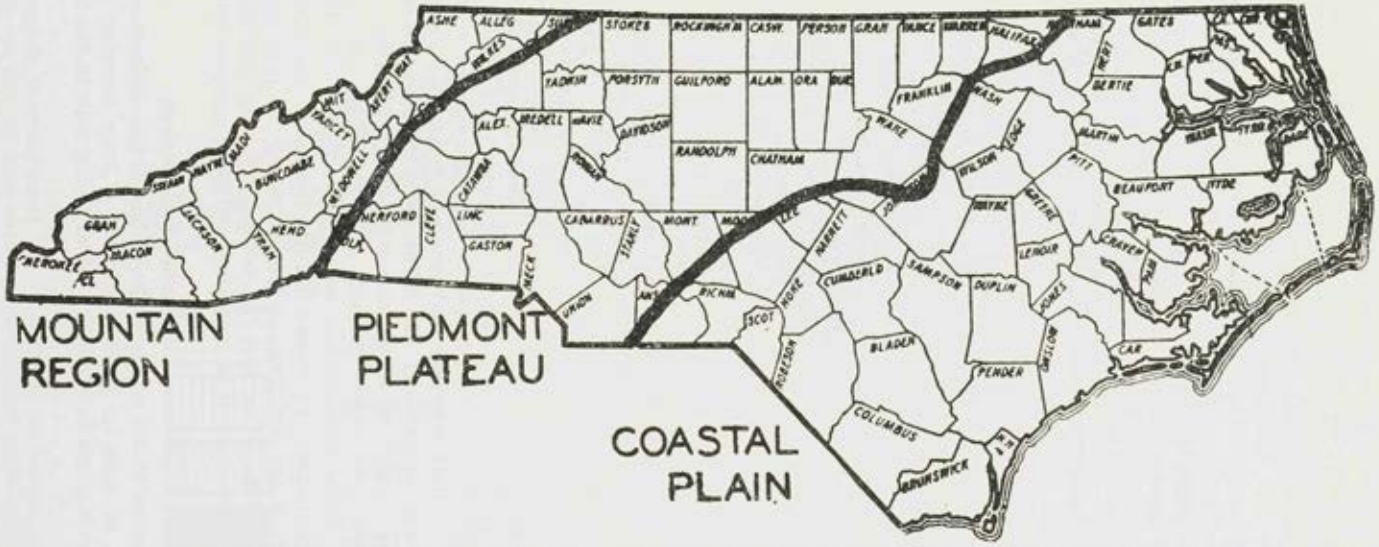


Figure 1—There are three general soil regions in North Carolina. Marked differences appear in the soils among regions and within a given region.

expected crop removal and other losses. With a VH level in the soil, somewhat less than normal fertilization can be applied resulting in utilization of the soil reserves. The organic matter is reported in terms of per cent. and the acidity reported in terms of pH.

To facilitate handling and manipulation of the large number of figures the data were punched on International Business Machine (IBM) cards and sorted according to the types of information desired[2]. The soil test results, the crop to be grown on the land, the amount of lime recommended, and the county name were entered on the cards.

The data were first summarized on a county basis by calculating the percentages of the samples falling in each of the five categories: VL, L, M, H and VH in phosphorus and potassium. The percentages of soils in five ranges of pH (less than pH 5·0, pH 5·0 to 5·5, pH 5·6 to 6·0, pH 6·1 to 6·5 and above 6·5) and in five ranges of organic matter (less than 1·0%, 1·0 to 1·5%, 1·51 to 2·0%, 2·01 to 2·5% and above 2·5%) were calculated also.

The above percentages were calculated in relation to the crop to be grown. This was done in each county for the four crops from which the largest number of soil samples were received. These data were then combined by type-of-farming areas and then on an overall state basis. North Carolina is divided into 100 counties which are grouped into twelve type-of-farming areas.

In order to construct the state maps showing fertility levels, it was necessary to obtain a weighted average or a single index of each county (8). This was obtained by multiplying the percentage of samples in the VL group by 1, in the L group by 2, in the M group by 3, in the H group by 4 and in the VH group by 5. The sum of these products was divided by 100 to give the index. The counties were listed in order from low to high index for each test, divided into four equal groups and each group given a different shading on the maps.

The amounts of fertilizer and lime used per acre were calculated by counties. The data on fertilizer consumption were obtained from the Farm Census Summary of North Carolina and are an average of the usage in 1946, 1947 and 1949. The data on lime consumption was obtained from PMA (1943 to 1948 average). In order to facilitate showing these data on maps the counties were listed from low to high usage for both fertilizer and lime and treated as described above.

Sample bias, that is, the failure of the samples to represent average fertility conditions in the county must be considered. For example, the more progressive farmers may be taking advantage of the soil tests. These farmers may be using more lime and fertilizer resulting in soils that are at a higher fertility level than the average of a county. A study is now underway in Duplin county to provide information on this problem. One-half the county is being systematically sampled and the results will be compared with the samples sent in by farmers.

General Soil Regions

In order to aid in explaining some of the differences in the fertility status of soils in North Carolina, a map showing the general soil regions is given in Figure 1. Most of the soils in the Coastal Plain are

[2] The authors are indebted to the Department of Experimental Statistics, N.C. State College for compilation of the data through the use of IBM cards.

AVAILABLE PHOSPHORUS IN SOILS OF NORTH CAROLINA COUNTIES

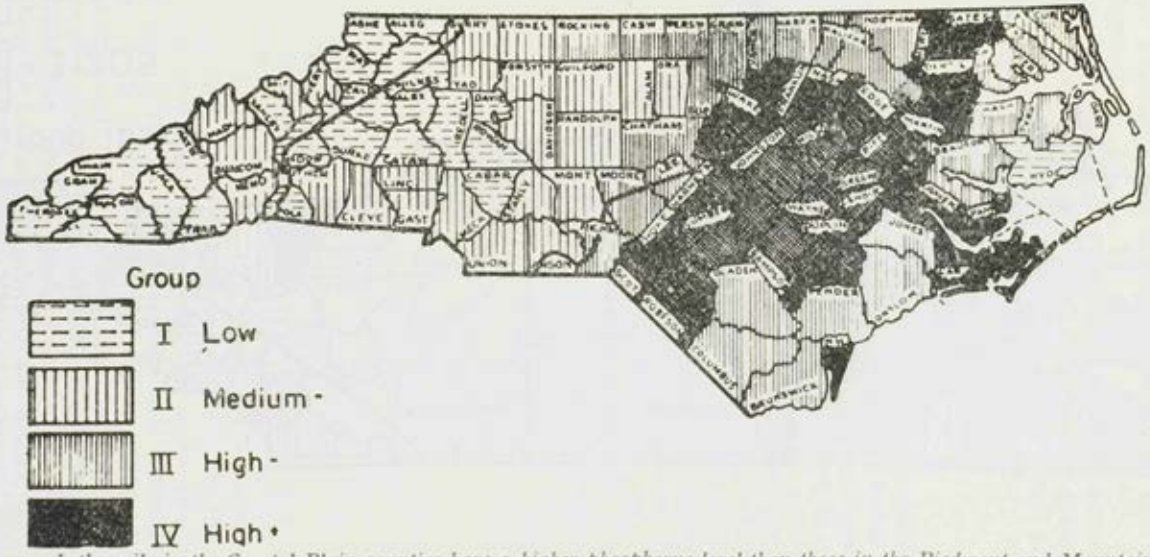


Figure 2—In general, the soils in the Coastal Plain counties have a higher phosphorus level than those in the Piedmont and Mountain counties.

FERTILIZER USAGE IN NORTH CAROLINA

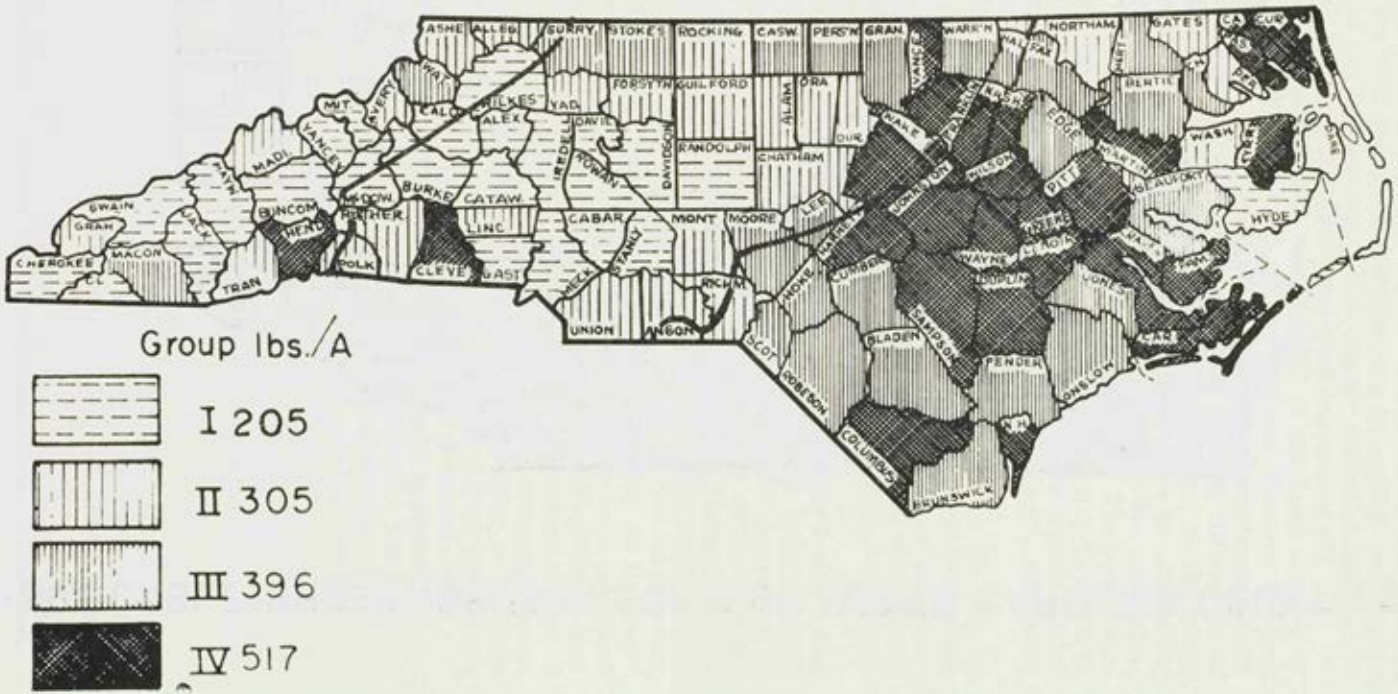


Figure 3—There is a much greater usage of fertilizer in the Coastal Plain counties. This is related to the distribution of cotton and tobacco acreage. (Fertilizer usage based on average of 1946, 1947 and 1949)

sandy loams and were formed from material carried down from the higher land in the Piedmont Plateau. The soils in the Piedmont and in the Mountain Regions range from sandy loams to loams and clay loams and were formed in place from the present rock. These rocks were of many kinds including sandstone, shale, and acid and basic crystalline types.

The soils in the Coastal Plain are generally lower in exchange capacity and contain lower amounts of bases. Phosphorus is generally less available in the Piedmont and Mountain soils due to a high phosphorus fixing capacity.

Figure 3—There is a much greater usage of fertilizer in the Coastal Plain counties. This is related to the distribution of cotton and tobacco acreage. (Fertilizer usage based on average of 1946, 1947 and 1949)

Type of Results Obtained

General fertility levels

Phosphorus: The soil phosphorus level varies greatly between counties and the counties having the highest phosphorus levels are in the Coastal Plain (Figure 2). These variations have been brought about primarily by differences in past fertilization practices as most of the virgin soils in North Carolina are extremely low in available phosphorus. When cropping begins the level of soil phosphorus gradually increases since much more phosphorus is added in fertilizers than is removed by crops or lost by leaching, erosion, and fixation. Calculations based on 1947 figures have shown that fertilizers used in North Carolina supply an average of more than five times as much P_2O_5 as is removed in harvested crops (3).

The fertilizer usage in North Carolina is shown in Figure 3. It was necessary to employ the data for average total fertilizer used per acre as the information for P_2O_5 applications was not available. A comparison of Figures 2 and 3 reveals the close relationship between fertilizer usage and phosphorus level in the soil. Actually the correlation coefficient on a county basis between soil phosphorus index and fertilizer usage was 0·78.[3]

The fertilizer usage and phosphorus levels can be rather generally related to the distribution of the acreage of tobacco and cotton. There is a considerable amount of tobacco in the Northern Piedmont and Upper and Middle Coastal Plain while the cotton acreage is highest in the Upper Coastal Plain and Southern Piedmont.

In Table I the soil tests for phosphorus are summarized in respect to the crop to be grown. It is interesting to note that 82% of the fields for tobacco tested H or VH in phosphorus. For cotton and peanut fields the values were 71% and 81%, respectively. In the case of tobacco and cotton, this high phosphorus level can be attributed directly to fertilization. With peanuts the high value is related to the heavy fertilization of the crops in rotation with peanuts, usually cotton. The truck crop soils, including those used for Irish potatoes and sweet potatoes were also well supplied with phosphorus.

On the other hand, the forage crop soils were relatively low in phosphorus. Of those for Ladino-grass pastures and alfalfa, 64% and 66% of the fields, respectively, were L or VL in phosphorus. This is a reflection of the low fertility status of the soils which are usually chosen for forage crop production.

Potassium: In contrast to phosphorus the potassium content of

[3] Highly significant at .01 level.

AVAILABLE POTASSIUM IN SOILS OF NORTH CAROLINA COUNTIES

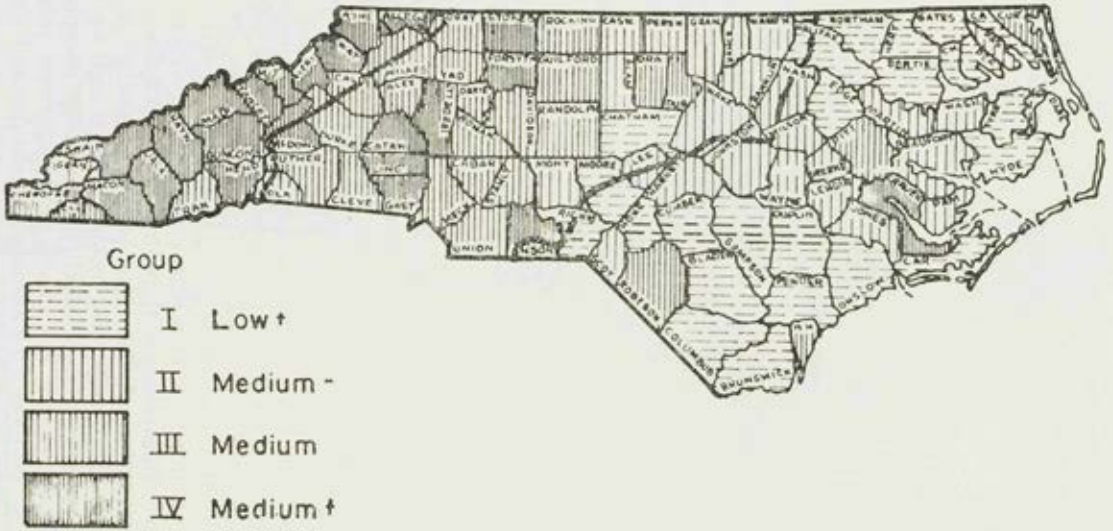


Figure 4—In general, the soils in the Coastal Plain counties have a lower potassium level than those in the Piedmont and Mountain counties. This is in contrast to phosphorus.

the soils is lowest in the Coastal Plain (Figure 4). These soils have a low native supply of available potassium as compared to those in the Piedmont and Mountains where many of the parent rocks are high in potassium-bearing minerals. Hence, the virgin soils in the latter areas may be rather well supplied with potassium.

In comparing Figure 4 with Figure 3, there appears to be an inverse relationship between the potassium content of the soils and amount of fertilizer used. The correlation coefficient between potassium index and fertilizer usage was -0.50.[4] This apparent discrepancy exists because the most heavily fertilized crops are grown in the Upper and Middle Coastal Plain regions where the soils were originally low in potassium. Calculations show that fertilizer supplied 158% as much potassium as was removed in harvested crops in North Carolina (3). Allowing for losses due to leaching, erosion and fixation, any increases in potassium levels in the soil would be relatively small.

On a broad basis, the content of potassium in soils is more closely related to soil association than to fertilization. It is realized, however, that on a given soil continued heavy fertilization will build up the potassium level. This has been demonstrated with Irish potatoes where 66% of the soils tested were H or VH in potassium (Table II). On the other hand, in the Mountain Region, the fact that 69% of the soils for burley tobacco tested H or VH in potassium is related in part to the types of soil on which burley tobacco is grown.

Peanuts and soybeans, crops which remove rather large amounts of potassium, have had a definite effect on the soil. Of these soils, 62% and 66%, respectively, tested L or VL in potassium. The generally low potassium status of the flue-cured tobacco soils is emphasized by the fact that 51% were in the L or VL category.

Lime: The data on pH emphasize the general acid condition of the soils of North Carolina. The most acid soils are in the Coastal Plain (Figure 5). This is related in part to the cropping system and in part to the nature of the soils. Tobacco is grown extensively in the Coastal Plain and little lime is used for tobacco. On the other hand forage and hay crops constitute a large portion of the crop land in the Mountains and in parts of the Piedmont and these crops receive more lime. In addition, in the Coastal Plain the soils, as compared

TABLE III. Acidity (pH) as related to crop to be grown (State average)

Crop to be grown	Percentage of samples testing				
	Below 5·0	5·0–5·5	5·6–6·0	6·1–6·5	Above 6·5
Tobacco (Flue-cured) ...	7	46	38	8	1
Tobacco (Burley) ...	1	19	28	30	22
Cotton	4	39	42	13	2
Corn	9	39	33	14	5
Peanuts	3	28	43	23	3
Soybeans	22	33	29	13	3
Ladino-grass	16	43	25	12	4
Other pastures	4	35	35	19	7
Alfalfa	4	28	26	28	14
Irish potatoes	53	34	9	4	0
Sweet potatoes	23	53	22	2	0
Other truck crops ...	18	34	31	12	5

[4]Highly significant at ·01 level.

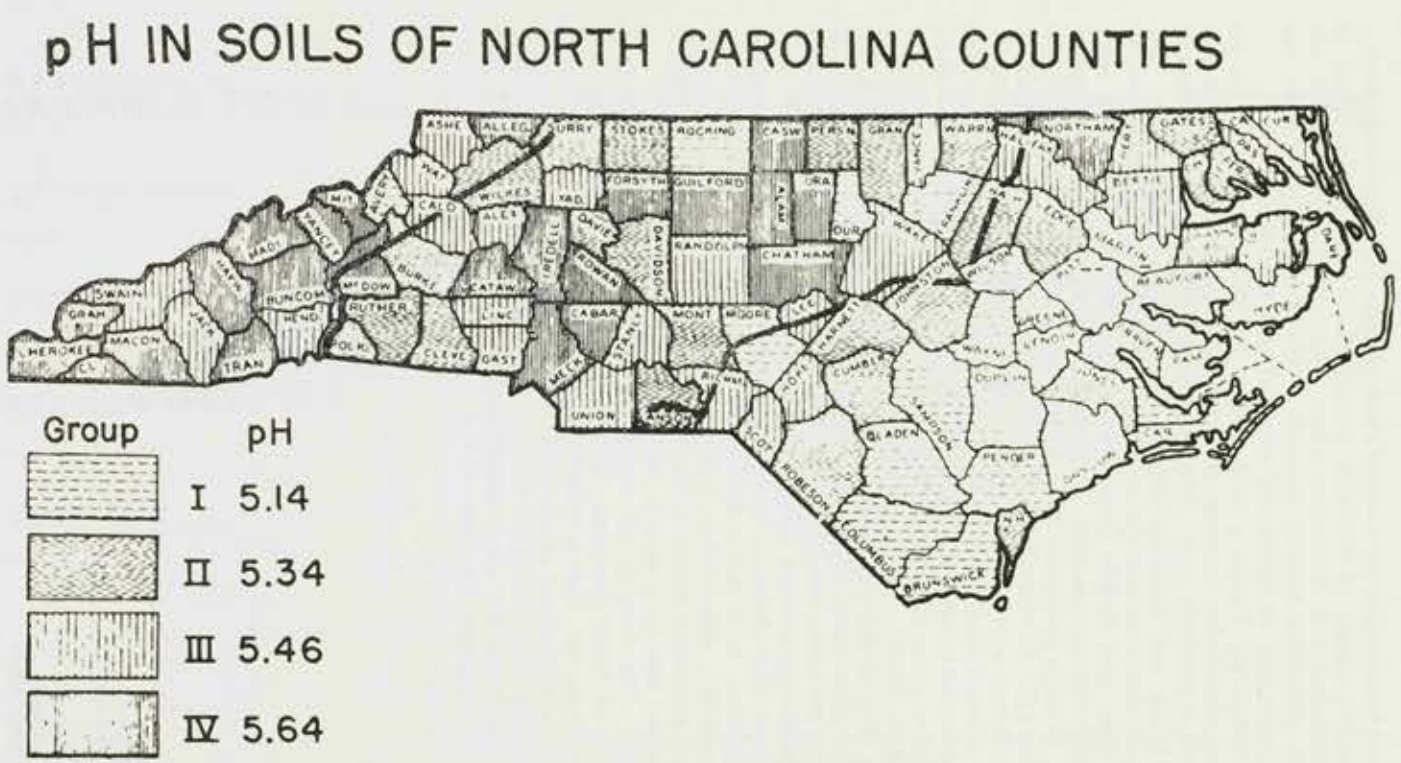


Figure 5—The soils in the Coastal Plain counties, particularly in the southern part, are generally more acid than in other parts of the State.

to those in the Piedmont and Mountains, are more sandy and more readily leached and, hence, lower in bases. The correlation coefficient between county values for pH index and average lime usage was 0·57[5].

The acid condition of soils on which most crops are being grown in North Carolina is further emphasized by the type of summary made in Table III. It can be readily seen that a high percentage of soils are below pH 6·0. This is too acid for most crops to produce good yields. In the case of cotton, peanuts and soybeans, a pH of about 6·2 is preferred yet 85%, 74% and 84% of the soils, respectively, are pH 6·0 or below. Data such as these emphasize the tremendous need for lime in North Carolina.

TABLE IV. Lime recommended on the basis of soil tests (State average)

Crop to be grown	Percentage of soils needing (lbs. per acre)					
	None	1,000–1,500	2,000	3,000	Over 4,000	Average amount needed–lb./A.
	%	%	%	%	%	
Tobacco (Flue-cured)	88	11	1	0	0	130
Tobacco (Burley) ...	97	3	0	0	0	30
Cotton	33	46	18	2	1	920
Corn	43	26	20	7	4	1,273
Peanuts	47	44	8	1	0	630
Soybeans	31	21	24	14	10	1,625
†Ladino-grass ...	16	8	22	25	29	2,430
Other pastures ...	33	9	20	22	16	1,843
†Alfalfa	35	10	21	20	14	1,760
Irish potatoes ...	99	0	1	0	0	20
Sweet potatoes ...	27	42	23	2	6	1,385

†Includes some maintenance.

The amounts of lime recommended for major crops are shown in Table IV. It will be noted that the forage crops, Ladino-grass, other pastures, and alfalfa, had the greatest need for lime with average amounts needed of 2,430, 1,843 and 1,760 pounds per acre, respectively.

Organic matter : The soils in the Lower Coastal Plain and in the Mountain Region are generally higher in organic matter than in the other portions of the state. The soils in the Lower Coastal Plain are more poorly drained and, hence, more organic matter has accumulated. The soils in the Mountain Region were developed under a cooler climate and have undergone less row cropping.

Special Uses of Summary

A soil test summary furnishes specific information that can be used by county agricultural leaders, extension specialists, fertilizer and lime industry agronomists and Experiment Station agronomists (9). A discussion of a few of the uses follows :

Local agricultural leaders : An example of the data for a county is presented in Table V. The top section (A) gives the average of the

[5] Highly significant at ·01 level.

results for all samples received from the county. This shows the general soil condition with respect to pH, calcium, phosphorus, potassium and organic matter. In the bottom section (B) similar information, along with the amounts of lime recommended, is shown for four crops in the county. This gives an indication of the fertility levels of soils on which various crops are being grown. It can be readily seen that pasture fields in the county are more acid and less fertile than many row crop fields. This emphasizes the importance of proper liming and fertilization in establishing productive pastures.

TABLE V—Percentages of samples in each pH, plant nutrient, and organic matter classification for the county as a whole and for crops in the county

*A. Soil Analyses for County**

pH		Plant Nutrient				Organic matter	
Range	%	Levels	Ca %	P %	K %	Range	%
Below 5·0	24	VL	14	6	12	Below 1%	24
5·0–5·5 ...	49	L	29	11	53	1·0–1·5 ...	25
5·6–6·0 ...	24	M	54	11	23	1·51–2·0 ...	20
6·1–6·5 ...	3	H	3	20	6	2·01–2·5 ...	12
Above 6·5	0	VH	0	52	5	Above 2·5	19

B. Soil Analyses as Related to Crops in County

pH		Plant Nutrient				Organic Matter		Lime Recom.	
Range	%	Levels	Ca %	P %	K %	Range	%	Rate	%
					(Tobacco (514 Samples)				
Below 5·0	16	VL	14	3	8	Below 1%	27	None	81
5·0–5·5	54	L	31	5	55	1·0–1·5	31	500–1,500	17
5·6–6·0	25	M	53	7	27	1·51–2·0	22	2,000	2
6·1–6·5	4	H	2	23	6	2·01–2·5	10	3,000	0
Above 6·5	0	VH	0	62	5	Above 2·5	10	4,000 or more	0
					Corn (154 Samples)				
Below 5·0	25	VL	12	4	14	Below 1%	27	None	29
5·0–5·5	50	L	30	15	55	1·0–1·5	21	500–1,500	34
5·6–6·0	21	M	54	12	22	1·51–2·0	16	2,000	16
6·1–6·5	3	H	3	18	4	2·01–2·5	12	3,000	11
Above 6·5	1	VH	0	50	4	Above 2·5	23	4,000 or more	9
					Ladino-Grass (61 Samples)				
Below 5·0	54	VL	16	26	33	Below 1%	7	None	3
5·0–5·5	28	L	33	26	50	1·0–1·5	13	500–1,500	5
5·6–6·0	15	M	44	21	10	1·51–2·0	13	2,000	7
6·1–6·5	0	H	6	21	5	2·01–2·5	16	3,000	21
Above 6·5	3	VH	0	5	2	Above 2·5	50	4,000 or more	64
					Sweet Potatoes (43 Samples)				
Below 5·0	26	VL	9	5	12	Below 1%	30	None	35
5·0–5·5	44	L	26	9	49	1·0–1·5	19	500–1,500	39
5·6–6·0	28	M	65	9	23	1·51–2·0	14	2,000	21
6·1–6·5	2	H	0	7	9	2·01–2·5	19	3,000	0
Above 6·5	0	VH	0	70	7	Above 2·5	18	4,000 or more	5

VL—very low; L—low; M—medium; H—high; VH—very high.

*Columbus County (928 soil samples).

LADINO-GRASS IN AREA 7
(382 SAMPLES)

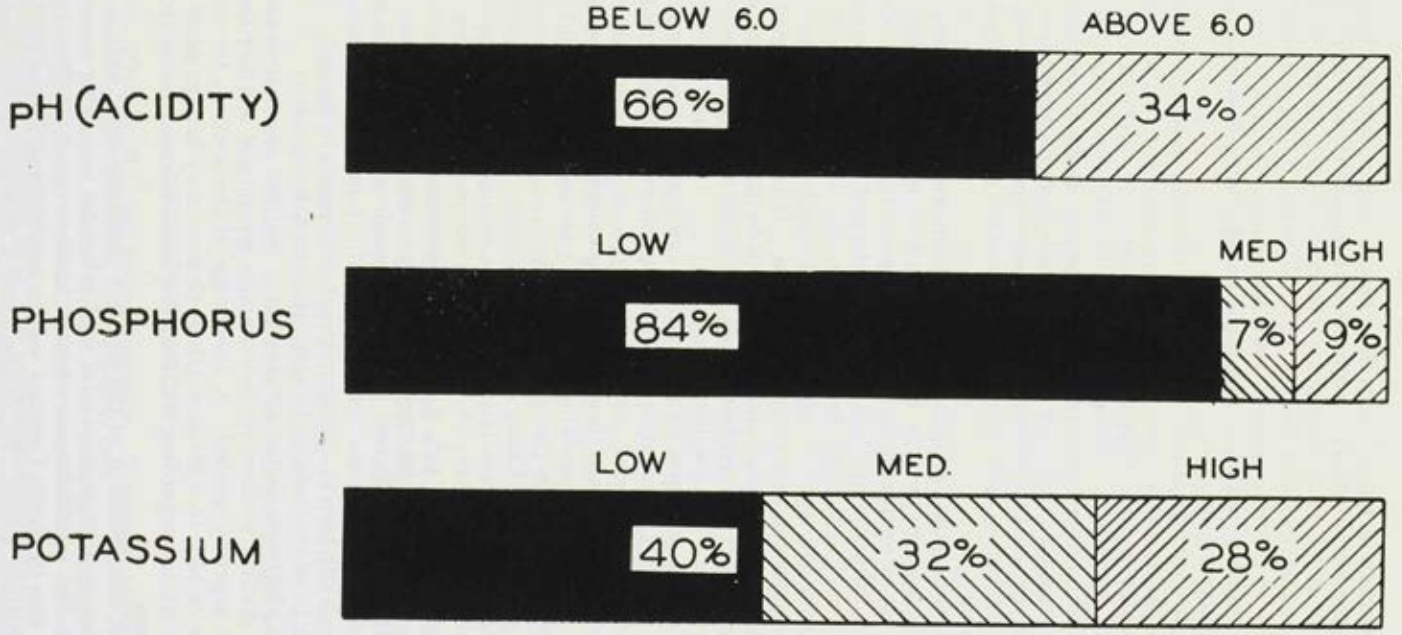


Figure 6—This emphasizes the low phosphorus status and acid conditions of the soils being used for Ladino-grass pastures in type-of-farming area No. 7.

The data in Table V also show that in this particular county most of the samples for tobacco recommendations are H or VH in phosphorus and L or VL in potassium. Information such as this is being used by local agricultural leaders and Extension tobacco specialists as one means of showing farmers that 4-8-10 and 8-0-24 fertilizers are more nearly in line with soil and plant requirements than past grades used extensively for tobacco.

Extension specialists : Agronomy Extension specialists can obtain information from a soil test summary as to the fertility level of soils on which various crops are being grown in a county or type of farming area. A method of presenting data for pH, phosphorus and potassium on Ladino clover-grass pasture soil samples in one of the type-of-farming areas is shown in Figure 6. Slides made from charts such as these have been prepared for several crops and are being utilized to show farmers the general fertility level of soils used for particular crops in an area or county.

Considerable variation may exist from one area or county to another. If the soils in an area are generally low in a plant nutrient element, the use of fertilizers high in this element is encouraged. On the other hand, where continued use of an element has produced a generally high level in the soil, lower amounts may be needed in fertilizers.

Local information such as this helps to create a greater interest in soil testing and recommendations. It is being stressed that while a table or chart may show the general fertility picture the only way to determine if a given field needs lime or extra phosphorus or potassium is to have a soil test made.

Industry agronomists : Fertilizer and lime industry agronomists can use soil test summaries in predicting what analysis fertilizers will be most recommended for specific crops in each area or county and where lime is most needed. For example, the data on soil samples for corn recommendations in Area 3 showed that 73% of the samples were H or VH in phosphorus and 65% of the samples were L or VL in potassium. Under these conditions, a high proportion of the fertilizer recommendations for corn would include a 6-6-12. On the other hand, in Area 10, 86% of the samples for corn were L or VL in phosphorus and 44% L or VL in potassium. Under these conditions, a 5-10-10 would be recommended to a considerable extent.

If the most efficient use is to be made of fertilizers, it is important that industry make available to the farmers the analysis fertilizer which will help to correct nutrient deficiencies in the soil. The industry can be of real service to agriculture in this capacity.

Experiment station agronomists : Soil test summaries can be helpful to station workers in determining where soil fertility investigations are urgently needed. A knowledge of the areas in the state that are low or high in a given nutrient element may help to point to the need for studies regarding fertilizer responses of crops being grown in these areas.

A consideration of the soil test summary along with a careful consideration of experimental work is helpful in making recommendations for the establishment of new fertilizer grades. One such example of this in North Carolina was in establishing a new grade of tobacco fertilizer, 4-8-10. In Tables 3 and 4, it will be noted that 82% of the flue-cured tobacco soils tested H or VH in phosphorus and 51% were

L or VL in potassium. This information was helpful in proposing a 4-8-10 fertilizer as a general substitute for 3-9-6, the old established tobacco fertilizer.

SUMMARY

It is recognized that the main objective in soil testing is to obtain a basis for making lime and fertilizer recommendations for individual fields. However, a summary of soil testing data on a state, type-of-farming area or on a county basis shows general fertility levels. Such summaries can be useful to local agricultural leaders, Extension specialists, industry agronomists and Experiment Station workers in promoting their respective programmes.

The soil test data obtained during the period July 1, 1949 to June 30, 1950, were summarized and the summary distributed to local and state agricultural leaders. Some of the more important types of information obtained and applications of the data were as follows:

1. The counties having soils with the highest phosphorus levels were in the Coastal Plain. This was related to past fertilization. The tobacco, cotton, and truck crop soils were relatively high in phosphorus, while a high percentage of the fields to be sown in Ladino clover-grass pastures were relatively low in phosphorus.

2. In contrast to phosphorus, the potassium content was highest in the Piedmont and Mountain regions. The potassium levels were related to the general soil associations. Crops such as peanuts and soybeans, which remove large amounts of potassium, have had a definite effect on the level of soil potassium, however.

3. The summary revealed the general need for lime with the soils of the Coastal Plain being somewhat more acid than those in the Piedmont and Mountain Regions. The forage crops, Ladino-grass, other pastures and alfalfa showed the greatest need for lime.

4. The soil tests, summarized on a county or type-of-farming area basis, help to point out to county agricultural leaders and Agronomy Extension Specialists the nutrients which are most likely to be deficient for given crops. The summaries can also be used to emphasize special fertilization needs.

5. Data in soil test summaries may be used as a basis for fertilizer and lime industry agronomists to predict what analysis fertilizer will be most recommended for specific crops in an area or county and where lime is most needed.

6. Soil test summaries can be useful to Experiment station workers in determining where soil fertility investigations are urgently needed. The summaries are also helpful in making recommendations for the establishment of new fertilizer grades.

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SESSION 9

BODENUNTERSUCHUNGEN IN DEUTSCHLAND UND IHRE BEDEUTUNG FÜR DIE PRAKTISCHE LANDWIRTSCHAFT

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Nach Abschluss der Prüfung von Laboratoriumsmethoden für die Bestimmung des Kali- und Phosphorsäurebedürfnisses der Böden durch die Internationale Bodenkundliche Gesellschaft (1) wurde in Deutschland eine Reichsmethodenprüfung durchgefürt mit der Zielsetzung, von den vorhandenen Methoden das Verfahren zu ermitteln, das billig, schnell und treffsicher arbeitet und als Schnellmethode zur systematischen Untersuchung der Böden empfohlen werden konnte.

Als Schnellmethoden kamen zur Nachprüfung:

(1) die Verdrängungsmethode von KAWE (2);

(2) die Methode von DIRKS-SCHEFFER (3);

(3) die Aspergillus-Methode von NIKLAS (4);

(4) der Mikro-Düngungsversuch von SEKERA (5);

(5) die Laktatmethode von EGNÉR (6).

Zur Untersuchung gelangten fast 1,000 Böden von mehrjährigen Feldversuchen, die über ganz Deutschland verteilt waren. Diese Böden waren ausserdem nach der Keimpflanzenmethode von NEUBAUER-SCHNEIDER (7) untersucht worden. Einige Proben wurden auch nach der Elektro-Ultrafiltrations-Methode von KÖTTGEN (8) und nach der thermokinetischen Methode von REINAU (9) geprüft.

Wie aus dem Bericht von HERRMAN (10) hervorgeht, war die Laktatmethode von EGNÉR die für Massenuntersuchungen der Böden auf Phosphorsäure geeignetste Methode; zur Bestimmung des Kalis konnte keine Methode für den genannten Zweck als geeignet gefunden werden. Es wurden deshalb weitere Methoden zur Bestimmung des Kalibedarfs geprüft, und zwar die Methode von EGNÉR (11), die Methoden NEHRING (12), SCHACHTSCHABEL (13) und RIEHM (14). Alle vier Methoden gaben übereinstimmende Werte, doch war die Methode RIEHM bei weiten am einfachsten durchzuführen (15). Zur systematischen Untersuchung der deutschen Böden wurde deshalb die Laktatmethode nach EGNÉR-RIEHM sowohl für die Bestimmung der Phosphorsäure als auch des Kalis angewandt. Für die Kalkbestimmung wurde ursprünglich die Methode GOY-ROOS (16) durchgeführt. Seit einiger Zeit verwenden wir aber die Methode von SCHACHTSCHABEL (17).

An allen landwirtschaftlichen Versuchsanstalten Deutschlands sind Bodenuntersuchungslaboratorien eingerichet worden, die durch spezielle Apparaturen in der Lage sind, bis zu tausend Böden täglich

zu untersuchen. Im folgenden sollen eine kurze Beschreibung der Bodenuntersuchung, wie sie jetzt bei uns durchgeführt wird, sowie einige Resultate, die wir dabei erlangt haben, gegeben werden. Das Problem wird in folgende vier Abschnitte geteilt:

I. Probenahme

II. analytische Untersuchung

III. Auswertung

IV. einige bemerkenswerte Resultate.

I. *Die Entnahme der Bodenproben* (18)

Wir arbeiten allgemein mit Durchschnittsproben von einer Fläche, die möglichst klein gewählt wird, etwa $\frac{1}{4}$ bis höchstens 2 ha. Die Probenahme geschieht mit einem Bohrstock. 15—20 Einstiche, die gleichmässig über die Fläche verteilt sind, werden zu einer Mischprobe vereinigt. Bei Ackerland entnehmen wir die Proben im allgemeinen auf 20 cm Tiefe, bei Grünland wegen der geringeren Bewurzelungstiefe auf 10 cm.

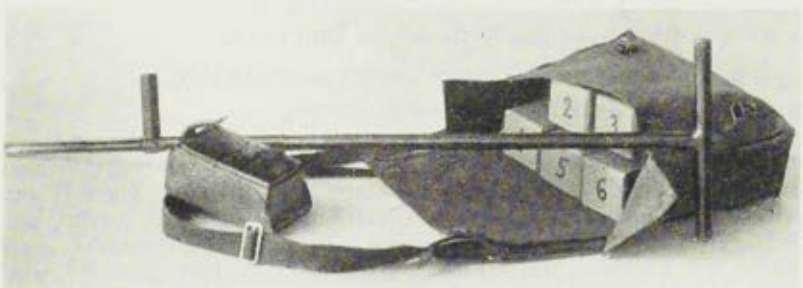


Abbildung 1—*Bohrstock mit Abstreifbecher und Probekartons für die Bodenprobenahme.*

Abbildung 1

Die günstigste Zeit für die Probenahme ist nach der Ente, vor einer Düngung, möglichst nach einer abtragenden Frucht. Im allgemeinen ist es ratsam, die Proben von den geschulten Probenehmern der Untersuchungsanstalten entnehmen zu lassen.

II. *Untersuchung der Proben im Laboratorium* (19)

Um die Untersuchung billig zu gestalten, muss ebenso wie bei der Probenahme auch bei der Untersuchung im Laboratorium jeder einzelne Handgriff und jeder Schritt genau überlegt sein. Es gibt z. B. Maschinen zum Bodensieben, Spezialwaagen, Spezialschüttelmaschinen, Spezialfiltriertische usw. Im allgemeinen sind die Bodenuntersuchungslaboratorien für Arbeiten am laufenden Band eingerichtet.

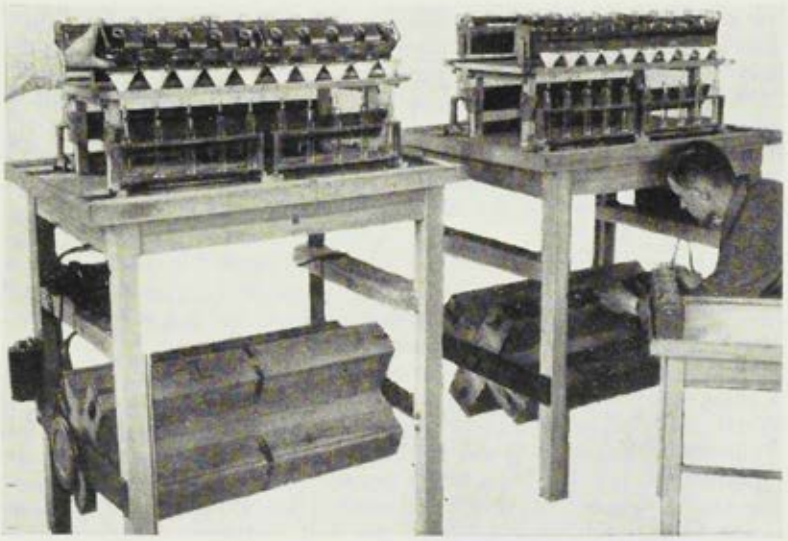


Abbildung 2—Schüttel—und Filtriertisch nach Riehm—Aptila.

Abbildung 2

Als Schüttelflaschen werden Steilbrustflaschen verwandt, die in den Kästen unter dem Tisch geschüttelt werden können. Die Flaschen kommen nach der Extraktion auf den Tisch. Mit einem Handgriff können 10 Flaschen filtriert werden. Das Filtrat läuft direkt in die Kolorimeterröhren. Ein Kapillarheber vermeidet, dass diese Röhren überlaufen.

Im allgemeinen führen wir in der an der Luft getrockneten und auf 2 mm gesiebten Feinerde folgende drei Bestimmungen durch:

(a) *Kalkbedarfsbestimmung nach* SCHACHTSCHABEL (17)

Die genannte Methode ist eine Vereinfachung der Bestimmung der hydrolytischen Acidität nach KAPPEN. Dabei wird nicht wie üblich filtriert und durch Titration des Filtrats die gebildete Menge Essigsäure bestimmt, sondern pH-Erniedrigung der Bodenemulsion gemessen. Die ganze Kalksbedarfsbestimmung erfordert aluso nur eine pH Messung.

(b) *Bestimmung des Phosphorsäure- und Kalibedarfs des Bodens nach der Laktatmethode von* EGNÉR-RIEHM (20).

Das Wesentliche an der Laktatmethode ist die Wahl des geeigneten Extraktionsmittels, eine schwache Milchsäurelösung, die halb mit Kalk neutralisiert ist. Der pH-Wert dieser Lösung beträgt 3,7; sie ist sowohl gegen Wasserstoffionen als auch gegen Calciumionen gut gepuffert, zwei Faktoren, die auf die Löslichkeit der Phosphorsäure grossen Einfluss haben. Für die Bodenuntersuchung besagt dies, dass man die verschiedensten Böden damit unter den gleichen Bedingungen extrahiert.

Das pflanzenaufnehmbare Kali ist im Boden grösstenteils in austauschbarer Form vorhanden. Zu seiner Bestimmung wurde von EGNÉR eine Monochloressigsäurelösung angewandt. Heute bestimmen

wir nach meinem Vorschlag auch den Kalibedarf im Laktatextrakt, so dass also der Boden zur Bestimmung des Phosphorsäure- und Kalibedarfs nur einmal extrahiert werden muss.

Die Phosphorsäurebestimmung geschieht nach der Molybdänblaumethode unter Zuhilfenahme eines speziellen lichtelektrischen Kolorimeters, die Kalibestimmung mittels der Flammenphotometrie. Neu ist hierbei, dass bei Anwendung von Leuchtgas als Heizgas die Ausfällung des Kalkes vor der Kalibestimmung nicht nötig ist (21).

III. *Auswertung der Untersuchungsergebnisse*

Durch die Kalkbedarfsbestimmung nach SCHACHTSCHABEL erhält man direkt die dz CaO, die man geben muss, um den Boden auf den gewünschten pH-Wert zu bringen.

Etwas schwieriger ist die Auswertung der Phosphorsäure- und Kalilaktatzahlen. Mit ihnen wird, unter Berücksichtigung der pH-Werte und der Bodenart, eine Bodenklasse bestimmt. Bei hohen Nährstoffzahlen werden die Böden in die Klasse I eingereiht und erhalten eine normale Düngung, etwa entsprechend dem Nährstoffentzug, so dass der gute Nährstoffzustand im Boden auch nach der neuen Ernte erhalten bleibt. Böden mit mittleren Nährstoffzahlen werden in die Klasse II eingereiht; sie erhalten eine verstärkte Düngung mit dem Ziele, möglichst bald in die Klasse I zu kommen, während Böden mit geringen Nährstoffzahlen der Klasse III eine sehr starke Düngung erhalten müssen.

Der Landwirt bekommt ausser den Untersuchungsresultaten eine Anleitung für die Aufstellung von Düngungsplänen unter Berücksichtigung verschieden hoher Ertragsstufen (22). Anhand dieser Anleitung kann er für die verschiedensten Verhältnisse je nach dem Ausfall der Bodenuntersuchung die zweckmässige Düngung ersehen. Ein Exemplar dieser Düngungsratschläge kann ich Ihnen hier austeilen.

Besonders bewährt hat sich auch die kartenmässige Darstellung der Resultate, worauf die Nährstoffklassen in bestimmten Farben eingetragen sind. Der Landwirt erhält damit einen guten Überblick über die Nährstoffversorgung seines Betriebes, wie aus Tafel 1 und 2 zu ersehen ist.

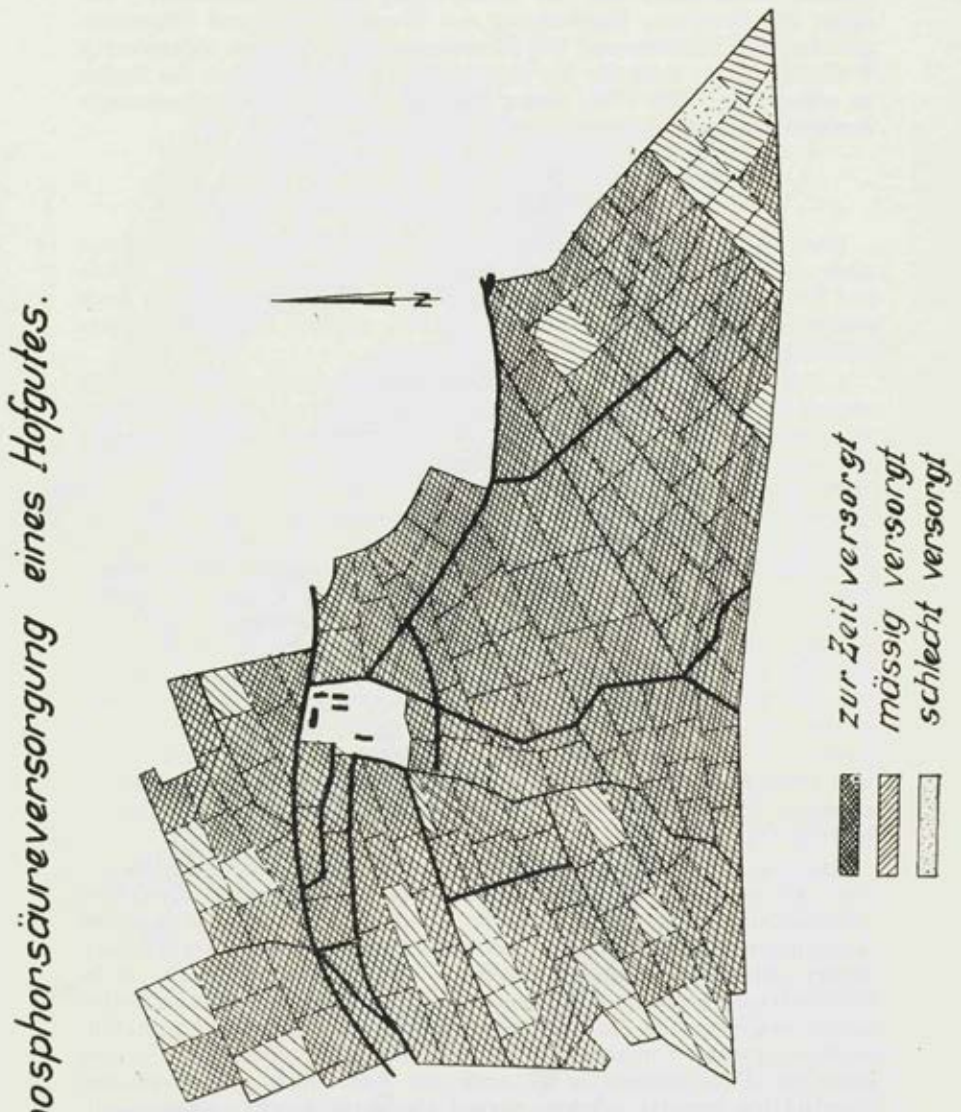
Tafel 1

Tafel 1 gibt die Phosphorsäureversorgung eines Hofgutes wieder. Der Boden ist verhältnismässig gut mit Phosphorsäure versorgt; nur an wenigen Aussenschlägen, die neu hinzugekauft wurden, ist die Phosphorsäureversorgung schlechter.

Tafel 2

Tafel 2 gibt die Phosphorsäureversorgung einer Gemeinde mit stark zersplittertem Besitz wieder. Die Bauern mit 4—5 ha Land besitzen mindestens 40—50 Parzellen, die über die ganze Gemarkung verteilt sind. Die einzelnen Bauern düngen verschieden stark, daher der grosse Unterschied in der Phosphatversorgung von nebeneinander liegenden Äckern. Im allgemeinen ist es so, dass die aufgeschlosseneren Bauern auch die besser versorgten Äcker besitzen. Auffällig ist, dass die Äcker in der Nähe des Dorfes in vielen Fällen am phosphatreichsten sind.

Mit der Bestimmung des Phosphorsäure-, Kali- und Kalkbedarfs haben wir natürlich nur einige von den Wachstumsfaktorn, wenn auch drei der wichtigsten, ermittelt. Nötig wäre vor allem die Bestimmung des Stickstoffbedarfs des Bodens; wie schon erwähnt,



Tafel 1.

ist dies zur Zeit nicht möglich, weil der Nitratgehalt im Boden ausserordentlich schwankt. Es sind aber Versuche im Gange, auch dafür eine brauchbare Methode zu entwickeln (23). Die Fachgruppe für Bodenuntersuchung des Verbandes Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten hat es sich zum Ziele gesetzt, Schnellmethoden zur Bestimmung der Spurenelemente, vor allem des Bors, zur Bestimmung des Humusgehalts und Humuszustandes, zur Bestimmung der Basenkapazität, also des sogenannten T-Wertes, sowie auch für die physikalischen Eigenschaften des Boden zu entwickeln. Mit Hilfe dieser Faktoren ist dann eine allgemeinere Bodenbeurteilung möglich.

IV. *Einige bemerkenswerte Resultate*

Nach den geschilderten Methoden sind in Deutschland bis jetzt über 10 Millionen Bodenuntersuchungen durchgeführt worden. Ohne auf Einzelheiten einzugehen, möchte ich Ihnen zum Abschluss noch einige bemerkenswerte Resultate mitteilen, die sich aus diesen Untersuchungen ergeben haben.

1. *Die Phosphatkarte von Deutschland* und den angrenzenden Gebieten zeigte, dass die Phosphatversorgung in Deutschland verhältnismässig sehr schlecht ist. Es ergaben sich aber insofern bemerkenswerte Unterschiede, als die Versorgung in den Westgebieten besser als in Mitteldeutschland war und die in Mitteldeutschland wieder besser als in Ostdeutschland. Die Hauptursache dafür ist, dass im Westen die Erzeugungsstätten für Thomasphosphat, dem in Deutschland früher gebräuchlichsten Phosphatdüngemittel, liegen und im Osten wegen der extensiven Landwirtschaft in diesem Gebiet, vor allem wegen des weiteren Transportweges, weniger Phosphatdüngemittel angewandt wurden. Ein weiterer Grund dafür ist, dass im Westen viel Kraftfutter aus dem Ausland eingeführt wurde und Nahrungs- und Futtermittel aus dem Osten herbeigeschafft wurden, ohne dass dadurch zum Ausgleich mehr Phosphatdünger nach dem Osten gebracht wurde. Es lassen sich enge Beziehungen zwischen Intensität der Bodennutzung und Phosphatgehalt finden, wie überhaupt ein enger Zusammenhang zwischen Thünen'scher Kreislehre und Phosphatzustand des Bodens besteht (24).

Ähnliche Betrachtungen lassen sich natürlich auch auf ganz Europa und auf die ganze Welt ausdehnen. Bei systematischen Phosphatuntersuchungen in solch grossem Rahmen werden aber manche Ausnahmen auftreten. Als besonders phosphatreich werden sich immer alte Kulturstätten erweisen, auch wenn sie heute nicht mehr intensiv bearbeitet werden. Die Phosphorsaüre wird im Boden kaum ausgewaschen, so dass eine einmal eingetretene Phosphatanreicherung unter Umständen jahrhundertelang bestehen kann. Daher kann die Phosphatanalyse ja auch zur Auffindung archäologischer Fundstätten benutzt werden, worauf als erster ARRHENIUS (25) aufmerksam gemacht hat. In Deutschland hat dann LORCH (26) diesbezügliche Untersuchungen nach einer von ihm verbesserten Methode durchgeführt, worüber er schon des öfteren selbst berichtet hat.

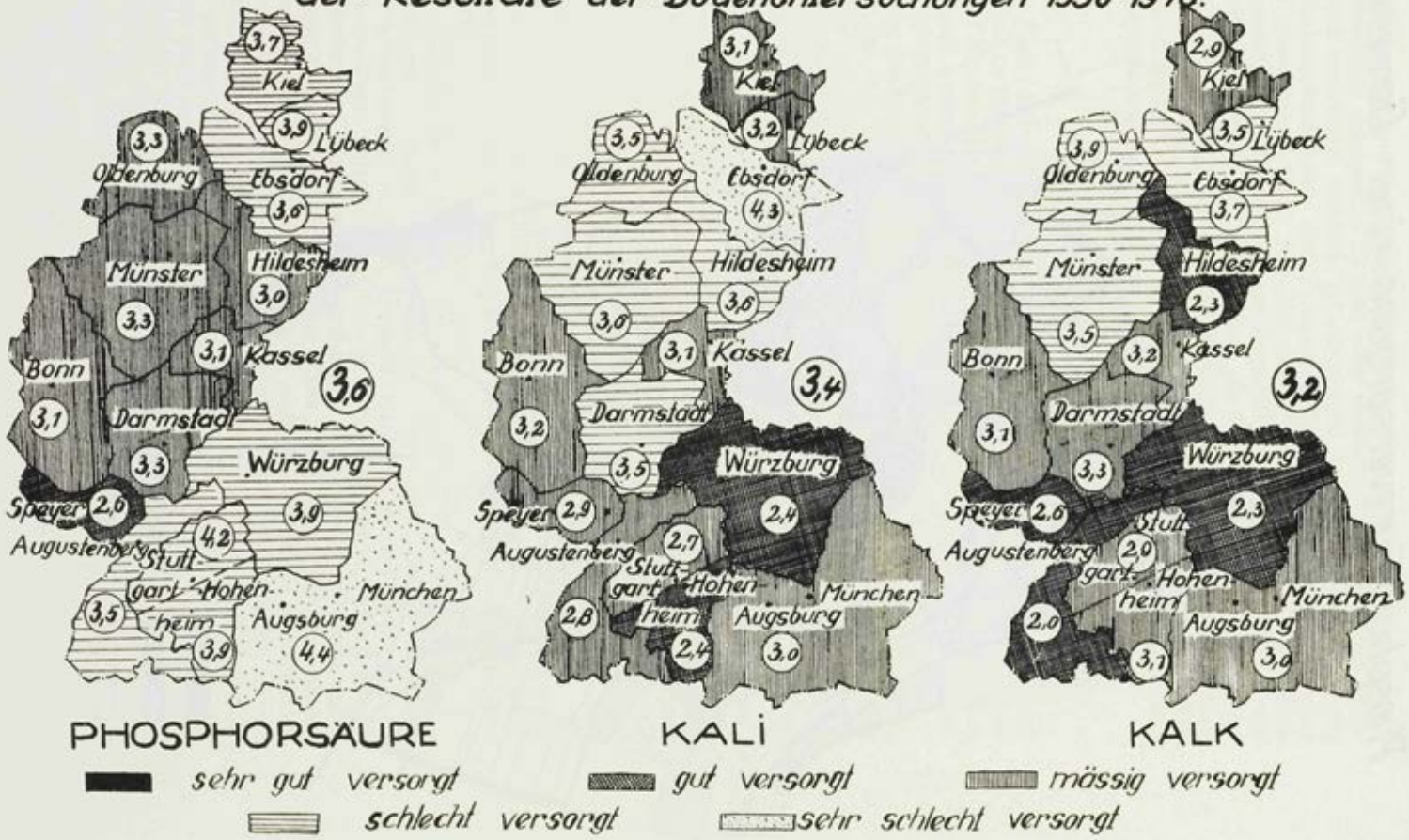
2. *Die Bodenuntersuchungen in den Westgebieten* ergaben folgende Resultate:

Phosphorsäureversorgung einer Gemeinde.



Tafel 2.

Nährstoffkarte der Westgebiete auf Grund der Resultate der Bodenuntersuchungen 1936-1948.



Tafel 3.

ÜBERSICHT 1. Zusammenstellung der Bodenuntersuchungsresultate der Westgebiete von 1936-1951

	Anzahl Proben	%—Anteil in Klasse I (zur Zeit versorgt)	II (mässig versorgt)	III (schlecht versorgt)
Phosphorsäure	5 444 975	21	33	46
Kali	3 725 975	24	39	37
Kalk	4 579 918	31	33	36

Die Übersicht 1 zeigt, dass fast die Hälfte der Böden von Westdeutschland schlecht mit Phosphorsäure versorgt ist, über ein Drittel ist schlecht mit Kali versorgt und ist stark sauer.

Tafel 3

Die Resultate sind auf Tafel 3 länderweise zusammengestellt. Man kann in grossen Zügen ersehen, dass die Böden im Süden des Gebietes schlechter mit Phosphorsäure versorgt sind als im mittleren Teil, während die Kali- und Kalkversorgung im Süden besser ist als dort. Was den Nährstoff Phosphorsäure anbelangt, geht dies parallel mit der Düngung; im Süden wird nur halb so viel Handelsdünger angewandt als im mittleren Teil. Bei der Kali- und Kalkkarte sind die Beziehungen nicht so einfach, weil hier der natürliche Kali- und Kalkgehalt des Bodens eine grössere Rolle spielt (27).

Die auf der Karte angegebenen Zahlen bedeuten Nährstoffnoten, die wie folgt erhalten werden:

Der Prozentanteil in Klasse I wird mit 1, in Klasse II mit 3 und in Klasse III mit 5 multipliziert, und die Summe der so erhalten drei Produkte, wird durch 100 dividiert.

Man erhält auf diese Weise Zahlen zwischen 1 und 5, wobei 100% in der gut versorgten Klasse und 5 100% in der schlecht versorgten Klasse bedeutet und 3 z. B. 100% in der mässig versorgten Klasse.

Wir erhalten so direkt Nährstoffnoten, die ähnlich wie Schulnoten bewertet werden können. Das Arbeiten mit ihnen hat sich als sehr brauchbar erwiesen. Die eine Zahl sagt uns sofort, wie die Nährstoffverhältnisse verschiedener Güter, verschiedener Gemeinden und verschiedener Länder sind. Die Noten sind besonders wertvoll bei laufenden Nährstoffkontrollen, denn sie sagen uns sofort, ob Änderungen eingetreten sind.

3. *Die geringere Anwendung an Handelsdüngemitteln in Süddeutschland* ist verursacht durch die *kleineren Betriebe* in diesem Bereich und vor allem durch deren *Feldzersplitterung*. Die Bodenuntersuchungen in Süddeutschland selbst, besonders in meinem eigenen Gebiet in Baden, zeigen nämlich einen grossen Unterschied zwischen Nährstoffgehalt der Klein- und Grossbetriebe. Während die arrondier-

ten Grossbetriebe auch bei uns im allgemeinen einen befriedigenden Nährstoffzustand besitzen, ist derjenige der Kleinbetriebe, besonders bei zersplittertem Besitz, ausserordentlich schlecht. Die Bodenuntersuchungen andererseits haben aber diese Kleinbetriebe schon veranlasst, mehr Düngemittel anzuwenden.

Besonders schlecht ist die *Versorgung des Grünlandes mit Nährstoffen*. Das ist einerseits darin begründet, dass während des Krieges für das Grünland keine Düngemittel zugeteilt worden sind, zum andern, dass die Bauern im allgemeinem das Grünland vernachlässigen schon aus dem Grunde, weil es meist weiter von dem Betriebe entfernt liegt.

Übersicht 2. Nährstoffversorgung der badischen Acker- und der Grünlandböden.
(Untersuchungen bis 1951)

	Anzahl der Bodenproben	Phosphorsäure			Kali			Kalk		
		z. Zt. versorgt %	massig versorgt %	schlecht versorgt %	z. Zt. versorgt %	massig versorgt %	schlecht versorgt %	z. Zt. versorgt %	massig versorgt %	schlecht versorgt %
Ackerland ...	211867	29,3	30,7	40,0	58,4	30,9	10,7	70,5	13,0	16,5
Grünland ...	73157	12,6	26,5	66,9	32,0	32,1	35,9	55,9	9,1	35,0
insgesamt ...	285024	25,0	28,1	46,9	51,8	31,2	17,0	66,8	12,0	21,2

Wie aus Übersicht 2 hervorgeht, sind die Grünlandböden bedeutend schlechter mit Phosphorsäure, Kali und Kalk versorgt als die Äckerböden. Das Resultat bleibt nicht auf Baden beschränkt, sondern zeigt sich in allen Ländern des Bundesgebietes.

Die schlechte Nährstoffversorgung der Grünlandböden bringt nicht nur eine geringe Heumenge, sondern vor allem auch eine schlechte Heuqualität mit sich. Die fast 500 Heuuntersuchungen, die wir im vorigen Jahr von Nordbaden durchgeführt haben, ergaben einen besonders niedrigen Leguminosen- und Kräutergehalt im Heu. Das bedeutet neben einem geringen Eiweissgehalt auch einen niedrigen Mineralstoffgehalt, vor allem einen kleinen Phosphorsäurgehalt. Im Mittel aller Proben betrug der Phosphorsäuregehalt nur 0,38% P_2O_5, von den Proben, die auf schlecht mit Phosphorsäure versorgten Böden gewaschen waren, sogar nur 0,34%, während der normale Phosphorsäuregehalt des Heus bekanntlich etwa 0,60% beträgt.

Eine wesentliche Besserung bei unseren kleinen Landwirten wird erst eintreten, wenn durch die Feldbereinigung eine Gebietszusammenlegung erfolgt ist. Wir arbeiten deshalb eng mit der Feldbereinigung zusammen und haben auch mit Hilfe der Bodenuntersuchung bemerkenswerte Resultate erhalten, die bei der Werbung der Bauern für eine Flurzusammenlegung benutzt werden können. So finden wir bei genauer Nährstoffuntersuchung der schmalen Ackerstreifen, dass der Nährstoffgehalt in der Mitte des Ackers immer bedeutend höher ist als der der Furchenteile. Entsprechend ist auch das Ernteergebnis der Furchenteile niedriger als des Mittelteils. Ein Beispiel hierfür gibt Übersicht 3.

ÜBERSICHT 3. Bodenzersplitterung, ungleichmässiger Nährstoffgehalt und Ernteergebnisse schmaler Ackerstreifen

Randstreifen und Mittelstück schmaler Äcker getrennt auf Nährstoffe untersucht und getrennt geerntet. (Angaben in Verhältniszahlen).

	Nährstoffe		Erträge	
	P_2O_5	K_2O	Körner bzw. Knollen	Stroh
Mitte	100	100	100	100
Hafer : Randdurchschnitt	60	43	72,5	67
Roggen : Randdurchschnitt	55,5	85	84	78
Kartoffeln : Randdurchschnitt	73	56	73	—
Futterrüben : Randdurchschnitt	87	72	53	—

Die Beispiele zeigen, dass in sämtlichen Fällen der Nährstoffgehalt am Rande der Parzellen geringer ist und entsprechend auch die Erträge niedriger werden. Der niedrige Nährstoffgehalt der Randstreifen ist dadurch verursacht, dass der Bauer mit der Düngung immer sehr vorsichtig ist. Er düngt vor allem die Mitte, um ja zu vermeiden, dass etwas Dünger auf das Feld des Nachbarn kommt.

Mit meinem Vortrag wollte ich Ihnen zeigen, wie die Bodenuntersuchungen in Deutschland zur Zeit durchgeführt werden und welche Bedeutung sie für die Landwirschaft bei uns haben. Der Hauptzweck der Bodenuntersuchungen ist, dem Bauern die notwendigen Unterlagen für die wirtschaftlichste Verwendung seiner Düngemittel in die Hand zu geben. Endziel aller Bodenuntersuchungen bleibt eine laufende Nährstoffkontrolle in regelmässigen Abständen von 3 bis 5 Jahren, um die Zweckmässigkeit der Düngungsmassnahmen zu kontrollieren, den Boden notfalls zu heilen, ihn gesund zu erhalten und damit hohe und sichere Erträge zu gewährleisten.

SUMMARY

The German State test of soil investigation methods, in which 12 different methods were compared and in which almost 1,000 soil samples from long-term field experiments were used, showed that for a systematic examination of soils in regard to their nutrient state the Lactate method is the most efficient. This method is therefore employed on a large scale in determining phosphate and potash needs. We use the SCHACHTSCHABEL method to determine calcium needs. The methods and their evaluation are briefly described.

The approximate 10 million soil examinations in Germany showed

that the calcium as well as the phosphate and the potash condition of the soils leaves much to be desired (compare Table 1 and Map 3). This is especially true of soils in the small holdings and of grassland. Soil examination can be most useful in field consolidation (compare Table 3).

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SESSION 9

LA DETERMINATION DE LA VALEUR RELATIVE DE QUELQUES TYPES DE SOL D'UNE MEME REGION

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Introduction

C'est grâce à l'initiative de l'Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture (IRSIA) que l'établissement systématique d'une carte des sols de la Belgique prit son essor dès 1947.

Le travail global des recherches pédologiques, dont le but est la confection de la carte pédologique de la Belgique, comporte trois phases successives :—

1. l'établissement de cartes indiquant les variations dans les profils de sol, telles qu'elles se sont développées au cours des temps sous l'influence de facteurs naturels et humains. La direction pour toute la Belgique est actuellement assumée par le Prof. Dr. R. Tavernier de l'Université de Gand.

2. la caractérisation pédologique des types de sol par une série d'analyses, effectuées au laboratoire. Il existe en Belgique trois laboratoires, notamment ceux des instituts agronomiques de Gand, de Louvain et de Gembloux, sous la direction respective du Prof. Dr. L. DE Leenheer, du Prof. Ing. J. Livens, et du Prof. Ing. G. Manil.

Au laboratoire on détermine la texture, la capacité de sorption, la matière organique, le pH et le calcaire, ainsi que la réserve en minéraux altérables. Ces analyses s'effectuent systématiquement sur tous les échantillons provenant de 80 à 60 profils par planchette de 8,000 hectare.

3. la détermination de la valeur agricole relative des différents types de sol d'une même région, au moyen de récoltes expérimentales. Cette tâche a également été confiée aux trois instituts agronomiques. C'est cette troisième phase du travail de recherches pédologiques que nous traiterons dans le présent article. Elle a été mise au point et appliquée la première fois par le premier auteur de cette note.

On sait de longue date que la fertilité d'une terre peut être mesurée par la quantité et la qualité de sa récolte. Si l'on veut déterminer, au moyen de parcelles d'essais et de récoltes expérimentales, la valeur agricole propre à un type de sol donné, *il faut que tous les facteurs extrapédologiques soient égaux sur les différentes parcelles comparées.* C'est dire que les différentes parcelles doivent profiter d'une même fumure, de labours et de soins identiques que l'ensemencement d'une

variété identique et la récolte doivent se faire sur les différentes parcelles à la même époque[1] que la rotation des cultures précédentes et les fumures enfouies pour chaque culture précédente soient les mêmes.

En conclusion de ce qui précède, il apparait que si l'on veut pratiquer la méthode décrite ci-dessus, on se heurte à des difficultés d'aménagement de parcelles expérimentales presque insurmontables. Le nombre de types de sol que l'on compare ne peut être également que très réduit, vu l'impossibilité pratique et pécuniaire de réunir un grand nombre de parcelles toutes traitées de la même façon.

Le principe et la technique de la méthode changèrent fort peu au cours des dernières années. Il n'en est pas de même pour les calculs des résultats et leur interprétation, qui évoluèrent au fur et à mesure que l'expérience grandissait.

1. *Le Principe de la Technique des Récoltes Expérimentales*

Si l'on admet que les différents types pédologiques d'une même série ont été choisis de telle sorte que leur valeur agricole soit réellement différente, on peut conclure, en éliminant tous les facteurs extra-pédologiques, que ces différents types de sol donneront une production différente.

Le lecteur américain pourrait se demander pourquoi la valeur agricole relative ne peut être déduite des informations de production fournies par un grand nombre d'agriculteurs. La raison est avant tout psychologique : les agriculteurs belges ont connu deux guerres mondiales c.à.d. deux périodes pendant lesquelles ils ont été harcelés . . . et pressés durement pour remettre toute leur production agricole. Ils ont appris à ne plus jamais dire la production réelle et à considérer les pédologues et leurs adjoints comme des agents probables d'un ravitaillement futur ou d'un controle des revenus (fisc) ; cette, mentalité des agriculteurs nous a obligé de recourir à une technique appropriée.

Nous basant sur la carte pédologique d'une région quelconque dressée au préalable par le Centre de Cartographie pédologique, nous faisons un premier choix d'environ 80 parcelles d'essai ; *le choix des parcelles doit être effectué de telle façon que sur chaque parcelle on retrouve deux ou trois types pédologiques différents.*

Puisque l'unité d'expérimentation et de comparaison est la *parcelle exploitée par le même fermier, tous les facteurs extra-pédologiques* tels que les labours, la fumure, la variété de céréale ou de betterave, l'entretien, etc., *restent constants* et les différences de production reflèteront la valeur agricole de chaque type de sol, sur la même parcelle, pour autant que des facteurs imprévus ne soient intervénus. Dans ce dernier cas, par exemple par suite d'une mauvaise structure locale, ou par la verse complète des céréales, les résultats sur la parcelle endommagée ne sont pas pris en considération.

La comparaison d'un grand nombre de parcelles avec des cultures différentes permet ainsi de fixer la valeur agricole relative de tous les types pédologiques d'une région. Mais cette valeur agricole relative,

[1] Le terme " la même époque " doit être pris ici, non dans son sens absolu, c.à.d. " la même dote ", mais dans son sens physiologique, c.à.d. la récol'e doit se faire au moment où la maturité normale de la plante est atteinte.

établie après une première année n'est exacte que pour les circonstances météorologiques de l'année écoulée. Elle constitue donc une première indication qui devra être précisée par des observations couvrant plusieurs années. A cause de l'empleur de la tâche fixée, nous avons dû nous contenter d'un cycle de trois années consécutives pour une même unité géographique (un paysage ou sous-paysage).[2]

2. *Méthode Opératoire*

Une carte des sols très détaillée est levée pour chaque parcelle d'expérimentation, afin de déterminer avec une grande précision les limites des différents types pédologiques. Pour dresser ces cartes, qui sont à l'échelle de 1/1,000, on effectue environ 35 sondages par hectare.

Ces cartes serviront à faire un choix décisif des parcelles les plus aptes à l'expérimentation.

Sur ces parcelles on indiquera l'emplacement exact des douze petits carrés sur chaque type pédologique dont la production sera récoltée. Chaque carré a une superficie de 2¼ m2 et se délimite facilement sur le terrain en mettant sur le sol un cadre en bois, mesurant 1, 5 m de côté. Toute la production à l'intérieur du cadre est récoltée.

Les céréales coupées sont séchées et battues au laboratoire, puis le rendement en grain est pesé à 1 gr. près.

Les productions moyennes (12 répétitions par type pédologique) ainsi obtenues permettent d'établir la valeur agricole relative des différents types pédologiques d'une même parcelle et par extention de tous les types d'une même région.

Dans le cas de céréales l'emploi du cadre en bois précité donne entière satisfaction. Il n'en est plus de même si l'on veut comparer les productions en pommes de terre ou en bettraves sucrières ou fourragères.

Dans le cas de récoltes expérimentales de pommes de terre on pèse immédiatement sur le champ le poids des tubercules provenant de douze plantes. La production moyenne se calcule au moyen de douze observations. Quant aux betteraves sucrières et fourragères on pèsera également sur le terrain 12 fois le poids de 15 racines par type pédologique.

3. *Exemple d'une Parcelle d'Expérimentation*

Les premières récoltes expérimentales en Belgique se firent en 1948 dans le paysage inversé des Polders anciens.

Nous donnons en exemple une parcelle d'essai située sur la commune de Lampernisse, et comprenant trois types pédologiques, A_4, A_5 et B_1, décrits ci-après.[3]

[2] L. DE LEENHEER et K. DE CAESTECKER, Revue de l'Agriculture du Ministère de l'Agriculture de Belgique, II (1949), No. 6 et Transactions of the International Congress of Soil Science (Amsterdam 1950), I, 352 et II, 237.

[3] F. R. MOORMAN. Planchette Lampernisse, 51 W, de la carte des sols de Belgique. Institut Géographique Militaire (Belge), Bruxelles, 1950.

(*a*) *les types pédologiques.*

A_4 : argile à argile lourde, passant à moins de 60 cm de profondeur à un sédiment plus léger ; pas de sable à moins de 60 cm.

L'allure moyenne de ce profil sur la parcelle étudiée est la suivante :

0 à 25 cm : argile lourde ; brun foncé
20 à 35 cm : argile lourde ; gris
35 à 40 cm : argile grise
40 à 65 cm : argile légère ; bleu gris+rouille
65 à 85 cm : sablon bleu gris+rouille
85 à 125 cm : sable bleu gris+ rouille+restes de coquillages

A_5 : argile lourde à argile, passant entre 60 et 100 cm de profondeur à un sediment plus léger.

L'allure moyenne du profil A_5 sur cette parcelle est comme suit :

0 à 25 cm : argile lourde, brun foncé
25 à 65 cm : argile lourde, gris
65 à 75 cm : argile grise+rouille
75 à 105 cm : argile légère ; bleu gris+ rouille
105 à 125 cm : sablon, blanc gris

B_1 : argile lourde reposant à plus de 100 cm de profondeur sur de la tourbe.

Le profil B_1 de cette parcelle se présente de la façon suivante :

0 à 30 cm : argile lourde ; brun foncé
30 à 70 cm : argile lourde ; gris
70 à 90 cm : argile lourde ; $+CaCO_3$
90 à 125 cm : argile lourde ; bleu gris+rouille

Par endroit on trouve dans les profils du type A_4 un sable légèrement argileux ; sur ces profils la végétation souffrira moins vite de la sécheresse. Les profils des types A_5 et B_1 sont bien représentatifs.

(*b*) *Circonstances culturales.*

Les renseignements suivants, se rapportant aux circonstances culturales, nous furent fournis par le fermier :

—Culture précédente : betteraves fourragères
—Fumure : 280 kg/ha nitrochaux.

Une fumure de potasse et de phosphore n'est jamias donée. Tous les trois ans une dose de fumier de ferme, la dernière fois dans l'arrière saison de 1947.

—Culture actuelle : froment
—Variété : Alba
—Date des semailles : 30 octobre
—Densité des semailles : 200 kg/ha
—Distance des lignes : 22 cm
—Récolte : 2.8.49

(c) *Carte détaillée de la parcelle examinée.*

Chaque petit point noir indique l'endroit où un sondage fut effectué. Les chiffres à côté des différents sondages du type A_5 donnent la profondeur à laquelle commence un sédiment plus léger. Les chiffres du dessus à coté des types A_4 donnent la profondeur du sédiment plus léger ; les chiffres du dessous la profondeur à laquelle apparait le sable.

Les petits carrés noirs signalent l'endroit, où on préleva une récolte d'essai sur une superficie de $2\frac{1}{4}$ m2.

(d) *Récoltes et résultats des pesées.*

12 récoltes d'essai ont donc été prélevées sur chaque type de sol, chaque échantillon étant la récolte d'une superficie de $2\frac{1}{4}$ m2 (carré de 1, 5 m de côté).

Ces récoltes expérimentales ont été numérotées de 1 à 12, de 21 à 32 et de 41 à 52.

Les céréales coupées sont séchées et battues au laboratoire ; puis le rendement en grains est pesé à 1 gr près.

Les rendements en grains pour chaque carré de la parcelle sont mentionnés dans le tableau suivant (P. 279).

Cet exemple choisi est bien représentatif pour le rendement de l'année 1949 des types A_4, A_5 et B_1 (rendements quasi égaux).

En fait, les observations déjà effectuées (1948), ainsi que les renseignements fournis par les cultivateurs, avaient démontré que le type B_1, bien plus humide que les deux autres, donnait d'ordinaire de moins bons rendements.

Les résultats obtenus en 1949 sont-ils contradictoires ? Non. N'oublions pas que le rendement des récoltes expérimentales est fonction des conditions climatologiques, qui cette année furent, particulièrement anormales. En fait les mois de juin et juillet de cette année furent anormalement chauds et secs. Cette période de sécheresse influence favorablement le rendement des types les plus lourds et les plus humides. Tout au contraire sur les types normales.

Ceci prouve que les productions relatives sur différents types de sols doivent être déterminées pendant plusieurs années de suite, et que l'interprétation des rapports obtenus doit se faire en fonction des données météorologiques des années écoulées.

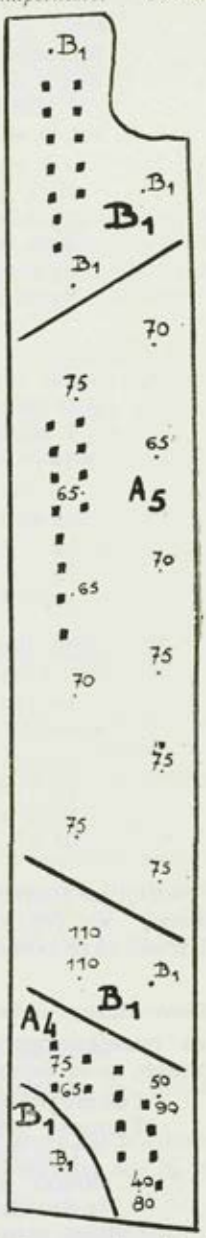


fig. 1 : carte détaillée d'une parcelle

Parcelle 59. *Froment* (1949)

Numéro des carrés	Poids en gr Type A_4	Numéro des carrés	Poids en gr Type A_3	Numéro des carrés	Poids en gr Type B_1
1	1358	21	1324	41	1348
2	1200	22	1236	42	1339
3	1280	23	1280	43	1395
4	1375	24	1215	44	1400
5	1346	25	1316	45	1434
6	1447	26	1518	46	1398
7	1387	27	1157	47	1226
8	1276	28	1315	48	1236
9	1373	29	1372	49	1301
10	1265	30	1281	50	1497
11	1077	31	1454	51	1408
12	1300	32	1388	52	1562
Moyennes	1307		1321		1379

4. *Elaboration des Résultats afin de déterminer la valeur agricole relative des différents Types pédologiques d'une même Région*

Il est aisé de comparer les rendements moyens de plusieurs types pédologiques figurant sur une même parcelle.

En effet, si les rendements moyens des types x—y et z de la parcelle A sont respectivement 1100, 1300 et 1600 (production moyenne exprimée en gr des petits carrés de $2\frac{1}{4}$ m2 de superficie), on calcule facilement leur rapport en multipliant les résultats par 100 et en les divisant par le plus petit rendement. Cela donne pour l'exemple cité le rapport de 100—118—145.

Le problème devient plus complexe quand il s'agit de comparer une série de rendements, obtenus sur différents types et provenant d'un grand nombre de parcelles expérimentales.

La solution resterait aisée si sur chaque parcelle se répétait le même type pédologique auquel on pourrait référer. Mais cette possibilité n'est pas à envisager, tout au moins pas pour les alluvions marines, où les profils pédologiques diffèrent dans de si fortes proportions qu'on ne trouverait nulle part des parcelles assez grandes pour les comparer.

Nous avons adopté au cours des deux premières années d'expérimentations une méthode d'élaboration des résultats assez primitive se basant uniquement sur les plus values. Cette méthode n'avait aucune base mathématique, mais elle donnait les résultats prévus et escomptés par les expérimentateurs. C'est ainsi qu'il fallut plus de deux ans pour la remplacer par une méthode d'élaboration mathématique : notamment la méthode des plus petits carrés.

Après cette importante transformation des résultats il restait encore un point faible ; en effet, le nombre de comparaisons de deux types pour une même culture sur différentes parcelles était encore trop faible. Statistiquement 3 ou même 4 répétitions de la même comparaison étaient encore insuffisantes pour obtenir des résultats sûrs, ayant un grand poids d'interprétation.

Nous pouvons enfin affirmer que pour l'année 1952 notre technique de récoltes expérimentales donnera mathétiquement et statistiquement

entière satisfaction, le nombre de répétitions pour chaque comparaison ayant été porté à 10. Ce dernier chiffre nous semble être en même temps le maximum de répétitions que les statisticiens peuvent demander à ce genre d'expérimentation, qui est effectué sur une échelle régionale (un paysage on sous-paysage).

(*a*) *Détermination de la valeur agricole relative en se basant sur les plus values* (1948-1949) :

1. Parmis les 12 observations de rendement (par type pédologique) on élimine celles dont l'écart vis-à-vis du rendement moyen était supérieur à 3,5 fois l'erreur moyenne. Les observations restantes servaient à calculer les moyennes corrigées par type.

2. Les moyennes corrigées permettent d'établir le rapport des productions sur deux ou trois types pédologiques différents d'une même parcelle, et par conséquent la plus value du meilleur type. (Le rendement le plus faible est présenté par 100).

3. Tous les rendements peuvent être enchainés dans une série, étant donné que les types pédologiques se rencontrent sur les diverses parcelles en différentes combinaisons.

EXEMPLE

Culture : *betteraves fourragères* (année 1948)

Rendements comparés des types A_3, A_4, A_5 *et* B_1 (polders anciens)

No des parcelles	Type A_3	Type A_4	Type A_5	Type B_1
59		100	131	103
57	100	121		
55		100		151
54		100	129	
53		100		125
50	100			147
35	100	142		
12	100	123		
Production comparée	100	129	168	159

Nous basant sur les parcelles n° 57, 35 et 12, nous pouvons établir la relation moyenne des productions des types A_3 et A_4 notamment : 100 à 129.

Ensuite on calcule les rendements moyens du type B_1, comparés au type A_4.

Nous calculons d'abord le nouveau rapport pour les parcelles 59, 55 et 53, le type A_4 étant porté à sa valeur moyenne 129. A ces 3 observations nous ajoutons celle de la parcelle 50. Les résultats sont :

No des parcelles	A_3	A_4	B_1
59		129	133
55		129	195
53		129	161
50	100		147
Production comparée	100	129	159

Les parcelles 59 et 54 nous donnent enfin la relation entre les types A_5 et A_4, notament 130 (A_5) pour 100 (A_4) ; le type A_4 ayant lui-même une valeur relative de 129 vis-à-vis de A_3, on en déduit le rapport entre A_5 et A_3, soit 168 pour 100.

La production relative devient ainsi : $A_3=100$; $A_4=129$; $A_5=168$; $B_1=159$.

Critiques de cette méthode des plus values

1. *Elimination de certaines observations.* La définition du type pédologique n'excluant pas des variations de fertilité dans un même type de profil, il est logique de trouver sur les différents petits carrés des rendements parfois fort divergeants. En éliminant certaines observations, on fausse la production moyenne dans l'un ou l'autre sens et l'on donne aux résultats une importance qu'ils n'ont point.

2. *Calcul des plus values.* L'élaboration des résultats ne peut donner la garantie exigée pour exprimer mathématiquement les comparaisons des rendements relatifs. La comparaison des rendements relatifs était arbitraire ; en effet on tâchait toujours d'obtenir des gradations maxima dans les résultats relatifs pour des types différents, ce qui entraînait des interprétations fautives. Dans différents tableaux de production obtenus au cours des années 1948 et 1949 on a constaté qu'il y avait moyen d'obtenir des rapports différents de chaque type de différentes manières, suivant l'ordre dans lequel on établissait les comparaisons.

3. *Les erreurs.* On ne tenait aucune compte de l'exactitude liée aux résultats. Ainsi on mettait sur le même pied des expériences avec de grandes erreurs moyennes (donc peu exactes) avec des expériences pour lesquelles l'erreur moyenne était minime.

4. *Les répétitions.* Le nombre de répétitions des mêmes comparaisons était trop faible. On s'était contenté au début de deux ou trois parcelles éxpérimentales, comparant les mêmes types, pour établir les rapports moyens de productivité.

C'est pour remédier aux griefs de l'ancienne méthode que nous avons mis au point en 1950 une nouvelle méthode d'élaboration mathématique des résultats des récoltes expérimentales. Nous avons poursuivi le but d'y exclure toute interprétation arbitraire des résultats et de donner les rapports des rendements les plus vraisemblables. En surplus nous y tenons compte de l'exactitude avec laquelle on a conduit les expériences, en attribuant un poids à chaque résultat, en rapport avec la grandeur de l'erreur.

Pour le bien fondé mathématique de la méthode nous avons pu faire appel à la bienveillance du Professeur Hirsch, de l'Institut Agronomique de l'Etat de Gand.

(*b*) *Calcul de la production relative des différents types d'une même région par la méthode des plus petits carrés* (1950)

Ce n'est pas notre intention d'expliquer et de prouver ici la méthode des plus petits carrés[4]. Aussi nous bornerons nous à donner un exemple des calculs effectués.

[4] R. DÖRFLING, Mathematik für Ingenieure (München : Oldenburg, 1950).

Exemple: Récoltes expérimentales dans les Polders Anciens. Céréales, 1950.

En possession des résultats des pesées on calcule pour chaque type la moyenne arithmétique et l'erreur moyenne selon la formule :

$$E\ M=\sqrt{\frac{\Sigma a^2}{n(n-1)}}$$

dans laquelle a est la différence entre le résultat expérimental et la moyenne arithmétique, n étant le nombre d'essais par type et par parcelle (12 répétitions).

Les différentes moyennes par type, avec leur erreur moyenne, sont réunies dans la *table I*. (*Table des récoltes.*)

Notons en passant que dans cette table on compare aussi bien des productions en froment que des productions d'avoine et d'orge.

De chaque résultat on calcule le logarithme et l'erreur moyenne sur le logarithme. L'erreur moyenne sur le logarithme est calculée de la façon suivante :

ex. log. 1014, 9=3,00642
log. (1014,9+23,3)=3,01107
log. (1014,9−23,3)=2,99634

dans laquelle 1014,9 est le rendement, avec l'erreur moyenne (E.M.) de 23,3.

L'E.M. sur le logarithme est alors la moyenne des différences de log. (1014,9+23,3) et log. (1014,9−23,3).

L'E.M. sur le logarithme 3,00642 est donc :

$$\frac{(3{,}00642-2{,}99634)+(3{,}01107-3{,}00642)}{2}=0{,}0098$$

Les logarithmes des récoltes avec leur erreur moyenne sont données dans *le Table II*. (*Table des logarithmes*).

Ensuite on calcule toutes les différences possibles des logarithmes (donc les rapports des récoltes) :

$x=a-b$	$r=f-g$
$y=b-c$	$q=a-c=x+y$
$z=c-d$	$p=b-d=y+z$
$v=d-e$	$t=b-e=y+z+v$
$m=e-f$	etc. . . . (voir table III).

a, b, c, d, e, f et g sont respectivement les logarithmes des productions des types pédologiques A_1, A_4, A_5, B_1, A_3, C_3 et P_4.

Les différences, ainsi que le carré de l'*E.M.*, le poids et le produit "poids par différence," sont également donnés dans *la Table III* (*Table des différences*).

L'erreur moyenne de la différence est calculée selon la formule

$$E.M.=\pm\sqrt{E.M._1{}^2+E.M._2{}^2}$$

dans laquelle *E.M.* est l'erreur moyenne de la différence $E.M._1$ et $E.M._2$ étant les erreurs moyennes des deux termes.

Comme poids on prend l'inverse du carré de l'erreur moyenne, donc

$$\text{poids} = \frac{1}{\text{le carré de l'erreur moyenne}}$$

La détermination des rendements relatifs des différents types de sol se réduit à calculer la valeur la plus vraisemblable des différences des logarithmes (donc des inconnues). Cela ce fait en appliquant la thèse des carrés les plus petits.

La forme générale des équations est la suivante :

$$x\Sigma a^2 + y\Sigma ab + z\Sigma ac + v\Sigma af + m\Sigma af + r\Sigma ag = \Sigma al.$$
$$x\Sigma ab + y\Sigma b^2 + z\Sigma bc + v\Sigma bd + m\Sigma bf + r\Sigma bg = \Sigma bl.$$
$$\text{etc.}$$

Les équations pour notre exemple sont les suivantes :

$377.686x + 67.586y = -111.304$
$67.586x + 383.417y + 234.812z + 108.872v = -7.316$
$234.812y + 940.451z + 655.820v + 373.826m + 204.948r = 48079.$
$108.872y + 655.820z + 766.980v + 484.986m + 248.540r = 47079.$
$373.826z + 484.986v + 484.986m + 248.540r = -44,6$
$204.948z + 248.540v + 248.540m + 585.634r = 5346.$

Après la solution des équations normales on obtient :

$x = -0,2910775$
$y = -0,0207771$
$z = 0,00936544$
$v = 0,1649650$
$m = -0,18506698$
$r = 0,02495775$

Etant donné que le type A_1 donne les plus petits rendements, on calcule tous les rapports des rendements en fonction de ce type ; cela donne :

$a - b = x = -0,291$
$a - c = x + y = -0,312$
$a - d = x + y + z = -0,302$
$a - e = x + y + z + v = -0,137$
$a - f = x + y + z + v + m = -0,322$
$a - g = x + y + z + v + m + r = 0,298$

Ces valeurs sont les logarithmes des rapports des rendements.

En cherchant l'antilogarithme, on trouve :

Type	A_1	A_3	A_4	A_5	B_1	C_3	P_4
Rendement relatif	100%	137,2%	195,4%	205%	198%	211,3%	198,4%

Pour les récoltes expérimentales de 1951 on a apporté à la méthode d'élaboration des résultats une légère amélioration.

Dans la détermination du poids on tient dorénavant compte de la

différence entre le résultat expérimental et le résultat provisoire. Aussi procède on de la manière suivante :

On détermine en premier lieu le poids provisoire qui est l'inverse du carré de l'erreur moyenne ; les solutions des équations normales donnent des valeurs à x, y, z, m et v, qui sont considérées comme provisoires. En effet, nous avons accordé aux résultats un poids provisoire, dépendant seulement de l'erreur moyenne du résultat expérimental. En outre, la différence entre chaque résultat et le résultat final joue un rôle dans le calcul du poids définitif.

Le calcul doit donc être repris, en tenant compte de la différence entre le résultat expérimental et le résultat final.

Le poids définitif devient alors l'inverse d'une somme de deux carrés, notamment le carré de l'*E.M.* plus le carré de la différence entre le résultat expérimental et le résultat provisoire.

Critique de la méthode appliquée au cours des années 1950 *et* 195

Cette méthode donne mathématiquement entière satisfaction, mais laisse statistiquement encore à désirer. En effet le nombre de répétitions reste trop faible et l'on compare encore directement diverses céréales.

En 1952 nous devions commencer la détermination de la valeur agricole relative des types de sol les plus importants de la région limoneuse belge. Aussi nous en avons profité pour élaborer un nouveau plan de travail conforme aux désidérata de la statistique, pour autant cependant que sa réalisation soit pratiquement possible.

Le programme de 1952 pour la nouvelle région à envisager, peut être résumé dans les quelques points qui suivent :

1. Un minimum de 10 répétitions (donc 10 parcelles différentes) pour 2 types pédologiques comparés directement.

2. La détermination de la valeur agricole relative des types de la région limoneuse s'effectuera au moyen de deux cultures seulement, notamment la culture du froment et celle de la betterave fourragère.

Les productions de différentes céréales ne seront donc plus comparées simultanément, comme cela avait été le cas précédemment.

3. Réduction du nombre de types comparés. Cette réduction découle directement du plus grand nombre de répétitions (10 à la place de 3 ou 4) et du fait que nous sommes limités par le temps.

Nous nous sommes proposés de ne comparer que les 4 types pédologiques les plus importants de la région limoneuse, étant donné que la comparaison de 4 types de sol au moyen de deux cultures (froment et betteraves fourragères), mais avec 10 répétitions, requiert déjà une cinquantaine de parcelles expérimentales.

SUMMARY

Determination of Productivity Ratings of Different Soil Types

Soil mapping is only one of the objectives of the Belgian soil survey, another objective being the determination of the productivity ratings of the different soil types in a district.

A psychological consequence of the two world wars is the difficulty

of obtainging accurate information from the Belgian farmer regarding his crop production, because he still keeps in mind the severe food supply control in war-time. Therefore, a special investigation technique had to be worked out.

The principle of this investigation was already explained in Transactions of the International Congress of Soil Science, Amsterdam 1950, vol. 1, page 352.

However, the method of calculating the results obtained in the field was unsatisfactory from the standpoint of both the mathematician and the statistician. The difficulties in both cases have been overcome. A mathematically justified method of calculation is based on the method of the smallest square values, an example of which method is given in this paper.

To satisfy the statistician, the three or four repetitions of the same comparison will be replaced by ten repetitions, but the number of crops to be compared will be reduced to two, namely wheat and sugarbeet.

TABLE I. (*Table des récoltes.*)

Productions moyennes en gr (12 *répétitions*) *de différents types des Anciens Polders, comparés à un type de la région sablo-limoneux* (*type* C_3). *Céréales* 1950. *Entre parenthèses : erreur moyenne*

Parcelles	A_1 *a*	A_4 *b*	A_5 *c*	B_1 *d*	A_3 *e*	C_3 *f*	P_4 *g*
P1	536,1 (11,8)	898,-(17,1)	1112,-(19,5)				
P2	680,7 (10,8)	1070,9 (22,5)					
P3	341,2 (20,-)	867,9 (20,8)					
P4			1083,7 (21,4)	1004,-(18,-)			
P6		722,2 (10,3)		761,7 (11,3)			
P7			821,4 (16,7)	811,6 (12,5)			
P8			867,-(13,6)		675,-(10,8)		
P9			747,7 (14,2)		507,6 (10,9)		
P10		827,7 (25,7)			456,7 (16,4)		
P11		899,7 (16,7)			547,7 (9,4)		
P13	598,-(10,8)	1213,3 (23,4)					
P76			799,3 (14,1)			838,-(12,5)	828,2 (20,-)
P77			940,-(12,5)				840,6 (23,1)
P79			940,-(20,4)			920,-(10,7)	932,8 (11,1)
P80						976,8(15,4)	840,9(25,3)
P81				1020,9 (17,9)		1054,7 (23,2)	1011,5 (30,9)

TABLE II. (*Table des logarithmes.*)

Parcelles	A_1 *a*	A_4 *b*	A_5 *c*	B_4 *d*	A_3 *e*	C_3 *f*	P_4 *g*
1	2,72935 (0,00946)	2,95332 (0,00815)	3,04610 (0,0755)				
2	2,83296 (0,00683)	3.02975 (0,00903)					
3	2,53352 (0,0235)	2,93847 (0,1029)					
4			3,03491 (0,0845)	3, 0173 (0,0772)			
6		2,85866 (0,0615)		2,88178 (0,0640)			
7			2,91455 (0,0875)	2,90934 (0,0664)			
8			2,93802 (0,0676)		2,82030 (0,0690)		
9			2,87373 (0,0817)		2,70561 (0,0914)		
10		2,91787 (0,1328)			2,65963 (0,01514)		
11		2,95410 (0,0799)			2,73854 (0,00739)		
13	2,77670 (0,0777)	3,08397 (0,0830)					
76			2,90271 (0,0759)			2,92324 (0,0064)	2,91814 (0,0104)
77			2,97313 (0,0573)				3,92459 (0,1177)
80						2,98981 (0,0067)	3,92474 (0,0129)
81				3,00898 (0,0075)		3,02313 (0,0094)	3,00497 (0,0131)
	100%	195,4%	205%	200,6%	137,2%	211,3%	198,4%

TABLE III. (*Table des différences.*)

Différences		E.M.²	Poids	Poids × Différences
$x=a-b$	$=-0{,}22407$	$-0{,}0001540$	64935	$-14545{,}-$
	$=-0{,}19679$	$0{,}0001272$	78616	$-15470{,}8$
	$=-0{,}40495$	$0{,}0001119$	89366	$-36188{,}8$
	$=-0{,}30727$	$0{,}0001297$	77101	$-23690{,}8$
$y=b-c$	$=-0{,}09268$	$0{,}0001234$	81037	$-7518{,}6$
$z=c-d$	$=+0{,}03318$	$0{,}0001315$	76046	$+2523{,}2$
	$=+0{,}00521$	$0{,}0001210$	82645	$+430{,}6-$
$v=d-e$				
$m=e-f$				
$r=f-g$	$=+0{,}00510$	$0{,}0001491$	67069	$+342{,}1$
	$=-0{,}00600$	$0{,}0000541$	184840	$-1109{,}-$
	$=+0{,}06507$	$0{,}0002127$	47015	$+3059{,}3$
	$=+0{,}01816$	$0{,}0002619$	38170	$+693{,}2$
$q=a-c$	$=-0{,}31685$	$0{,}0001480$	67568	$-21408{,}9$
$x+y$				
$p=b-d$	$=-0{,}02312$	$0{,}0000794$	125940	$-2912{,}-$
$y+z$				
$t=b-e$	$=+0{,}25824$	$0{,}0004049$	24697	$+6377{,}8$
$y+z+v$	$=+0{,}21556$	$0{,}0001188$	84175	$+18144{,}8$
$s=c-e$	$=+0{,}10872$	$0{,}0000939$	106500	$+11578{,}-$
$z+v$	$=+0{,}16812$	$0{,}0001501$	66622	$+11200{,}4$
$w=c-f$	$=-0{,}02053$	$0{,}0009870$	101310	$-2080{,}-$
$z+v+m$	$=+0{,}00934$	$0{,}0001480$	67568	$+631{,}1$
$k=c-g$	$=-0{,}01543$	$0{,}0001659$	60277	$-930{,}1$
$z+v+m+r$	$=+0{,}04854$	$0{,}0001717$	58241	$+2927{,}-$
	$=+0{,}00334$	$0{,}0001157$	86430	$+288{,}7$

Schéma des comparaisons qui sera mis en pratique pour la première fois en 1952, dans la région limoneuse

Froment					Betteraves fourragères				
Parcelle	Type A	Type B	Type C	Type D	Parcelle	Type A	Type B	Type C	Type D
1	x	x	x	x	24	x	x	x	
2	x	x	x		25	x	x		
3	x	x			26	x	x	x	
4	x	x	x		27	x	x		
5	x	x			28	x	x		
6	x	x			29	x	x		
7	x	x			30	x	x		
8	x	x			31	x	x		
9	x	x	x		32	x	x		
10	x	x			33	x	x		
11		x	x	x	34		x	x	x
12		x	x		35		x	x	x
13		x	x		36		x	x	
14		x	x	x	37		x	x	
15		x	x		38		x	x	
16		x	x		39		x	x	
17			x	x	40		x	x	
18			x	x	41		x	x	
19			x	x	42			x	x
20			x	x	43			x	x
21			x	x	44			x	x
22			x	x	45			x	x
23			x	x	46			x	x
					47			x	x
					48			x	x
					49			x	x

SESSION 10

THE EVALUATION OF SOIL ANALYSIS

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The chemical determination of available plant nutrients in the soil has been the aim of chemists for more than 100 years, since the days of LIEBIG and BOUSSINGAULT. To-day, I think, the chemist has at his disposal methods by which he is able to determine the available quantities of at least some plant nutrients, for example potassium. In other cases he is, perhaps, not able to determine the amounts of available plant food, but is able to arrive at figures so closely correlated with these amounts, that his figures may be regarded as valid expressions of the unknown amounts. Several of the methods used for the determination of available phosphorus lead, I think, to such correlated values of the real amounts.

The chemist can, however, at best, only answer the question: how much available plant food, say phosphoric acid, does the soil contain? But the farmer is not at all interested in this answer. He wants the answer to quite another question: will superphosphate pay? And no analytical method can answer this question.

In the evaluation of soil analysis, it is, in my opinion, important to emphasize the fundamental difference between the question the farmer wants to have answered and the question the chemist is able to answer. Many misunderstandings and much disparagement of laboratory methods have arisen from neglect of this difference.

In the following, I shall use the determination of phosphorus as an example, but any remarks may just as well be applied to the determination of any other nutritive element.

The farmer is interested in the effect of superphosphate. The fertilizer bill is paid by the increase in yield caused by the fertilizer. And now it is a well established fact that even if the effect of superphosphate depends upon the amount of available phosphoric acid in the soil, it does not solely depend on this. Other factors may greatly influence the effect.

As an example I shall only point to the phenomenon often met with in the field experiments, the positive interaction between nitrogen and phosphorus. The greater the dressing with nitrogen, the greater the effect of phosphorus.

To illustrate this, I quote the average results from 19 Danish experiments, in which dressings with superphosphate have been combined with basal dressings of nitrate of lime.

Effect of superphosphate

Superphosphate—kilos per hectare	Basal dressing—kilos nitrate of lime per hectare		
	0	100	200
	Fodder units per hectare		
1000	420	620	730
2000	570	780	700

The effect of superphosphate increases, as the amount of nitrogen is increased.

But the interaction between phosphorus and other factors means that we shall never be able, from any laboratory determination of available phosphoric acid, to answer exactly the question put forward by the farmer : how will superphosphate pay ?

If we examine a number of field-experiments with superphosphate, we find that the effect of superphosphate may vary considerably from one experiment to another, even if the determination of available phosphoric acid has given identical results. And we find identical effects of superphosphate on soils with different content of phosphoric acid. Everybody engaged in soil analysis knows this fact only too well, and some so-called practical-minded agriculturists therefore reject soil analysis as a means of advising the farmers about the effect of fertilizers. But taking in account the limitations of soil analysis, it is nevertheless possible to utilize the results to the advantage of the farmers.

It is evident, that if the soil analysis shows that the content of available phosphoric acid in a soil is low, the farmer will never be able to obtain high yields on this soil without phosphatic fertilizers. It is possible, even probable, that he will have to use other means too, nitrogen, drainage, etc., but phosphorus is necessary in every case.

On the other hand, if the content of phosphoric acid is very high, he can save the expenses on phosphatic fertilizers. Only if he uses extraordinarily heavy dressings with nitrogen, irrigation or other means to obtain very high yields, can he expect an effect from superphosphate.

But, of course, most soils are neither very poor nor very rich, and then the difficulties arise.

To utilize soil analysis it is necessary to compare the analytical results with the results from a great number of appropriate field-experiments. For this " calibration " of the soil analysis two different ways have been chosen.

The first is to compare the analytical results with the effects caused by a certain amount of fertilizers. As an example I shall give the results from about 2,000 Danish experiments with barley, dressed with 200 kilos of superphosphate per hectare (in addition to basal dressing).

Average effect of 200 kilos of superphosphate

Phosphorus values*	0—2	2—4	4—6	6—8	8—10	10—12
Effect (kilos kernel per hectare) ...	161	114	84	65	52	42

*One unit of " phosphorus values " corresponds to 20 p.p.m. of P_2O_5, soluble in diluted nitric acid at pH 2·5. One unit is approximately 50 kilos of P_2O_5 per hectare.

It will be seen how the average effect of superphosphate decreases with increasing " phosphorus values." Now, how can this calibration of the soil analysis be utilized ?

It needs no explanation that the average effect, say 161 kilos of

kernel, is the average of widely differing single results and the table has to be interpreted in the following way.

If the phosphorus value of a given soil is between 0 and 2, some hundred field-experiments have shown the average effect of superphosphate to be 161 kilos of kernel. Nobody can exactly tell what the effect will be on this soil, but the *probability* that superphosphate will give a profitable return is far greater than with soil whose phosphorus value is between 6 and 8, in which case the average effect is only 65 kilos of kernel.

If wanted, it is possible, knowing the distribution of the single results, to work out probability tables showing for each phosphorus value the probability of a certain effect. And the farmer may then decide whether he regards the probability of a profitable return as high enough to justify the use of superphosphate.

This line of utilizing soil analysis we have followed in Denmark. I admit, it does not give the farmer the definite answer to his question: will superphosphate pay? But, I think, this way of presenting the calibrated soil analysis is a sober one, giving all that the chemists in co-operation with the experiment workers are able to give. It emphasizes the limitations of soil analysis, and to the agricultural advisers, who are often consulted by the farmers, this method of presentation encourages the search for such factors as may cause the effect to deviate from the average effect. This line of calibrating soil analysis suffers from the disadvantage that it cannot answer the question: how much superphosphate should be used in a given case? This disadvantage is caused by the design of the field experiments, where only one quantity of superphosphate is used.

It could be overcome by experiments with increasing quantities of superphosphates, but such experiments we do not yet have in a number allowing the calculation of probability tables.

The other line followed in the utilization of soil analysis is based on the correlation between the analytical results and the yields instead of the increases in yields. As this line, I think, is more commonly followed and has some distinct advantages, I should like to go a little into details.

One advantage is, that in field-experiments the yields can be determined with greater accuracy—or lesser inaccuracy—than differences in yields.

The relation between available plant nutrients and yields are often expressed by the well-known MITSCHERLICH equation. In Denmark we prefer another equation, the hyperbolic equation

$$y = \frac{ax}{b + x}$$

where y is the yield, x the amount of a given nutrient, a and b constants. The constant a corresponds exactly to the MITSCHERLICH constant A, being the maximum yield obtainable. The constant b corresponds to the MITSCHERLICH constant C ("Wirkungsfaktor,") and it will easily be seen, that $x=b$ gives $y=a/2$, just the same relation as we have by using the MITSCHERLICH equation. But the hyperbolic equation

is easier to handle than the MITSCHERLICH equation and fits experimental data at least as well, often better. Now, if we turn to some experimental data, I may give the results from experiments with fodder sugar-beets. We have derived the equation

$$y = \frac{150 \cdot x}{1{\cdot}5 + x}$$

where y is the yield in quintals (=100 kilos) dry matter per hectare, and x the "phosphorus value" of the soil (x=1=50 kilos P_2O_5 per hectare) (2·5 million kilos).

This equation has been calculated on the basis of about 800 field-experiments in different years and on different types of soils.

Nobody will expect, I think, that all observed yields should correspond exactly to the equation. The equation expresses the average relation between phosphorus values and yields—and what may be read from this equation? The interpretation is, that under average conditions (average dressing with farmyard manure and with nitrogen, average pH, average drainage, etc.), a yield up to 150 quintals may be obtained, if the soil contains sufficient available phosphoric acid.

The equation further tells us, that if the phosphorus value is 1·5, we will only have half the yield we could have, and that the phosphorus value 6 corresponds to 80 per cent. of the obtainable yield.

This reasoning leads to a consideration of the factor b, which is analogous to the efficiency factor ("Wirkungsfaktor") C in the MITSCHERLICH equation.

It is well known that MITSCHERLICH postulates that the efficiency factor is invariable for a given nutrient, i.e. is independent of soil, crop, climate, etc. A thorough examination of several thousand Danish experiments has shown that this is not the case. The efficiency factor, be it b or C, varies from one experiment to another. But the efficiency factor for a given nutrient varies about an average value, which is different from one plant nutrient to another. And now it has to be remembered that any concave curve is an approximation to the real yield-curve, i.e. the graphical presentation of the relation between the amount of nutrient and the yield. It is, therefore, no wonder that by using the average value for the efficiency factor, it is possible to get a fairly good approximation to the experimental data.

This point is important. It means, that despite the variability of the efficiency factor it is possible by using the average value to draw sufficiently exact conclusions for practical purposes.

The constant a (MITSCHERLICH'S A) will vary much, dependent as it is in the first place on the crop, and for a given crop dependent on soil, climate, basal dressing, etc. But if we take the crop fodder sugar-beets, an examination of the data from experiments in which the phosphorus values have been varied, as a rule by different dressings, we find that we get fairly good approximations by using the value 1·5 for b, regardless of the value for a.

This enables us to generalize and calculate the following table, showing the relative yield corresponding to different values of available nutrient, expressed with b as a unit.

Yields, in percentage of maximum yield a. at varying values of nutrient

Nutrient	Yield	Nutrient	Yield	Nutrient	Yield
0·1 *b*	9·0	0·6 *b*	37·5	2·0	66·7
0·2 *b*	16·7	0·7 *b*	41·2	3·0	75·0
0·3 *b*	23·1	0·8 *b*	44·4	4·0	80·0
0·4 *b*	28·6	0·9 *b*	47·4	6·0	85·7
0·5 *b*	33·3	1·0 *b*	50·0		

From this table we may take it that the phosphorus value of a soil has to be 6—7 (4 *b*—5 *b*), when the phosphoric acid shall not be the limiting factor.

I want again to emphasize, that the use of an invariable value for the constant *b* is an approximation and I further want to emphasize, that in every case we cannot consider *b* (MITSCHERLICH's *C*) as independent of the crop. In Danish experiments *b* was found to be lower for cereals than for roots.

The line described above was originally proposed by MITSCHERLICH and has in the U.S. an enthusiastic advocate in WILCOX. But I may point to one disadvantage. The farmer cannot pay his fertilizer bill by an increase in yield of, say, 10%. He has to pay the bill by means of so many kilos of barley—or some other crop. The farmer, therefore, is not interested to learn that if his phosphorus value is 2, he will only have 67% of the maximum yield, and that, increasing the phosphorus value to 3 by means of superphosphate will increase his yield by 12·5%. He will immediately ask two questions: what is the weight of 12·5% and how much superphosphate must be applied to obtain this 12·5%, i.e. to raise the phosphorus value from 2 to 3?

It therefore seems that this way of interpreting the results of soil analysis is not better than the first way, using the increases in yield. Nevertheless I think that the latter way is the better, but some explanation of my reasons will be necessary.

The basal idea is, that the best economy—at least with respect to phosphoric acid, but to other plant nutrients too, except nitrogen—will be, that the soil contains "enough" of available plant nutrients. In modern agriculture, with its high working expenses, not the least being the high labour wages, it is a misconceived economy to save fertilizers. Apart from being in good "lime condition," the soil has to be in such "phosphorus condition," "potash condition," etc., that high yields can be produced.

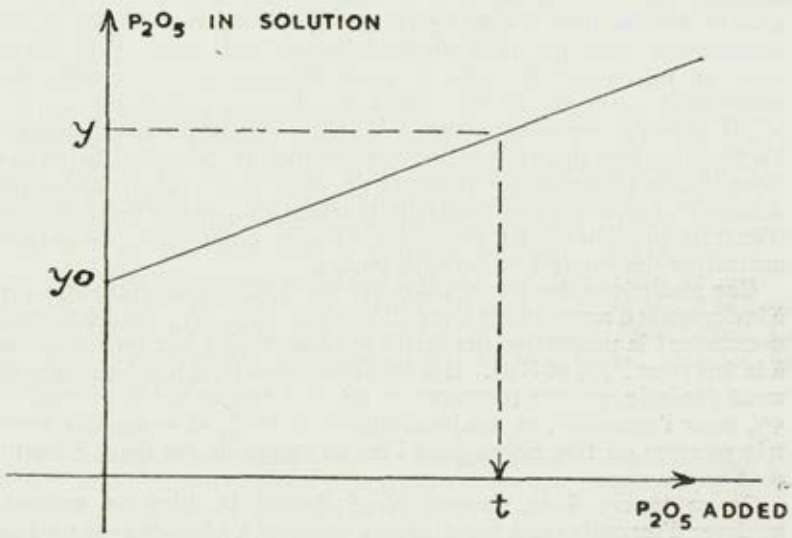
The effect which the application of superphosphate—and potash—has on soils, poor in these nutrients, is to be regarded as a soil amelioration. The phosphorus level has to be raised to the appropriate value. When this level has been established, the application of superphosphate may then be reduced to what is necessary for maintaining the proper level. The farmers have to regard the phosphorus problem in just the same way as they have learned to regard the lime problem. And—if this view might be accepted—it is important to determine the average value of the constant *b* (MITSCHERLICH's *C*) for the different nutrients and the different crops in order to point out the proper level.

But if this view is accepted, one important problem arises: is it possible to tell how much superphosphate must be applied to a given soil to raise the phosphorus level to a certain value? It seems to be

possible. And furthermore, I think that different methods of analysis allow for this possibility.

The principle I shall explain by means of the Danish method for determining the phosphorus values. In this method the soil is extracted by dilute acid, formerly nitric acid, now sulphuric acid. The amount of phosphoric acid going into solution is the basis for the calculation of the " phosphorus value " of the soil.

If now small amounts of phosphoric acid are added to the solvent before extraction one finds, of course, more phosphoric acid in the soil extract than by using the pure solvent. But the relation between phosphoric acid in the extract and the phosphoric acid added to the solvent is a rectilinear one, as shown in the figure.



The slope of the line may vary very much from one soil to another, from 0·95 for a light, sandy soil to 0·1 for an ochraceous peat soil.

If a soil has the phosphorus value *yo* and it is desired to raise this value to *y*, it will be seen from the figure how much phosphoric acid —*t*—one has to add to the soil to obtain the value *y*. This method of analysis, i.e., to add small amounts of the element to be determined to the solvent, was first applied by the late P. Damsgård-Sørensen, even though he used the rectilinear relationship for a somewhat other purpose. But the principle has turned out to be very useful and is now applied in determining phosphorus, potassium and manganese deficiency, enabling the chemist to tell the farmer how much fertilizer he has to apply to obtain a certain level of available nutrients in the soil.

The idea that it is possible for the chemist to tell the farmer what profit he may get by using fertilizers, we have to dismiss. But the chemist may be able to tell the farmer how much fertilizer he has to use to be sure that his yield is not limited by lack of phosphorus, potash, manganese and other plant nutrients. And I think that the chemist then will have met reasonable demands and that soil analysis will turn out to be a valuable means to the farmer.

SESSION 10

APPLICATION PRATIQUE DE L'ANALYSE CHIMIQUE DES TERRES EN FRANCE

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Jusqu'à ces dernières années, les analyses de terre effectuées en France, en nombre relativement petit (quelques milliers à 5.000 environ par an) ont eu davantage pour but de définir les caractères naturels de chaque type ou espèce de sol, que de déterminer les modifications apportées par l'homme à chaque parcelle de terre. Or il est apparu, comme dans d'autres pays de vieille culture morcelée, que la composition chimique de la couche labourée varie souvent davantage dans un même terroir, selon le passé cultural, que la composition moyenne d'une espèce de sol à une autre, du moins en ce qui concerne le pH (pour les terres non calcaires), l'humus (pour les sols minéraux), l'acide phosphorique, et dans une moindre mesure, peut-être, la potasse. Pour l'acide phosphorique notamment, la carte à l'échelle cadastrale a souvent l'aspect d'une mosaique reflétant l'importance des apports d'engrais phosphatés au cours des décades antérieures, ou la concentration des fumiers en certains points.

Une statistique des terres analysées par les Stations Agronomiques à la demande d'agriculteurs a été effectuée en 1939 (1) ; on a déterminé notamment la proportion des terres se situant dans une zone moyenne à la fois pour P_2O_5 et K_2O. Il a été ainsi constaté, d'une façon absolument générale, que ces terres moyennes sont en très faible proportion, 5% pour l'ensemble, et, toujours moins de 10%, alors que les terres très pauvres ou très riches pour l'un au moins de ces deux éléments sont nombreuses.

On se trouve donc souvent placé devant le dilemme suivant : analyser d'innombrables parcelles, ou renoncer à adapter avec quelque précision la fumure à la composition du sol, si ce n'est dans certains secteurs ayant conservé une certaine uniformité, comme des pays de pâturage où l'emploi des engrais ne s'est pas développé.

Certes, dans les régions soumises depuis longtemps à la culture intensive avec large emploi d'engrais minéraux, l'analyse des terres conduit assez rarement à conseiller des fumures PK s'écartant beaucoup de celles basées sur la restitution des quantités exportées en moyenne au cours d'un assolement, sauf dans le cas de terres particulièrement enrichies que l'on peut laisser s'appauvrir pendant un temps limité. Mais dans les régions d'agriculture peu évoluée, la connaissance des éléments particulièrement déficients, dont l'application suffit momentanément pour accroître à peu de frais les rendements, aiderait au développement nécessaire de l'emploi des engrais.

Tout récemment, un mouvement s'est dessiné en faveur d'une multiplication des analyses de terre, à l'instigation des services de vulgarisation ou d'organisations professionnelles. Le dispositif auquel on tend à s'arrêter actuellement consisterait à centraliser les analyses sur des laboratoires régionaux, Stations Agronomiques ou laboratoires annexes sous leur contrôle ; pour les conclusions pratiques à tirer des analyses, les conseillers agricoles s'appuieraient à la fois sur la docu-

mentation générale de la station et sur leur expérience locale. Un contact direct avec l'exploitation paraît en effet nécessaire pour formuler un avis judicieux. Les formules de renseignements imprimées se sont révèlées d'une faible utilité.

Les Méthodes

Prélèvement des Echantillons

En régle générale, chaque échantillon est prélevé en un emplacement déterminé, sans chercher à constituer un échantillon moyen de la pièce examinée, mais tout en mélangeant un volume de terre suffisant pour compenser les accidents locaux. Les échantillons ont été le plus souvent prélevés jusqu'à présent par les agriculteurs eux-mêmes, ce qui n'est pas l'idéal ; les conseils du technicien sont particulièrement utiles dans le choix des points de prélèvement.

pH.

Il est en général mesuré dans l'eau, avec rapport terre / eau = 1/2. L'emploi d'une solution d'un sel neutre ($CaCl_2$) 0,02 N par exemple pour compenser les variations de la concentration en électrolytes dissous et se rapprocher des conditions naturelles, qui facilite d'ailleurs beaucoup la lecture pour la méthode colorimétrique encore assez utilisée, n'est pas entré dans la pratique courante. Certains opèrent sur la terre humectée jusqu'à l'état pâteux (électrode de verre). Il serait sans doute souhaitable, dans le cas particulier du pH, d'adopter une méthode uniforme (par exemple pour pouvoir généraliser les résultats d'expériences culturales sur les phosphates naturels en terres peu acides).

Besoin en Chaux.

Les anciennes méthodes pour la détermination conventionnelle du déficit de saturation en bases, acétate de Ca, selon KAPPEN par exemple, sont encore utilisées. Mais dans les sols légèrement acides, fréquents en France, les valeurs trouvées sont très inférieures aux quantités qui peuvent être épandues sous forme de marne ; par ailleurs, certains sols de limon ne conservent leur optimum structural qu'en présence d'une petite quantité de calcaire. La connaissance du pH, jointe à une documentation sur le type de sol examiné, suffit dans beaucoup de cas.

Calcaire.

Il serait utile d'apprendre aux agriculteurs eux-mêmes à reconnaître la présence du calcaire ; il n'est pas rare de voir chauler des terres contenant une quantité notable de calcaire.

Une importance particulière s'attache à l'estimation du pouvoir chlorosant des sols où l'on se propose de planter des vergers ou des vignes sur porte-greffes sensibles au calcaire. La méthode préconisée par G. DROUINEAU (2) (10 gr. de terre ; 240 cc oxalate NH_4 0,2 N ; 2h.d'agitation) a fait ses preuves à cet égard.

Acide Phosphorique

Pour les terres non franchement calcaires, la méthode à l'acide citrique est la plus courante (30 gr. ; 150 cc acide citrique 2% ; 2 fois 4 h. d'agitation).

Pour les terres franchement calcaires, la méthode SCHLOESING DE SIGMOND à NO_3H dilué est utilisée faute de mieux. Certains utilisent dans tous les cas la méthode de TRUOG (SO_4H_2 à pH 3,0 avec grand rapport solvant/terre : 400 cc/2 gr.).

La méthode rapide acéto-acétique de MORGAN est utilisée (après quelque modification de la technique coeruleo-molybdimetrique) par certains laboratoires, et également par des particuliers ou des organismes non officials. La Station Agronomique qui l'a le plus employée (Dijon) la considère comme satisfaisante. D'autres laboratoires la jugent inférieure aux autres. Des ingénieurs de maisons d'engrais, appliquant cette méthode à l'aide d'une trousse ont trouvé une bonne corrélation entre ses résultats et l'importance des fumures phosphatées dans le passé.

Le choix de la méthode n'a sans doute pas une importance capitale si l'on se borne à comparer des terres de même nature. Mais en pratique, cette condition ne peut être strictement observée. Or, il est possible que certaines méthodes donnent une image particulièrement déformée de l'activité des phosphates du sol. En effet les acides dilués énumérés (SO_4H_2, NO_3H, acétique), à l'exclusion de l'acide citrique, ne séparent que l'une des formes d'acide phosphorique participant aux équilibres entre phases solides et liquides dans le sol en place ; de sorte que les terres où cette forme prédomine (tèrres alcalines même non calcaires) se trouvent surestimées par rapport à celles où la forme extractible par les alcalis dilués l'emporte. C'est pourquoi les méthodes tendant à séparer l'ensemble des 2 formes, comme c'est le cas en partie pour l'acide citrique seraient sans doute préférables pour comparer des térres (non calcaires) de nature variée.

Potasse

On dose en général la potasse échangeable (épuisement par acétate d'ammonium neutre). La méthode rapide acéto-acétique est utilisée, également en tenant compte éventuellement dans le dosage de l'ammonium présent, ou en le bloquant par le formol. Elle ne sépare naturellement qu'une fraction de K échangeable, d'autant plus petite que le pouvoir absorbant du sol est plus grand ; elle tient donc compte dans une certaine mesure du degré de saturation du sol en K ; il est cependant douteux que ceci constitute un avantage.

Humus et Azote

L'azote total est en étroite corrélation, avec la teneur en matière organique totale pour les sols labourés minéraux soumis aux mêmes influences climatiques générales et à des systèmes culturaux analogues. Il renseigne mieux sur l'état humique que le carbone dosé par oxydation humide, et surtout mieux que la perte au feu corrigée.

Conclusion

La plupart de ceux qui ont confronté les résultats d'expériences culturales au champ, bien conduites et suffisamment prolongées avec les résultats d'analyses de terre, reconnaissent à ces dernières une bonne valeur pratique, à la condition de ne comparer que des terres de nature voisine. Une difficulté de l'extension des analyses de terre réside dans le risque de se laisser aller peu à peu à un automatisme

dangereux des conclusions pratiques, à measure que la tâche de chaque conseiller s'alourdira. Cependant par des consultations s'appuyant sur les analyses de terre, et données sur place de façon suivie à un petit nombre d'agriculteurs éclairés susceptibles de faire école dans chaque village, il apparait possible de contribuer largement au progrès de la fertilisation.

(1) *Annales Agronomiques*, **9**, Novembre-Décembre, 1939.
(2) *Annales Agronomiques*, **12**, 1942, 441.

SESSION II

THE DEVELOPMENT OF SOIL FERTILITY RESEARCH IN THE NETHERLANDS

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1. *Introduction*

International congresses and committee meetings have had the inestimable value of establishing contacts between investigators from all countries and facilitating an efficient exchange of scientific data. Joint research has, however, so far been confined to methods of soil research with a bias towards laboratory work. This also applies to the joint labour of testing laboratory methods for the determination of the potash and phosphate needs of soils (Oxford 1935, Königsberg 1936 and Stockholm 1939). The present time with its many possibilities of communication and exchange of views may be ripe for all sorts of studies of a specialistic nature that are based on jointly organized field-trials. The advantage would be that in the co-operating countries interest would be focussed upon the problem of soil fertility and its importance for practical farming and the national economy.

With this object in view this paper on the development of soil fertility research in the Netherlands will especially refer to the close co-operation between field and laboratory experiments, which may be called a special characteristic of this development. This fact, we trust, may be a sufficient justification for choosing a subject which specifically deals with experience in our own country.

2. *General characteristics of the development*

The lectures delivered on "Soil Science and its application in the Netherlands" during the Fourth International Congress of Soil Science at Amsterdam, naturally touch various aspects of fertility research, although it was not emphasized as a central point of discussion.

Agricultural research in the Netherlands, which was not developed until the end of the 19th century, was with its small staff of scientific workers at the time confronted with so many problems of a diverse nature, that little attention could be devoted to soil scientific questions.

The characterization of the heavier soils was then based on the determination of weathering silicates, the mechanical composition, the humus and calcium carbonate contents and later also on the adsorption capacity and the mutual relation of the exchangeable cations. With the aid of these factors and a general knowledge of the profile and the agro-hydrological condition of the soil it was possible to draw a comparison between the different clay districts and to approach the value of new areas. The extent of this soil survey was comparatively small, however. Its character returns in later years in the chemical and physical soil descriptions in connection with hydrological problems (1).

The many lighter soils (especially the diluvial sandy soils) soon

claimed the attention of agricultural research, because the cultivation of crops was threatened by deficiency diseases. First it was the "Veenkoloniale Haverziekte" (grey spot disease), occurring after overliming of these humic sandy soils, which could be remedied by applying sulphate of manganese. Later, frequent mention is made of three soil defects, i.e. "Veenkoloniale Haverziekte," "Hooghalense Ziekte" (low pH)[1] and "Ontginningsziekte" (reclamation disease)[2], and an attempt was made by regulating the lime status to create favourable growing conditions (2). The investigation of the lime status dominated soil fertility research for a good many years.

It is characteristic of the Netherlands that nearly half its agriculture is carried on on diluvial sandy soils that are poor in plant nutrients (content of particles $< 16\mu$ less than 10% and humus contents of 2 to 14%). It is, therefore, not surprising that farmers soon began to appreciate the possibilities offered by the developing fertilizer industry. Also older clay soils which had been under cultivation for several centuries and had been exposed to the leaching influence of a surplus of rainwater (26% drainage water of the average of 705 millimetres rainfall), showed a favourable reaction to fertilization. Moreover, the rapidly increasing population (at present 275 per square kilometre) necessitated an intensive use of the soil and stimulated the reclamation of heath and moorland.

The following table gives an idea of the increase in population and a rise in the use of fertilizers.

Year	*Population*	*Use of Fertilizers in Tons of 1,000 kgs*		
		N	P_2O_5	K_2O
1920	6,865,000	25,000	70,000	2,000
1930	7,936,000	60,000	100,000	90,000
1940	8,923,000	100,000	110,000	110,000
1950	10,200,000	164,000	121,000	150,000

The above quantities are applied to 2,400,000 hectares of land under cultivation (1,080,000 ha. arable and horticultural land and 1,320,000 ha. grassland), i.e. 73% of the total area. If at present the average dressing of grassland (predominantly permanent grassland) is assumed to be 60 kgs N, 40 kgs P_2O_5 and 30 kgs K_2O per ha., the average quantities for arable land are 80 kgs N, 65 kgs P_2O_5 and 100 kgs K_2O per ha.

From this it will be clear that soil fertility research early in the 20th century was first and foremost required to state where, in what quantities and in what form fertilizers should be applied. In those years the important point was to raise the yield per ha. as much as possible. In a country like the Netherlands it was (and is) almost impossible to leave land with a rather poor soil to occupy land in a more fertile region. By dint of hard work and intensive manuring reclaimed heath and moorland could be rendered productive. In fact, soil testing acquired increasing importance since about 1920 and re-

[1]Much later it was shown that magnesium deficiency played an important part in the development of this disease (3).

[2]A cure was effected by adding town refuse compost and sulphate of copper, respectively. Mulder proved the cause of this defect (4).

ceived a fresh stimulus by the foundation of the Soil Testing Laboratory. Investigations were not confined to soil research ; due attention was also paid to the usefulness of chemical crop research for the determination of the various aspects of soil fertility. The applicability of the various methods was subjected to a severe test. Not only the yield, but also the quality of the crops was taken as a measure of the soil fertility. In this connection also the relation between single soil values and the botanical composition of grassland may be referred to (5).

However, the system of single values, which was gradually developed, should not only be looked upon as a means of providing dressing advice for the benefit of farmers. It has, especially through the efforts of O. DE VRIES, expanded to a system of soil fertility analysis.

Besides easily variable factors related to the fertility status, factors that are difficult to vary and which are related to the more permanent characteristics of the soil, were incorporated as single values in this system. This led to regional investigations, the results of which could be compared.

The importance of soil survey and soil mapping has been emphasized especially since 1940 by the Agricultural University at Wageningen (6). The results of the work of the Soil Survey Institute were put forward in 1950 on the occasion of the Fourth International Congress of Soil Science in an English edition of a book by C. H. EDELMAN : " Soils of the Netherlands." Also, city and rural planning, a necessity because of the steady increase in population, availed itself of the results of soil research. As far as the problem of soil fertility is concerned, it frequently proves that so much independent significance, in a quantitative respect, should be attached to soil factors which can be distinguished in the units of the Soil Survey, that their combination into units leads to a too simple representation of the soil fertility. Of late years a close co-operation has developed between the work of the Soil Survey and the above-mentioned direction of the single values.

3. *From the determination of single values to a system of soil fertility analysis*

It requires considerable specialized study to recognize a factor of soil fertility and to express it in a figure. But it is equally important to test the single value thus obtained for its significance. In industrial language this may be called a semi-technical application of a method. The specialist investigator in this way acquires a larger sphere of work and may come to realize the limited significance of his creation.

In testing the single values, large-scale fertilizer experimental fields and other trial-fields have been employed. Soil fertility is determined by means of field-trials and laboratory research should rather be looked upon as a link between trial-field work and farming practice. The obtaining of data concerning soil fertility and the testing of single values have therefore gone hand in hand. The development of field experimentation is inconceivable without soil research and other laboratory work. However, in the following chapter it will be made clear that in connection with the numerous uncertainties and interactions many difficulties attach to the rendering of advice to individual farmers on a basis of single values.

Investigations have taught us that the single values in respect to their influence on the soil fertility, cannot be considered separately but have to be studied in their interactions. It is not only the interplay of fertilizing factors we are concerned with, but also the influence of more constant soil factors upon these (humus and clay contents, lime status, etc.). This interaction required the laying out of series of trial-fields and trial-spots, distributed all over the country, and the development of a field-trial technique. Thus the knowledge of soil fertility was enlarged to a high degree. It proved to be possible to make a thorough soil fertility analysis of an agricultural region and to use it in evaluating agricultural conditions of the whole region (7).

The relations obtained between the results of field and laboratory experiments call for an interpretation. Biological knowledge of the habits of the crops and physical, chemical and biological insight into the processes in the soil are indispensable. For example, the study of ion activities may contribute to a correct understanding of the types and the mutual level of the yield curves (8). It is remarkable to what extent in general more fundamental research can be directed and promoted by a systematic elaboration of these single-value tests. It has led us to the conviction that relations between single values can form an important contribution to physical-chemical soil research of a more fundamental character. It goes without saying that in this respect, too, allowance should be made for interactions.

The execution of the above-mentioned combination of field and laboratory research naturally requires a well-equipped mechanism for trial-field management and soil testing, which in its turn tends to stimulate the development of this system of investigation. The fact that the application of the results of soil testing is very closely connected with the results of field research is the cause that the latter exerts a preserving influence, and is sometimes inclined to be conservative. Conversely, soil testing with its direct interest in farming practice, aims at quick and cheap determinations, so that there is hardly any risk of rigidity in the determination system selected. It will be clear that a uniform system of soil testing which is carried out throughout the country, is a first requisite for the control of the soil fertility of the whole country.

The Advisory Service, which has greatly extended in the last few years, constitutes an indispensable support in developing the system of soil fertility research and promotes its efficiency to a high degree. Finally it is worth noting that agricultural colleges and schools are of inestimable importance, because education and agricultural training impart confidence in scientific methods.

4. *Scientific development of soil fertility research on a basis of single values*

Working with single values in field-trials leads to a preference for many experimental treatments in series with a small number of, or even no, parallel plots to a smaller number of experimental treatments with many parallel plots (9).

The reason is that a single value represents a soil status which is subject to variations from spot to spot and also shows differences between parallel plots of one treatment. This is an inducement

to plot data of crops (contents, yields, qualities, etc.) against the single values of all the trial-plots and also to represent the results graphically. This procedure was even encouraged because of the aim to obtain optimum yields by means of fertilizers. The realization of complete yield curves was thus attempted. Working with parallels is especially practised when it is not possible, or not immediately possible, to express quantities of fertilizers applied in a change of soil factor. Lime experiments and nitrogen trial-fields may be regarded as extremes in this respect. In fact, the addition of lime soon brings about a change of the lime status, whereas as yet there is no question of an exact measure for the "nitrogen status" of the soil. Fertilizer trial-fields with phosphate and potash are in an intermediate position in this respect. In a series of fertilizer trial-fields with phosphate or potash, respectively, we are concerned with both "status" and "quantity." In this way it is possible to express yields with a different "status" as percentages of the optimum yields and to plot the relative figures thus obtained against the single values of the untreated plots. In the further development of our research it appeared that this procedure may include a restriction, i.e. a relative yield may be high because the optimum yield remains low through some limiting influence. The latter is often evident in fixation phenomena. It should, therefore, never be omitted to plot the absolute yields of the plots treated in the same way from all the experimental fields of one series (first the untreated plots) against the single values. This development led to the replacement of series of simple fertilizer quantity fields, laid out in an agricultural region, by experimental spots distributed over this region and possibly receiving diverse treatments. Their results may be treated by a graphic method of statistical analysis—the so-called polyfactor analysis (10).

The yield curves obtained by the graphic method are always drawn by hand through the dot diagrams. An attempt is always made to reduce the deviation of dots by eliminating the influence of other single values, after which a correction of the curves can be introduced. We are here concerned with problems of curvilinear adjustment. Investigators of different training and working in different spheres of activity have employed this working method, which no doubt brings out the perspectives of their investigation more clearly than would otherwise have been possible (11). In general, little consideration has been given to the mathematical basis of the method. The criticism that the reliability of the results obtained may possibly have been sacrificed to the clearness is justified. The problem is now being thoroughly studied by mathematicians.

In former years observations were given on standard deviations of various aspects of trial-field work and on analysis methodology. First this work dealt with questions like the most desirable size of the experimental plots, standard deviation of the yield determination and of the analysis of the soil (12) and later it was continued by evaluating usefulness of various methods of soil research. The latter problem was accurately studied and the standard deviations of soil sampling, of analysis and of yield determination, together with methodical error and the efficiency, were distinguished (13).

The methodical error in a restricted sense is caused by the insufficient agreement between the ways in which the various methods give a

measure for the characteristic of the soil to be determined. The efficiency refers to the extent to which a method can express the reaction of the crops. Several methods of determining phosphate and potash were compared and studied in relation to the crop yields; for phosphate :- P-citric acid, P-number (soluble in water at 50°C,) P-HCl, P-DIRKS-SCHEFFER, P-content (of the crop in an early growing stage), P-NEUBAUER, P-Aspergillus; and for potash :- K_2O-1N HCl, K-5% HCl, K-Asp., K-Neub. and K-content of the crop. Also several methods of determining the pH or the lime status of the soil were subjected to a critical examination, i.e. pH-H_2O and pH KCl (without drying the samples and after drying, respectively) and the V-number (degree of saturation). In this way valuable data were obtained.

5. *Soil fertility in the Netherlands and its control*

It is possible through co-operation between field and soil research to make an estimate of the possibilities of improving the fertility of the soil by manuring and soil improvement. This was done after the Second World War with respect to various factors (14). For example, the yield of arable land could be increased by 15-20% on an average in case of a more rational application of fertilizers, i.e. by 10% in case of a more efficient addition of nitrogen, by 1-2% with phosphate, 2-3% with potash and 3% with lime. Also with magnesium and trace elements improvements could be made. For permanent grassland this percentage was estimated at 20% through improving the phosphate status and potash status of the soil, provided at the same time other improvements were effected, e.g. in drainage conditions. The possibilities with nitrogen on grassland are naturally great; the yield could definitely be increased by 40% on condition that changes are also introduced in the management of the farm.

More intensive applications of organic manure on arable land, together with improvement of the soil structure, would bring about considerable improvements in many agricultural districts. But as yet it is impossible to give an average percentage. The methods to describe the nitrogen condition of the soil and the soil structure, which are needed to form a link between the results of the field-trials and the farming practice, are still in process of experimentation at the laboratory and are tested on the trial-fields. The possibilities of improvement of permanent grassland through a more intensive use of organic manure are, on the strength of statistical investigations, estimated at 5%.

These estimates tend to focus our attention on factors which are too much neglected. Thus it proves that losses of lime and magnesia are still insufficiently supplied, so that deficiencies in these respects are increasing.

In the Netherlands, effecting improvements is left to the initiative of the farmers, who are assisted and instructed by the Advisory Service. It is our opinion that regional investigations and conjointly organized improvements may, with Government support if necessary, ultimately lead to the desired end. In a few cases this is put into practice. In this connection consideration is given to the possibility of effecting improvements in the fertility status during re-allotment

and reclamation operations. Co-operation between soil survey and fertility analysis will doubtless have a beneficial effect on regional development.

Two other investigations of considerable extent may be worth mentioning: production level research and the investigation of the agro-hydrological condition of soils under cultivation. The former research, conducted by the Central Institute for Agricultural Research, deals with the determination of the yield in 3,400 places (1 : 600-700 ha.) over a few years, at the same time taking account of many details about farm management, crop cultivation and soil fertility. The results are statistically represented and treated in various directions. The investigation of the agro-hydrological status of the soils, which is financed from the M.S.A. funds, aims at procuring rational methods to control the water condition and to acquire an efficient distribution of the available amount of water. In both these investigations measur ing and weighing will, in many cases, be replaced by estimations and advantage will be taken of the estimation technique which has been developed in the last few years (15).

6. *Final remark in connection with the task of the Commission for Soil Fertility and Plant Nutrition of the International Society of Soil Science*

In the foregoing chapters we have not confined ourselves to a survey of soil fertility research but have also pointed out the importance of putting its results to practical effect. It seems to us that this close contact between field and laboratory research, which is the best stimulus in this direction, should be the basis for an international exchange of information. Our International Society can do much along these lines, the more so as its scope of activities is getting more and more extensive. Commission IV will, by means of results of fertility investigations in the countries and regions concerned, be in a position to indicate the lines on which the international co-operation of the commissions for Soil Physics, Soil Chemistry and Soil Biology should be conducted and to acquaint many soil scientists of characteristic differences in soil fertility and production level between countries in the same climatic zone.

It will not be difficult to find subjects which lend themselves to international experimentation and discussion. We would suggest, for example, the relation between organic fertilizers, structure and nitrogen condition of the soil or the exchange between lime and potash status or the various aspects of the phosphate problem.

It is our intention to illustrate these subjects by examples at the meeting.

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SESSION II

VERIFICATION OF CHEMICAL SOIL AND PLANT ANALYSES: GENERAL CONSIDERATIONS

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It is necessary that the methods employed when investigating the co-variation between chemical soil or plant analyses and the production of dry matter take into consideration the knowledge one has at any time of the shape and position of yield curves in the co-ordinate system.

Investigations on the shape and position of the yield curve under the influence of the factors of production of dry matter must, in the main, be carried out on the basis of the determination of yield from pot or field experiments, to which are added increasing amounts of a plant nutrient in minimum so that the relationship between the production of dry matter and the amount of the nutrient in question added can be determined; in such experiments one or two additional plant nutrients have often simultaneously been varied systematically. Generally the investigations so far have been carried out without appreciable control e.g., climate factors, etc.

When investigating the shape of the yield curve it is further essential that such investigations are carried out by determining the relationship between the production of dry matter and the absorbed amount or amounts of plant nutrients which are or may come in minimum. That investigations of this nature should be carried out in this way appears from diagrams 1, 2 and 3 in which the abscissa and the ordinate units are the same in all three figures.

Fig. 1 (all the following figures are more or less schematical) shows the relationship between the production of dry matter and the addition of increasing amounts of a plant nutrient (t), which is in minimum. Fig. 2 shows the relationship between the amount absorbed (o) of the plant nutrient in question and the amount added (t). The shape of this curve would hardly be altered by work with true coefficients of absorption. Finally, the graphical representation in Fig. 3 shows the relationship between the production of dry matter and the absorbed amount (o) of the plant nutrient in question.

This method (Fig. 3) of investigating the shape of the yield curve has two advantages. If the curve is S-shaped it may be difficult to observe in the graphical representation in Fig. 1; but as the coefficient of absorption must fall as the t-value rises, the concave part of the yield curve (observed at small t-values) will be easier to observe on investigating the relationship between the production of dry matter and the absorbed amount (o) of the plant nutrient in question (Fig. 3). It is furthermore obvious that the steepness of the yield curve (rate of production of dry matter) in Fig. 3 depends on the size of the coefficient of absorption and its variation with increasing t-values. This method of investigating the shape of the yield curve has further-

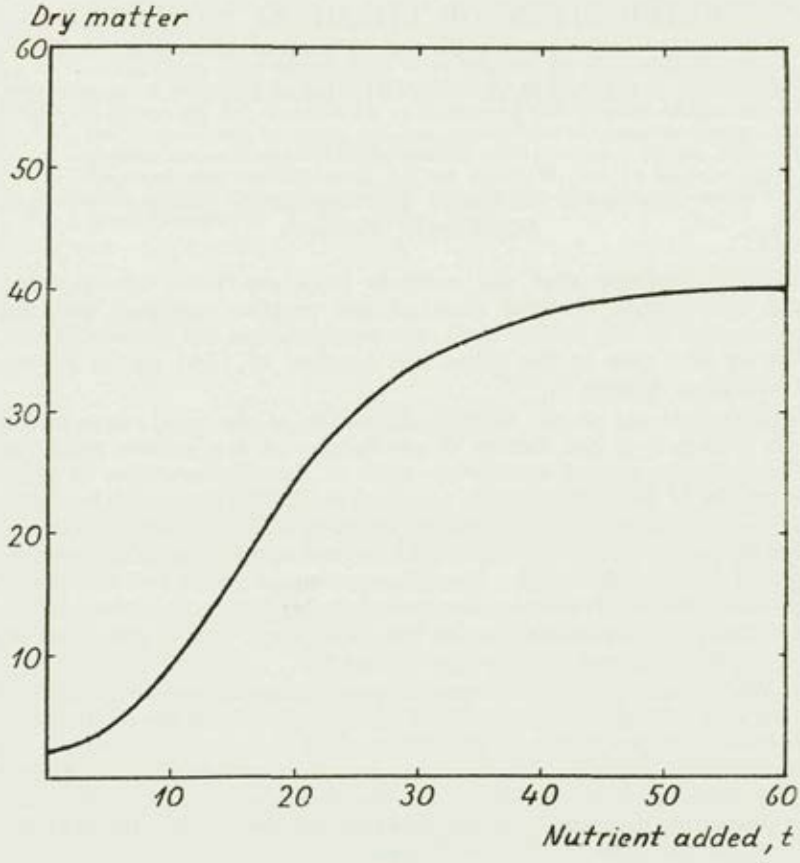


Fig. 1

more the advantage that one of the extreme points of the actual yield curve coincides with the zero point of the co-ordinate system; this extreme point is accordingly fixed.

Fig. 4 shows a schematical graphical representation of actual experimental results from both pot and field experiments which further illustrate the advantage of this method of investigating the course of the yield curve. The parts of the curves which are fully drawn are based on experimental results, while the parts of the curves shown with dotted lines represent interpolations between the zero point of the co-ordinate system (one of the extreme points of the curves) and the lowest determined yield corresponding to the smallest experimentally determined absorption (o) of the plant nutrient in question. Apart from the border-line cases of little practical importance which could be imagined to arise when seed containing certain plant nutrients is sown in a growth medium which does not contain the nutrients in question, it is certain that the three types of yield curves 1, 2 and 3 (Fig. 4) must all have one of their extreme end points in the zero point of the co-ordinate system, because both production

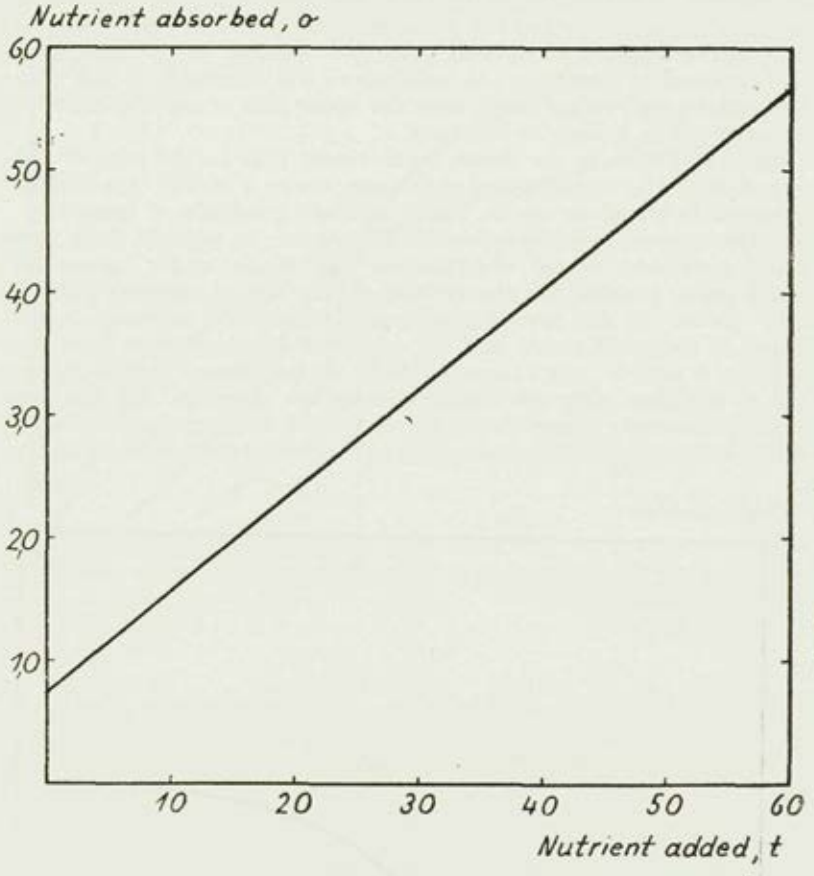


Fig. 2

of dry matter without absorption of the plant nutrient and absorption of the plant nutrient without production of dry matter are equally inconceivable from a physical point of view.

The factors which determine the shape and position of the yield curve (interactions) can be divided into four large groups.

1. *The soil factors in the widest sense.* Here are included pH-values, available amounts of nitrogen, potassium, phosphorus, manganese, and copper, etc., available water, amounts of farmyard manure, etc.
2. *Climate factors.* The quantity and quality of the light ; the temperature of the air (and soil) ; the degree of humidity of the air.
3. *Crop.* Family, genus, species, variety.
4. *The stage of development of the harvested crop* (time factor).

Whether we observe the whole S-shaped curve or a part of it, or whether the curve is S-shaped at all is, as far as we know at present,

determined by variations in the above-mentioned factors. According to our experience so far, the possibility of observing the S-shaped yield curve appears to depend upon the severity of the deficiency of a nutrient in question. In soils where the deficiency is not very pronounced (i.e., rather small) only the upper part of curve 1, curve 2, or curve 3 (Fig. 4) may be observed.

Our experience so far shows furthermore that in the case of the macro-elements, nitrogen and potassium, curve 2 in Fig. 4 is seldom observed in its whole course under ordinary condition of manuring; but one can supposedly meet the case—also as regards these two plant nutrients—where observations are made under conditions which make possible the observation of the part of curve 3 which is fully drawn. In the case of phosphorus, which with reference to the shape of the yield curve may be described as an element behaving between a macro- and a micro-element, the fully drawn part of curve 2 can in addition, although less frequently, be observed. In the case of micro-elements, observations are very often made under conditions which make possible the observation of the fully drawn curves 2 and 3.

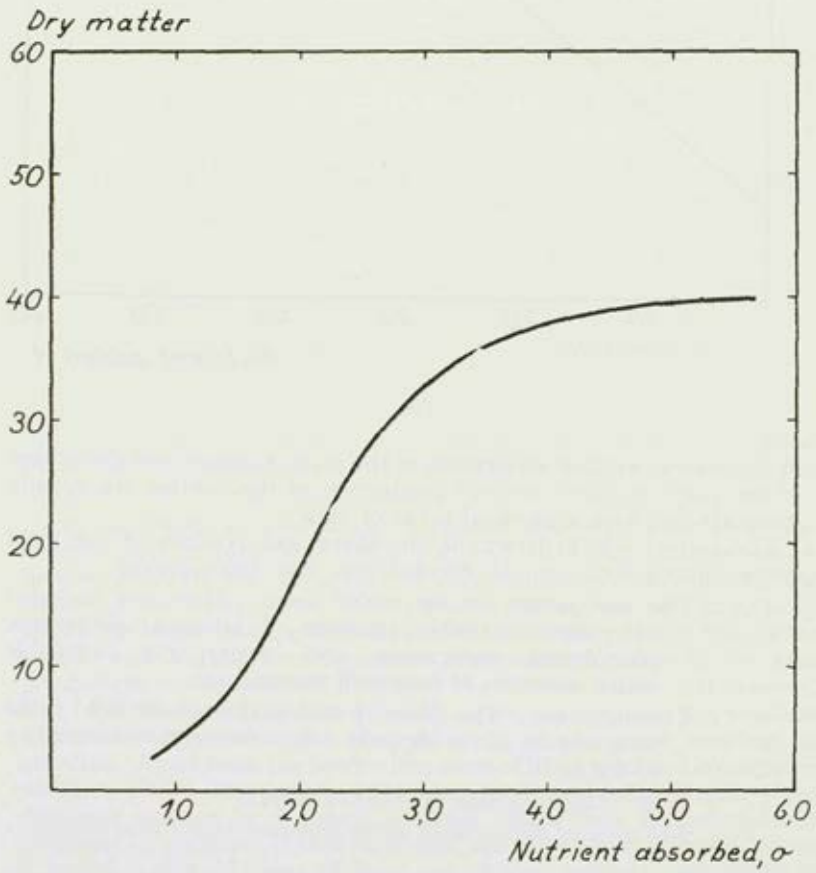


Fig. 3

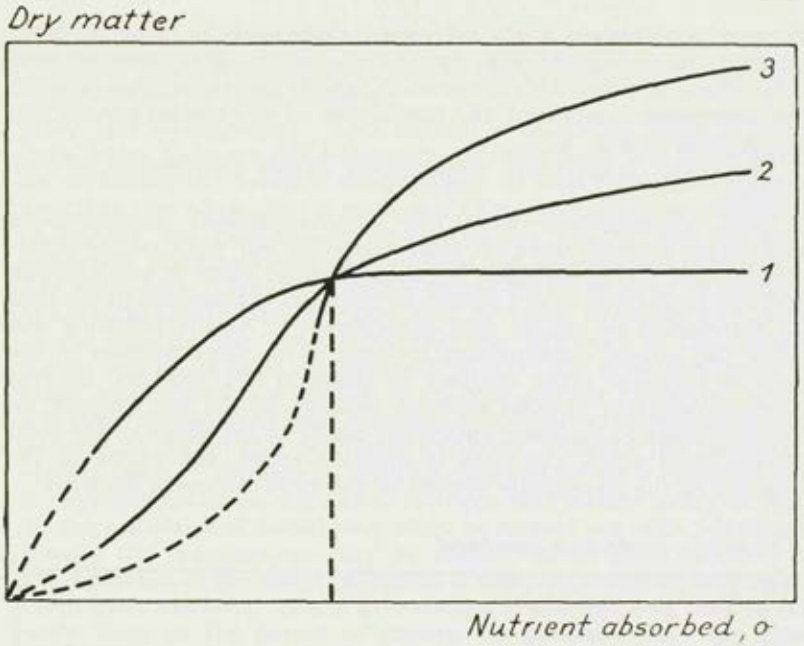


Fig. 4

It is further possible that a large addition of other factors of dry matter production not in minimum, may displace the yield curve in the case of the plant nutrient which is in minimum towards curve 3 (in Fig. 4).

Other experiences show furthermore that certain crops with a high capacity for absorbing a given plant nutrient in minimum in a given soil will give the impression that we have a soil relatively rich in the nutrient in question, i.e., we observe the upper parts of the curves, while another crop with a low absorbing capacity may give evidence of an S-shaped curve.

Finally, the yield curve seems to be most markedly S-shaped in the case of young, immature plants. Only little is known about the influence of the climate factors on the shape and position of the yield curve.

At present the following criteria seem usable in support of an opinion as to whether work is being done under conditions where the S-shape of the yield curve may be observed.

1. For the same crop, the lower the yield (at the basic treatment), the greater the probability of an S-shaped yield curve being observed.

2. If there is a very marked deficiency of the plant nutrient in question (basic treatment), the amount of supporting tissue in grasses will be low.

3. Typical and widespread symptoms of deficiency of the plant nutrient in question in the replications which receive basic treatment make it probable that the S-shape of the yield curve is observed.

4. If the yield curve is S-shaped, the chemical composition of

the crop with respect to the percentage content of the plant nutrient, which is most in minimum, and for the other plant nutrients will often show the courses of the curves as regards the relationship between the percentage content of the production of dry matter graphically represented in Fig. 5.

These four criteria are methodically rather independent of one another.

What consequences have the above-mentioned considerations and future research work on yield curves for our work on the determination of the co-variation between chemical plant or soil analyses and the production of dry matter of plants as experienced in the field or determined by pot or field experiments? As the following will show, the general consequences are mainly the same whether in the case of chemical plant analyses or chemical soil analyses, because the interpretation of these analyses depends, in the last instance, on whether there exists basic knowledge partly of the shape of the yield curves from which the yield in question arises, and partly of the position in the co-ordinate system of the yield curves in question.

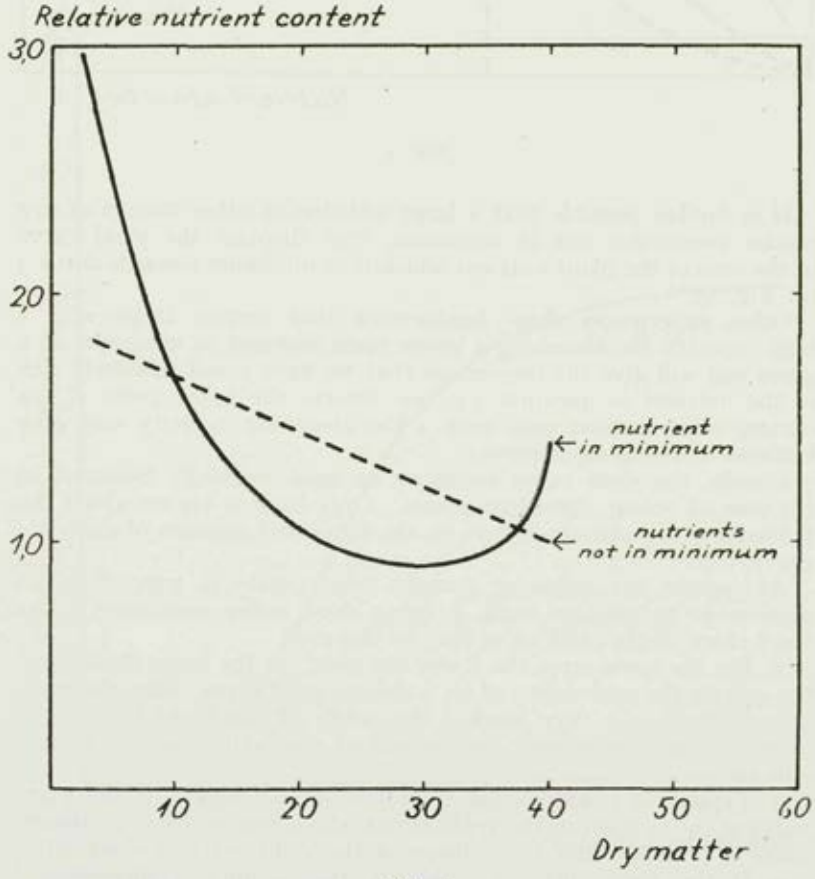


Fig. 5

4. Verification of chemical plant analyses

Several different methods are used in the interpretation of chemical plant analyses (or tissue analyses).

(*a*) *Spot investigations.* This method is of special value in those cases where there are still few results available from field experiments for evaluating the results of the analyses. At least three plant samples are taken (the whole crop or parts of it after a preceding investigation), in healthy, less healthy, and bad crops (*see* Fig. 5), and the most important plant nutrients contained in the samples are determined. The whole plant, organs, or parts of organs can be sampled for analysis. When sampling for analysis, care must be taken to choose such parts of the crop (or the whole crop) that the difference in the analysis figures will be as large as possible (Fig. 5); the same care must be taken when choosing a method of analysis and the extracting agent. For many elements the total contents (in dry matter) should supposedly be used to obtain this maximum variation, while in the case of an element as e.g., nitrogen, a fractionation resting on a chemical and a physiological basis, e.g., total nitrogen and nitrate nitrogen (e.g., in the leaf-stalks of beets) may often be carried out with advantage. Finally the examinations may be carried out in early summer, as the difference in the analytical results is then, as previously mentioned, often most marked; this is in accordance with the fact that at this early stage in the period of growth we generally have the most pronounced symptoms of deficiency in agricultural and horticultural crops.

According to this interpretation variations in the soil factors 1, (page 311) are reduced to a minimum, e.g., by sampling simultaneously with as small a distance as possible; this is generally most easily effected for micro-elements according to their steep yield curves. All the remaining factors grouped under 2, 3 and 4 (page 311) are kept constant or as nearly so as possible by this method of sampling. It is of vital importance that this elimination be successfully carried out when sampling as otherwise one may happen to measure the effect of the displacing of the yield curve in a horizontal direction (positive or negative direction along the abscissa), or in a perpendicular direction (positive or negative along the ordinate) under the influence of other factors of production of dry matter having a disturbing, as yet partly unknown, influence on this method of interpretation. By simultaneous sampling with as small a distance as possible one ensures as far as possible that the varying yields corresponding to the samples originate from the *same* yield curve (the same plant nutrient). This simplifies the interpretation as used in Fig. 5 where special attention then is paid to the *shape* of the yield curve.

(*b*) *Interpretation by means of experimental results from qualitative field experiments.* Fig. 6 shows the relationship between $\triangle$dry matter (curve 1, Fig. 4) and the percentage content in the crop of the nutrient in minimum. According to this interpretation variations occur from place to place and from one year to another in (1) the soil factors, and (2) the climatic conditions. On the other hand (3), the nature of the crop and often (4) the time of sampling, i.e., the stage of development of the crop, may be kept constant. Variations of factors within

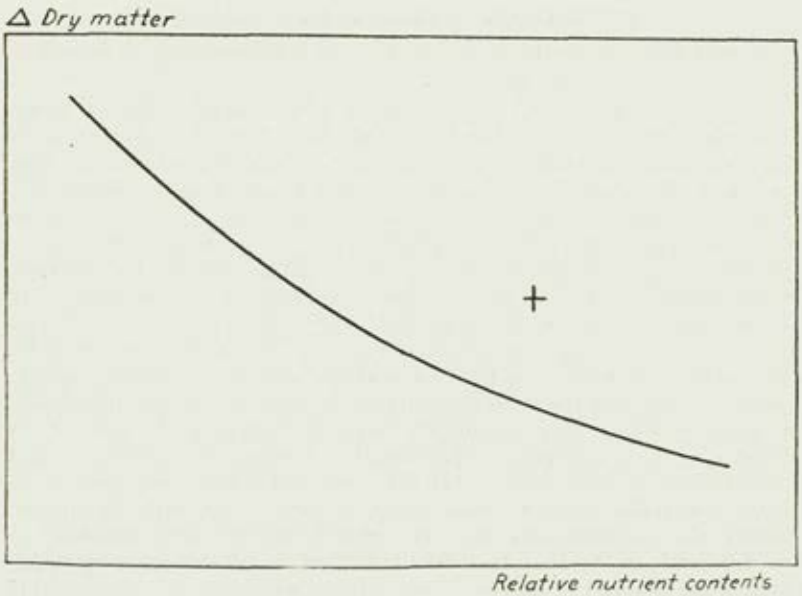


Fig. 6

the factor groups (1) and (2) may cause a displacing of the curves (Fig. 4), so that the relationship in Fig. 6 cannot be synonymous; e.g., the perpendicular dotted ordinate in Fig. 4 gives the same production of dry matter and the same absorption, i.e., the same percentage content of nutrient, but △ dry matter is widely different. This condition is also clearly shown by curve 2 in Fig. 4; here the law of diminishing returns does not hold and serious misinterpretations may arise in the interpretation unless the utmost care is taken. We may, in other words, find that for instance, a high percentage content of the particular nutrient in minimum is associated with a low production of dry matter, in which case there is the possibility of a large increase in yield (cf. cross in Fig. 6). This would mean a serious error in the interpretation.

The varying shape and position of the yield curve in the co-ordinate system under the influence of variations within factor groups (1) and (2) may, in this form of interpretation, necessitate a rather thorough statistical grouping of the experimental results under consideration. This grouping must proceed from physical and chemical, and gradually also climatic, determinations of the conditions for production of dry matter (factor groups (1) and (2), page 311) present in the various cases, special regard being paid to the factor or factors which experience has shown to have the greatest influence on the shape and position of the yield curve.

(c) *Verification by means of results from quantitative field experiments.* Results from such experiments make it possible to determine the optimal percentage contents (the percentage contents which give

the greatest net yield) of the plant nutrient which is in minimum. The method will not be outlined but it is evident as a matter of course that the various shapes of the curve and its various positions in the co-ordinate system from case to case can complicate this interpretation to a very considerable degree.

B. Verification of chemical soil analyses

The verification of chemical soil analyses is in principle entirely analogous to the verification of the chemical plant analysis. The following results may be used in the interpretation: (a_1) results from spot investigations, (b_1) results from qualitative field experiments, and (c_1) results from quantitative field experiments.

(a_1) *Spot investigations.* The basis of the verification is the same as for chemical plant analyses. Figs. 7, 8 and 9 show the transition from the ordinary yield curve (Fig. 7; curve 2 in Fig. 4), which represents the relationship between the production of dry matter and the amounts of a plant nutrient added (and present originally in the soil), which is in minimum, e.g., Mn, to the yield curve (Fig. 9), which represents the relationship between the production of dry matter and the soil's content of available manganese (aMn).

The transition from the abscissa's units in Fig. 7 to the corresponding units in Fig. 9 is shown in the graphical representation in Fig. 8, which can be drawn on the following basis:

According to e.g., FREUNDLICH'S adsorption equation we have

$$v = K\,(aMn)^n \qquad \text{(1)}$$

where v is the amount of manganese adsorbed by the soil and aMn is the equilibrium concentration of manganese expressed in aMn values,

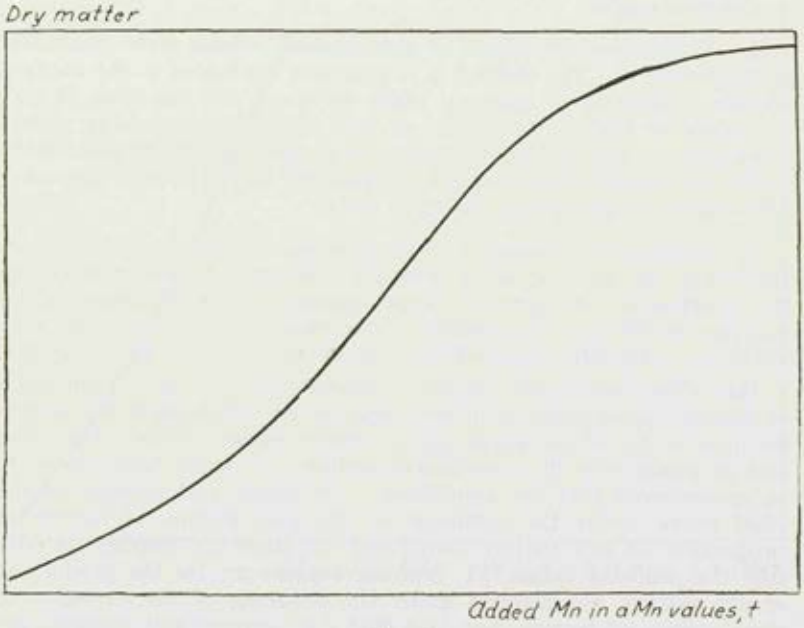


Fig 7

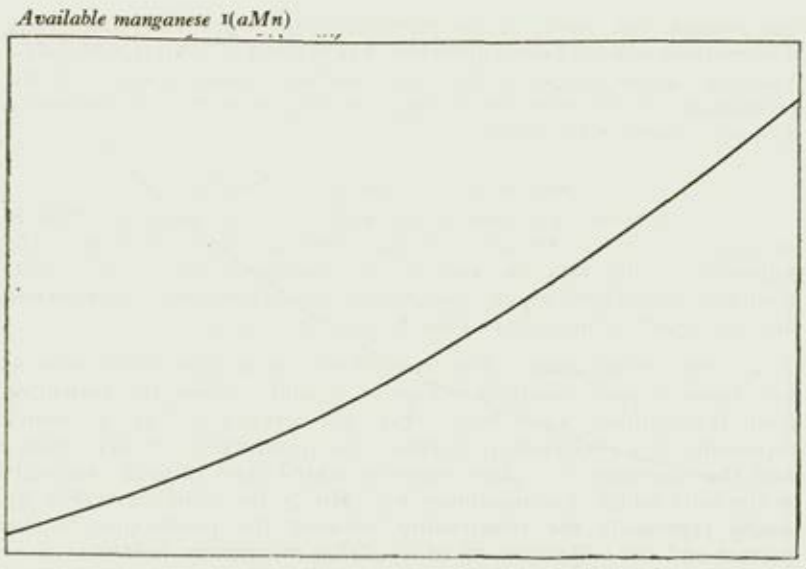


Fig. 8

while K and n are constants; if t is the amount of manganese added expressed in aMn values, we have

$$t - v = (aMn) \qquad (2)$$

In general, work is done with the part of the curve in Fig. 8 which is almost straight.

(b_1) *Verification by means of experimental results from qualitative field experiments.* The method is in principle analogous to the method for the verification of chemical plant analyses. On the basis of e.g., the curve in Fig. 9, we obtain at first rising increments in yields, △dry matter, next falling increments in yields, and finally (not shown in Fig. 9), sharply rising negative increments in yields with increasing aMn values (constant increments of aMn).

(c_1) *Verification by means of results from quantitative field experiments.* Here, too, the method is in principle analogous to the method for the verification of chemical plant analyses. For example, under varying conditions it is possible to determine, e.g., the optimal aMn values, i.e., the aMn values which economically are most advantageous.

The above-mentioned general considerations on the verification of chemical plant and soil analyses rest on the rather slight knowledge we have so far of the shape (in its whole course) of the yield curve and its position in the co-ordinate system. It ought furthermore to be remembered that the expression: the shape and position of the yield curve under the influence of the four groups of factors of production of dry matter mentioned on page 311, implies not only that the ordinate values, i.e., various expressions for the production of dry matter, are changed under the influence of the variation of these groups of factors, but also that e.g., certain soil analyses are

influenced—even on uncropped soil—by a long series of these factors of production of dry matter ; in other words it is difficult in functional investigations of this nature to disentangle causes from effects (interactions). Causes and effects must be treated summarily. At present the investigations concerned are purely technical.

At the practical carrying out of the verifications of statistical grouping for the methods, (b) and (b_1), (c) and (c_1), one must first and foremost work with the factors of production which experience has shown

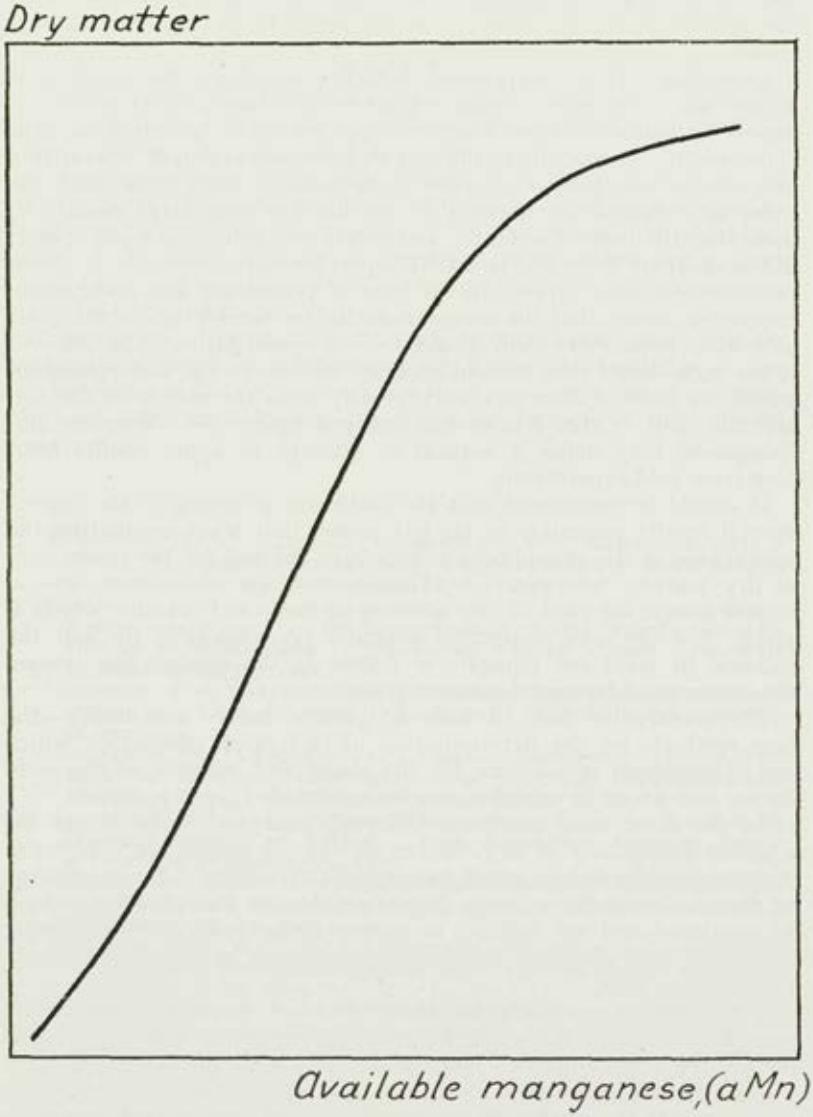


Fig. 9

to have a great influence on the shape and position of the yield curve, and which can be regulated provided that the factors in question can be expressed numerically. The factors of production of dry matter which are less important as regards the position and shape of the yield curve and those which cannot be regulated (e.g., climate factors) or determined (purely analytically) will, at the practical carrying out of the verification, mean an uncontrollable variation of the yield figures; this variation, the size of which to some degree depends on whether the experimental results are obtained from short—or long—term field experiments, must enter into the final answer to the agriculturist and cause a varying error to be attached to this answer.

According to Danish experience so far it is possible in the verification in the case of phosphorus and copper to use results (crops harvested mainly at maturity) from long-term qualitative or quantitative field experiments. This is due to the fact that the soil's content of available phosphorus and copper changes rather slowly with time, and the collected experimental material so far has not been large enough to show that the type of soil, etc., and rotation of crops have any special influence apart from the fact that superphosphate ought to be given exclusively to root crops. In the case of potassium and manganese, experience shows that the verification can be carried out on the basis of results from short-term qualitative or quantitative experiments; it has been shown that the soil analyses for manganese and potassium which are used in Denmark vary greatly with the nature of the soil and the crop. Other less mobile analysis figures for potassium and manganese may make it natural to attempt to apply results from long-term field experiments.

It should be mentioned that the statistical grouping of the experimental results accessible so far has shown that when evaluating the importance of the phosphorus available in the soil for the production of dry matter, determined by Danish methods of analysis, special regard should be paid to the amount of farmyard manure which is given. For the same content of available phosphorus in the soil, the increase in yield for phosphorus added is the smaller the greater the amounts of farmyard manure given.

The problem is then to find—at present *purely statistically*—the best methods for the determination of factors of production which are of dominant importance for the shape and position of the yield curve, and which in addition can be regulated.

At the same time the more thorough analysis of the causes for a given production of dry matter should, of course, be continued. A group of these factors which causes great variations in the production of dry matter is the climate factors, and even though they cannot be regulated and are difficult to express numerically, it is becoming more and more necessary that the research work be extended to cover this field as well.

The question as to whether the method of the spot investigation should be used in the verification or the methods which are based on results from short—or long—term field experiments of different kinds, depends on several conditions, and also in various ways on the quantity and the quality of the results of field experiments available. In countries and in fields of work where results from field experiments

are for different reasons still scarce, the method of spot investigation can be used with great satisfaction if the working rules laid down here are adhered to.

But in any case it is of decisive importance that investigations on the co-variation of the results of the analyses and the results of the experiments, and (or) the observations on the growth of the crop in the field, be followed by a parallel increased basic knowledge of the probable shape and position in the co-ordinate system of the underlying yield curves.

SUMMARY

1. General studies of the shape of the yield curve and its position in the co-ordinate system are important for the choice of a method for the evaluation of chemical plant and soil analyses.

2. Investigations into the shape of the yield curve in the case of ordinary plant nutrients ought to be done by determining the relationship between the production of dry matter and the absorbed amount of the plant nutrient in question, consideration being paid to the other factors of production of dry matter which experience has shown to be the most dominant.

3. The method of verification in a more restricted sense (co-variation investigations) must in practice rest on a general knowledge of the probable shape of the yield curves and their position in the co-ordinate system as influenced by several dominant factors of dry matter production.

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SOME BASAL CONCEPTS IN THE APPRECIATION OF PROBLEMS OF SOIL FERTILITY

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SUMMARY

Soil fertility problems in South Australia are such that the most profitable line of approach to their full understanding is based on the study of the climatic and geochemical factors responsible for the chemical characteristics of the native soils. Field experience with fertilizers is to be correlated with these characteristics.

The assessment of the level of fertility in Australian soils presents a problem which is in general quite different from that presented by countries with long and traditional experience in farming and with high densities of population. Soil differences imposed by man's activity in Australia are as yet slight and where present have usually occurred within living memory. Unexploited native soils are still common for comparison even in well settled districts and there are still available very large areas with original soil characteristics, although it is necessary to be able to recognise evidences of accelerated erosion associated with both pastoral and agricultural exploitation. It has become of interest, therefore, in studying the fertility level of these natural soils to endeavour to relate this to such controlling factors as climate, mineral content and recent geological history.

One exception to this point of view may, perhaps, be recorded at this stage. The Queensland Bureau of Sugar Experiment Stations (KERR and VON STIEGLITZ, 1938) has used routine laboratory methods for determining soil fertility. This is to be expected from the highly specialized nature of the crop, with its regulated area and high fertilizer needs.

In South Australia with an agricultural history of little more than one hundred years, the dominant soil factor has been the level of phosphorus and the almost universal response of crops and pastures to superphosphate. The use of this fertilizer for field crops has been well established for 50 years and for pastures increasingly so during the past 25 years.

In broad-scale agriculture, nitrogen has been supplied by the encouragement of legumes such as peas and annual medics on the crop land, and subterranean clover in pasture land. The use of subterranean clover is particularly important during the developmental phases on the native soils in the regions of higher rainfall.

It is now established that this 50 years of use of superphosphate on arable land has been sufficiently long to build up useful reserves of phosphorus in the soil and the recent work of C. H. WILLIAMS (1950) was primarily designed to test the methods by which the usefulness of these reserves could be determined.

The extension of pastoral development into regions of favourable rainfall but with poorer soils has revealed the existence of substantial

areas of soils which need, in addition to phosphorus, one or more of the micro-elements of which copper, zinc and molybdenum have so far proved to be the most significant. The history of these developments in South Australia has been surveyed recently by PRESCOTT (1951).

Generally speaking in all South Australian studies relating to these developments the soil deficiencies have been established by field trials rather than by laboratory tests. Intermediate pot experiments have proved useful, particularly for the study of specific problems. On at least two occasions in Australia a valuable lead was given by spectrochemical examinations of plant and animal material. The association of copper deficiency with ataxia in lambs in Western Australia was discovered in this way as was also the molybdenum deficiency of clover in South Australia.

Of immediate interest to the soil chemists working in the Waite Institute laboratories in Adelaide are the problems associated with the soils derived from laterite formations on Kangaroo Island where considerable development is taking place on the soils of the Seddon and associated series. These soils in their native state show marked deficiencies in phosphorus, nitrogen and copper. Molybdenum appears to be important for legumes and there is a suggestion from field indications of a response to zinc and in pot experiments of incipient deficiencies in potassium and manganese.

The deficiencies of phosphorus and nitrogen are extreme and biological activity is so low in the virgin soil that added ammonia or urea does not nitrify. The status of the native phosphorus in these soils is well shown in the following comparison with the results obtained by WILLIAMS in the case of soils from the older agricultural areas of the State.

TABLE I. Native phosphorus as PO_4 p.p.m. extracted from South Australian soils.

	Soluble in acetic acid and hydroxyquinoline	Soluble in 0·1N sodium hydroxide	
		inorganic fraction	organic fraction
Red Brown Earths ... (mean values)	35	68	186
Mallee Soils (mean values)	44	36	122
Seddon series	1	19	17

One problem under investigation is the reason for the low uptake of added copper, particularly by oat plants showing substantial increases in grain yields, even when amounts of up to 112 lb. per acre of copper sulphate are applied.

The great contrast between the Seddon series and the soils of the Red Brown Earths is made more remarkable when it is realized that so far as can be ascertained the two sets of soils are derived from the same geological parent materials. The differences are imposed by

the process of laterite formation which took place in Pliocene or possibly Miocene times and which differences have remained throughout the subsequent geological history.

As emphasized earlier the soil chemist is concerned with securing some logical explanation of these observed differences. The relevant considerations will be in general climatic and geochemical.

Climatic considerations

The classical example of a discussion of the possible relationship of climate to soil fertility is that of HILGARD (1893) who compared soils from the arid and humid regions of the United States. His values for total potassium and phosphorus as revised (1921) are summarized below

	mean values	
	K_2O %	P_2O_5 %
U.S. Arid soils	0·67	0·19
Humid soils	0·18	0·12

From the point of view of an Australian worker the values for phosphorus are high and call for some explanation.

One of the first generalizations reached in the study of Australian soils was the correlation between soil reaction expressed as the pH value and the rainfall. In general acid soils were associated with high rainfalls. Assuming calcium to be the predominating exchangeable cation the full possible range of soil reaction from pH 8·4 for fully saturated soils to pH 4·0 in fully acid soils was found in nature and could be related in South Australia to soil moisture conditions.

This relation proved so well founded that it was possible to suggest that the acidity encountered in the so-called sand plains of Western Australia under arid conditions could only be related to a former humid climate which on geo-morphological grounds could be identified with that responsible for the formation of laterite in other parts of the same region.

While in general, the changes that take place under leaching conditions are irreversible, the simple development of acidity due to loss of exchangeable calcium can under certain conditions be reversed if calcareous material of wind-borne origin reaches the soil during a subsequent climatic or geological period. Special aspects of this circumstance in explanation of some of the characteristics of the Mallee soils has been dealt with by CROCKER (1946).

Losses of plant nutrients generally under conditions of heavy rainfall and high leaching are less well understood. If such clay minerals as illite and montmorillonite are unstable the loss of potassium can be expected, while the losses that take place under water logged conditions need fuller investigation. Denitrification under such conditions is well understood but the possible loss of phosphorus, as hydrogen phosphides, needs to be considered. The low phosphate content of some of the Australian laterites may well be due to such losses.

The most important aspect of fertilizer practice associated with the range in soil acidity encountered in South Australia is the choice of phosphatic fertilizer. Rock phosphate under moderate rainfalls

is known to give a delayed response after a number of years, but its use for the rapid establishment of new pastures of subterranean clover is not favoured, as this clover is fairly sensitive to the form of phosphate available. The Seddon series of soils to which reference has been previously made shows, however, a noteworthy response to the thermal silico-phosphates. With the current difficulties in Australia over the supply of sulphuric acid—the conditions under which rock phosphate and the thermal phosphates are effective has become a matter of immediate interest.

Geochemical considerations

By far the most useful concept of recent years is that of successive cycles of weathering introduced by CONWAY (1945) and based on the multimodal distribution of elements in a series of rocks lithologically similar in other respects.

The low phosphorus content of Australian soils as compared say with those of North America can best be explained by assuming the parent rocks to have been through a greater number of cycles of weathering.

The distribution of phosphorus in igneous rocks is much the same for all the continents and the low values in soils would be puzzling without some such explanation. In South Australia the soil richest in phosphorus is that derived from a volcanic ash of basaltic character and of Pleistocene age, undoubtedly in the first cycle of weathering. The next group in order of phosphorus content is that derived from some of the pre-Cambrian limestones. The Red Brown Earths derived principally from shales and similar rocks also of pre-Cambrian age come next and then the brown soils of light texture of the Mallee group. The difficult soils of the so-called Ninety Mile Plain and the laterites of Kangaroo Island contain even less phosphorus. There is indeed a strong suggestion of discontinuity in the phosphorus contents in keeping with CONWAY'S suggestions, over a range of from 0·01% of total P_2O_5 to 0·20%, and within this range there is no real correlation with current climatic conditions. Assuming CONWAY'S value of a loss of 39% with each successive cycle of weathering, the parent material of some of our soils may have been subject to six or eight such cycles.

In spite of these low values for phosphorus, potassium may be quite high owing to the predominance of illite as the clay mineral in many of the soils. According to CONWAY illite is returned to the land with the marine sediments. The colloidal material of the narrow clay horizon of the *Laffer sand* of the Ninety Mile Plain is almost pure illite. The Seddon soils on the other hand are exceptional for South Australia in that the clay is kaolinite and the finest sand fractions show the presence of gibbsite—both occurrences emphasizing the lateritic character of the soil profile. The influence of alumina as expressed by the gibbsite on the availability of plant nutrients is at present under investigation.

With respect to the micro-elements used in South Australian fertilizer practice no overall geochemical pattern has as yet emerged. Responses to molybdenum are most likely to occur in soils containing the ironstone gravel associated with lateritic profiles. Responses to zinc and copper, while they can in general be related to specific

soil types as defined by the soil surveys, do not yet show any clear relationship to geological history. Manganese responses are most characteristic of the volcanic soil of Mt. Gambier, particularly where the soil has been affected by the accession of or admixture with calcareous materials.

Conclusions

Generally speaking, in South Australia, the responses of virgin soils to a wide range of fertilizers has offered a challenge to the understanding of the basal factors concerned in determining the fertility level of these soils. These basal factors are in general of climatic and geochemical character. Former climatic cycles are of importance. The number of cycles of weathering to which the parent materials of the soils has been subjected is the geochemical consideration showing most promise.

A fuller knowledge of the mineralogy of the various soil fractions should be of assistance in elucidating some of these factors.

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Appendices

APPENDIX NO. I

MOBILITE DES IONS PHOSPHORIQUES "FIXES" DANS LE SOL ETUDIEE AU MOYEN DE P_{32} *

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RESUME

L'emploi de P_{32} a déjà permis de constater que des échanges continuels d'ions phosphoriques contre des mêmes ions phosphoriques ont lieu dans le sol entre phases solide et liquide, même après établissement de l'équilibre de rétention-libération des phosphates. Les auteurs ont cherché à préciser sur quelles fractions de P_2O_5 minéral du sol portent ces échanges. Ils ont traité un sol argileux (limon des plateaux) par une solution phosphatée marquée (P_{32}), suffisamment diluée pour qu'elle ne cède pas de P_2O_5 au sol, et ils ont étudié l'allure des échanges d'ions phosphoriques au cours du temps. La courbe obtenue présente la même forme que celle relative à l'appauvrissement en P_2O_5 d'une solution plus concentrée : elle comporte une brusque descente initiale, suivie d'échanges lents. Cette observation confirme le résultat d'études chimiques antérieures, à savoir que les phosphates fixés au cours de la deuxième phase (ceux qui deviennent difficilement extractibles par les acides dilués) continuent à participer aux équilibres entre adsorbant et solvant.

SUMMARY

The use of P_{32} has revealed that continuous exchanges of phosphate ions against other phosphate ions of the same type occur between the solid and the liquid phases in the soil, even after the retention-liberation equilibrium of phosphates has been established. The authors have tried to determine which fractions of the mineral P_2O_5 in soil are capable of taking part in exchange reactions. They treated a clay soil with a labelled phosphate solution (P_{32}) which was dilute enough to avoid giving P_2O_5 to the soil. A study was made of this phosphate ion exchange in the course of time. The curve shows the same shape as that of the loss of P_2O_5 from a more concentrated solution : a sudden initial drop followed by slow exchange. This observation confirms the results of previous chemical studies, namely that the phosphates which have been fixed during the second phase (those which become extractible with difficulty by means of dilute acids) continue to contribute to the equilibria between adsorbent and solvent.

* Cet article va paraître dans le deuxième volume.
This paper will be published in Volume II.

DER GEFASSVERSUCH ZUR BESTIMMUNG DER BODENFRUCHTBARKEIT *

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ZUSAMMENFASSUNG

(1) Der Gefässversuch wurde als pflanzenphysiologische Methode zur Bestimmung mehrerer Faktoren der Bodenfruchtbarkeit entwickelt. Besondere Bedeutung für die Anwendung und Düngerberatung kommt dem von MITSCHERLICH entwickelten Verfahren zu.

(2) Der Gefässversuch zur Bestimmung des Düngebedürfnisses nach MITSCHERLICH wird in allen Phasen der Durchführung beschrieben. Es werden behandelt: die Entnahme und Vorbereitung der Bodenprobe, das Versuchsgefäss, die Füllung des Gefässes, die Düngung der Gefässe, die Ernte und Bestimmung der Trockensubstanz, die Auswertung der Ertragsergebnisse unter Anwendung des "Ertragsgesetzes."

(3) Bei der Düngerberatung ergibt sich auf Grund der mit dem Gefässversuch erfolgten quantitativen Bestimmung des Düngebedürfnisses die Möglichkeit einer Nährstoffstatik. Diese kann durch eine Rotation der Fruchtfolge (4-8) Jahre bis zu einer neuen Probeentnahme und Untersuchung durchgeführt werden. In der Nährstoffstatik sind neben der anorganischen Düngung die organische Düngung und die von den Pflanzen aufgenommenen Nährstoffmengen zu berücksichtigen.

(4) Es werden folgende, mit der Methode MITSCHERLICHS verbundene Probleme diskutiert und teilweise durch Versuchsergebnisse ergänzt:

(*a*) Anstelle der Bestimmung des Stickstoff-Bedürfnisses im Gefässversuch erfolgt die Feststellung der zweckmässigsten Stickstoffdüngung besser im Feldversuch. In den Böden der gemässigten und feuchten Klimate ist die Stickstoff-Bilanz sehr labil. Zu hohe Stickstoffdüngung ruft andererseits Ertragsdepressionen hervor.

(*b*) Obwohl MITSCHERLICH eine verhältnismässig hohe Pflanzenzahl pro Flächeneinheit empfiehlt, ergibt ein Vergleich der physiologischen Daten aus Feld- und Gefässversuchen, dass das Gleichgewicht zwischen Pflanzenbestand und Wachstumsfaktoren in beiden Verfahren ähnlich ist. Unter dieser Voraussetzung können der dichte Pflanzenbestand und die intensive Durchwurzelung im Gefäss nur als günstig bezeichnet werden. Geringe Pflanzenzahlen können den Wasserhaushalt in feinerdereichen Böden nicht so gut erschöpfen wie dichte Pflanzenbestände.

(*c*) Das Problem der Versuchsdurchführung in Boden / Sand-Gemischen wird untersucht. Neben der Aufnahme der Nährstoffe, welche dem Mischungsverhältnis weitgehend entspricht, muss die in der Pflanze erfolgte Verwertung der Nährstoffe zur Substanzbildung berücksichtigt werden. Letztere wird durch die Vielzahl der Wachstumsfaktoren beeinflusst, was an dem Beispiel des Kalk und des

* Dieser Vortrag wird im zweiten Band herausgegeben.
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Natrium-Faktors nachgewiesen wird. Als pflanzenphysiologische Methode ermittelt der Gefässversuch die im Boden "physiologisch wirksame Nährstoffmenge." Die Sandverdünnung sichert die Auswertbarkeit der Ergebnisse, vor allem in nährstoffreichen Böden.

(*d*) Die von MITSCHERLICH empirisch auf Grund des Vergleiches von Feld- und Gefässversuch festgelegte Berücksichtigung des Untergrundes wird besprochen. Es erscheint zweckmässig, die Probe aus der Gesamttiefe der bearbeiteten und gedüngten Ackerkrume zu entnehmen und dies bei der Auswertung der Ergebnisse zu berücksichtigen.

(*e*) Die Methode MITSCHERLICH wird unter weitgehend konstanten und optimalen biologischen Bedingungen durchgeführt. WIESMANN variiert die Methode, indem er sich von der Anwendung des allgemeinen Ertragsgesetzes, unabhängig von den klimatischen Bedingungen jedes Jahres, freimacht. Das Verfahren führt praktisch zu ähnlichen Ergebnissen. Bei der Auswertung von 27000 Feldversuchen konnte MITSCHERLICH die Anwendbarkeit des Ertragsgesetzes nachweisen.

(5) Der Gefässversuch ist von MITSCHERLICH auch zur Bestimmung des Kalkbedürfnisses des Bodens vorgeschlagen worden. Neben Hafer wird hier der Senf als Versuchspflanze benutzt. Für die Düngerberatung hat sich das Verfahren nicht durchgesetzt, zumal die billigeren Methoden zur "S" und "T" Bestimmung quantitative Auswertung gestatten.

(6) Die Ermittlung physikalischer Bodenfruchtbarkeitsfaktoren im Gefässversuch wird erwähnt.

(7) An Versuchsergebnissen wird gezeigt, dass der Gefässversuch zur Untersuchung des Wachstumsfaktors "Wasser" benutzt werden kann. Als Funktion des Feinerdegehaltes folgen sowohl die Erträge, als auch die Wasseraufnahme einer Geraden. Die Wasserverwertung steigt mit dem Feinerdegehalt und fällt mit der Höhe der Wassergaben. Innerhalb jeder Bodenart steigt die Wasseraufnahme als Funktion der Wassergabe nach der logarithmischen Funktion. Dasselbe gilt für die Verwertung der aufgenommenen Wassermengen zur Substanzbildung. Bei Extrapolation der funktionellen Zusammenhänge entspricht der gefundene Wert für "totes Bodenwasser" der Hygroskopizität (nach MITSCHERLICH). Der Wert für das "ungenutzte Bodenwasser" liegt stets über dem Wert für "totes Bodenwasser" bzw. der Hygroskopizität. Der Faktor "ungenutztes Bodenwasser/totes Bodenwasser" $\left(\frac{Wu}{Hy}\right)$ fällt mit dem Feinerdegehalt und steigt mit der Höhe der Wassergabe. Da der Gefässraum intensiv durchwurzelt ist, werden die Beziehungen unabhängig von der Nachlieferung des Wassers innerhalb des Bodens festgestellt.

SUMMARY

(1) The pot experiment technique was developed as a plant physiological method for determining several factors in soil fertility. In the use of this technique for making fertilizer recommendations the process developed by MITSCHERLICH has been particularly significant.

(2) MITSCHERLICH's technique for determining fertilizer requirement is described in detail under the following heads: the taking and

preparation of soil samples, the pot technique, filling and manuring of the pots, harvesting and determination of dry matter, and the evaluation of the yield result by use of the " yield law ".

(3) In fertilizer recommendations the possibility of nutrient equilibrium arises, based on the quantitive determination of fertilizer requirement ascertained by the pot method. This can be accomplished by a rotation of crop years (4-8) until new samples are taken and examined. In the nutrient equilibrium, organic fertilizer and nutrient matter taken up by the plant, are considered in addition to inorganic fertilizer.

(4) The following problems connected with MITSCHERLICH's method are discussed and partially supplemented by results of experiments :

(*a*) Nitrogen requirement is better determined in field than in pot experiments. The nitrogen balance is very variable in soils situated in medium and damp climates. On the other hand, too much nitrogen fertilizer causes yield depression.

(*b*) Although MITSCHERLICH recommends a relatively high plant number per surface unit, a comparison of the physiological data from field and pot experiments shows that the balance between plant numbers and growth factors is similar in both. On this assumption the density of plant population and intensive root development in the pot may be considered favourable. Small numbers of plants cannot exhaust the water content in fine-textured soils to the same extent as larger numbers do.

(*c*) The problem of carrying out experiments in soil-sand mixture is examined. In addition to the uptake of nutrients, which corresponds largely to the proportions of the mixture, the utilization of nutrients by plants for the formation of plant matter must be considered. The latter is influenced by numerous growth factors. This is exemplified by the lime and sodium factors. As a plant physiological method, the pot experiment technique determines the " physiologically effective nutrient content." The dilution with sand ensures the evaluation of results, above all in soils rich in nutrient matter.

(*d*) The empirical consideration of the subsoil by MITSCHERLICH as a result of field and pot experiments is discussed. It appears appropriate to take the sample from the total depth of the cultivated and manured crumb-structure surface soil and to consider this in the evaluation of results.

(*e*) The MITSCHERLICH method is carried out under controlled constant and optimum biological conditions. WIESMANN varies the method, in so far as he dispenses with the use of the general yield law independent of the climatic conditions each year. This process leads in practice to the same results. In the evaluation of 27,000 field trials MITSCHERLICH was able to prove the practicability of the yield law.

(5) The pot experiment technique was proposed by MITSCHERLICH also for determining the lime requirement of the soil. In addition to oats, mustard is used as a test plant. The process did not prove worth while for fertilizer recommendation, especially as the cheaper methods of " S " and " T " determination permit quantitive evaluation.

(6) The investigation of physical soil fertility factors by the pot experiment technique is discussed.

(7) Experiments have shown that the pot experiment technique can be used to examine the growth factor "water." As a function of the "fine earth" content the yields as well as the water intake follow a straight line. Water utilization increases in proportion to the "fine earth" content and decreases proportionately with the increase in the level of the water given. In each type of soil, water intake rises as a function of the amount of water supplied according to the logarithmic function. The same holds as regards the use of adsorbed water for the formation of plant matter. In extrapolation of the functional connections, the value for "dead soil water" corresponds to the hygroscopicity (according to MITSCHERLICH). The value for "unused soil water" is always greater than the value for "dead soil water" or hygroscopicity. The "unused soil water/dead soil water" $\left(\frac{Wu}{Hy}\right)$ factor decreases with the "fine earth" content and rises with the increase in the amount of water supplied. As the pot space is completely filled with roots, the ratios are determined independently of subsequent additions of water to the soil.

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