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## Chemistry Department

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## CHEMISTRY DEPARTMENT

By E. M. CROWTHER

### FERTILIZER EXPERIMENTS

Much of the work of the department is concerned with the analysis of problems of soil fertility and manuring by combining investigations in the laboratory, pot culture house and field experiments. Manurial experiments on sugar beet have been conducted in collaboration with the agriculturists of the sugar beet factories at some twenty centres each year since 1933, and the responses to fertilizers have been compared with those of laboratory examinations of soil samples taken before the fertilizers were applied to the plots. In many of the years leaf and root samples have been examined at the end of the growing season. This series of field experiments and an additional one on alternative forms of nitrogen fertilizers were continued in 1949. Arrangements for future experiments on this crop are under review.

In a much smaller series of experiments in co-operation with the staff of the Home Grown Threshed Peas Joint Committee and the National Agricultural Advisory Service from 1946 to 1949, the average responses to nitrogen and phosphate fertilizers were trivial and those to potassium fertilizer were profitable only on soils deficient in readily soluble potassium. Thus, grouping the experimental centres by soil analyses made by a rapid method in which the soil was extracted for one minute with 0.3 N.HCl the average responses to potassium fertilizer were :

	Readily soluble potassium in soil mg. K <sub>2</sub> O%	No. of experiments	cwt. additional peas per acre from 2 cwt. muriate of potash per acre
Low ...	0-6	7	2.1
Medium ...	7-8	5	0.3
High ...	Over 8	13	-0.1

In these experiments the fertilizers were applied broadcast shortly before sowing. With this method of application there is little justification for manuring peas, except where acute potassium deficiency is suspected. It will be shown in a later section of this report that suitably placed fertilizers may give good responses where broadcast fertilizers fail.

For many years manurial experiments designed and analysed at Rothamsted have been carried out on tropical plantation crops. In one series started on newly budded rubber in Malaya in 1934 and supervised by Dr. W. B. Haines, growth in girth showed marked and very rapid responses to ammonium sulphate and mineral phosphate but not to sulphate of potash. The trees with nitrogen and phosphate were ready for tapping many months before the untreated trees. In 1948 and 1949 it was possible to remeasure the girths of the trees and to obtain several rounds of sample-tappings from two of the experiments, which had, of course, had no further treatment or attention after 1940. In one experiment the number of tappable trees was least on plots which had received no nitrogen or phosphate from 1934 ; there was a significant increase in the yield of latex from the earlier nitrogen dressings on plots which had also

received phosphate. In another experiment on a different estate the numbers of tappable trees and the yields of latex per tree tapped were higher on plots which had received mineral phosphate from 1934 to 1940. These results provide an interesting example of the way in which suitable manuring in the early stages of the growth of trees may show improvements over long periods.

In experiments on both mature and newly planted oil palm started in 1940 in two estates in Nigeria and one in the Belgian Congo, the effects of nitrogen, phosphate and potassium fertilizers were small and irregular in the early years, partly because it was not possible to maintain regular manurial dressings during the war. Progressive changes with time showed, however, moderate improvements from potassium fertilizer in several experiments and small improvements from nitrogen. In most of the experiments, including those started at the time of planting, there were negligible effects from phosphate fertilizers. Significant improvements in yield from phosphate were obtained only on a single kind of soil at one of the three estates.

Since 1945 several members of the department have co-operated with the Research Division of the Forestry Commission in investigations on nutrition problems in forest nurseries. A general summary of the principal findings is given in a separate section of this Report.

#### *Phosphate fertilizers*

It is well known that superphosphate may have relatively small residual effects on certain kinds of soil, especially very acid ones, and it is often assumed that other kinds of phosphate fertilizer are therefore to be preferred on these soils. Although we have not yet been able to make long-term experiments to measure the residual value of different kinds of phosphate fertilizers on acid soils, we have had a number of experiments in which superphosphate has given excellent results on acid soils in the year of application. Of the alternative kinds of fertilizer tested only silicophosphate has given higher yields and phosphate recoveries than superphosphate, and the superiority was very small. Very good results have been obtained from superphosphate in forest nurseries and forests, even on acid soils, and sometimes the advantage from superphosphate has been outstanding in comparison with Bessemer basic slag and ground mineral phosphate. These results are consistent with the view that a special merit of water-soluble phosphate applied at or shortly before sowing is to stimulate early root growth and establishment, which may be of the greatest importance in dry springs. This feature of soluble phosphate fertilizers can be fully exploited where safe methods can be found for placing the fertilizer close to the seed. It may then become possible to rely on moderate annual applications instead of attempting to build up large reserves in the soil. There are other conditions in which it may be desirable to maintain a continued supply of available phosphate over longer periods. Some possible methods are being tested. Newly planted forest trees have received compound fertilizer (5% N, 10%  $P_2O_5$ , 5%  $K_2O$ ) compressed into one-ounce pellets, one on each side of the tree. Somewhat unexpectedly it was found that during the drought of 1949 over 90 per cent of the nitrogen, phosphorus and potassium had diffused out of the pellets after a few months. The pellets appeared unchanged but they

retained little but gypsum. Although these observations suggest that the pellets may not act slowly enough for the purpose intended, the rapid outward diffusion of the soluble salts may reassure farmers who doubt the activity of granular fertilizers when they find apparently unaltered granules at the end of a season. To slow down the rate of action of phosphate granules or pellets it may be necessary to select relatively insoluble ingredients. Another method under test is to mix superphosphate with bulky organic materials, such as chaffed green bracken, with the object of producing a less soluble calcium phosphate within the pieces of organic matter. Such material might remain accessible to plant roots but be brought only slowly into contact with the soil.

*Long-term residual effects of superphosphate and farmyard manure*

An account is given in the Field Experiments section of this Report of the striking residual effects shown in the Hoos Field Exhaustion Land in the barley crop of 1949. Plots which had received either superphosphate or farmyard manure for many years before 1901 but none since gave fair barley crops whilst those which had received no phosphate in the wheat and potato experiments before 1901 showed most acute symptoms of phosphate deficiency. Plant samples taken on 14th May 1949 gave the following yields and analyses.

Treatment before 1901	Dry matter cwt. per acre	P <sub>2</sub> O <sub>5</sub> % of dry matter	P <sub>2</sub> O <sub>5</sub> in crop cwt. per acre
No phosphate ...	1.1	0.32	0.004
Superphosphate ...	3.4	0.48	0.016
Farmyard manure ...	5.4	0.57	0.031

The fact that the phosphoric acid percentage increased regularly with the yield suggested that available phosphate was the principal controlling factor. The extra phosphate content on the better plots with manurial residues amounted, however, only to from 1 to 3 lb. P<sub>2</sub>O<sub>5</sub> per acre. Analyses for readily soluble soil phosphate showed differences over a tenfold range. The yields of barley followed the soil analyses quite well, except that plots without potassium before 1901 gave poorer plants for a given level of soil phosphate than those with either farmyard manure or potassium sulphate before 1901. This shows a residual benefit from potassium fertilizer. Samples taken on the same day from the permanent barley plots in the same field gave about 0.6% P<sub>2</sub>O<sub>5</sub> in the dry matter for plots without superphosphate and from 0.8 to 1.0% P<sub>2</sub>O<sub>5</sub> in the dry matter from plots with superphosphate every year. Another experiment in the same field shows that the residual effect of superphosphate in this slightly calcareous soil falls off only very slowly from the second to the fifth year after application. The observations on the exhaustion land show that a small fraction of added phosphate and potassium may remain available for many years.

*Rate of action of nitrogenous fertilisers*

Crop residues, farmyard manure and composts may liberate available nitrogen over many months, whilst most nitrogen fertilizers, including such organic materials as dried blood and crushed hoof, act very rapidly. This may allow serious losses of nitrate by leaching, and in very acid soils even ammonium may be lost. For many crops growth might be steadier and manurial practice

simplified if slowly acting nitrogen fertilizers could be prepared. Among the waste products we have tested the best results have been obtained from a plastic waste derived from formalized casein. Even slower and more prolonged action has been obtained in pots from crushed hoof which was inactivated by treatment with formaldehyde. A number of synthetic products, including several batches of urea-formaldehyde condensation products, have been tested. The rates of action have been assessed from pot experiments on repeatedly cut perennial ryegrass, the effects of dressings incorporated in the soil at the beginning of the experiment being compared with graded dressings of urea applied as top-dressings in factorial combinations on three occasions. In this way it is possible to assess the amount of available nitrogen supplied at different stages in the growth of the crop and to reduce the disturbance from the delayed response of the crop to nitrogen absorbed at an earlier stage. The absolute amounts of slowly available nitrogen obtained from any of the forms tested was small by comparison with the amounts of rapidly available nitrogen. No material tested gave results comparable with the same total amount of nitrogen applied in repeated dressings of a soluble form. For a given amount of early growth the amount of late growth increased in the order: urea, hoof, urea-formaldehyde products, formalized casein, formalized hoof. The results confirmed American findings that for urea-formaldehyde products both the early and the late supplies of available nitrogen increased with a conventional estimate of the "soluble nitrogen" in the product. It appears that much more experimental work will be required on the production and testing of urea-formaldehyde products before commercially useful materials can be prepared.

#### *Fertilizer placement*

Experiments comparing fertilizer placed near the seed with that broadcast were carried out in 1948 on sugar beet, mangolds and threshed peas. Two methods of broadcasting fertilizer were tested. Early dressings applied after ploughing were worked deeply into the soil by the cultivations given in preparing the seedbed. Late dressings were applied to the seedbed and were harrowed in shallowly. Fertilizer was placed three inches below the soil surface in bands at one inch and at three inches to the side of the seed.

Heavy dressings placed one inch to the side of the seed damaged the germination of sugar beet, mangolds and peas; bands three inches to the side of the seed were safe. Complete dressings of fertilizer for row crops should be placed not less than two inches to the side of the seed.

National Compound Fertilizer No. 2 (9%N, 7.5% P<sub>2</sub>O<sub>5</sub>, 4.5% K<sub>2</sub>O) gave similar yields of sugar beet and mangolds when broadcast and when placed in bands at safe distances to the side of the seed. For such crops grown on average soils there is no advantage from placing fertilizer beside the seed except that the labour involved in applying the fertilizer separately is saved. Further experiments in 1949 have compared a phosphate-potash fertilizer (15% P<sub>2</sub>O<sub>5</sub>, 13% K<sub>2</sub>O) broadcast and placed in a band two inches to the side of the seed. Preliminary results show that placed and broadcast fertilizer have again given similar yields.

Phosphate-potash fertilizer (10% P<sub>2</sub>O<sub>5</sub>, 20% K<sub>2</sub>O) was applied in experiments on threshed peas in 1948. Bands placed at the side of the seed gave consistently higher yields than the same quantity of fertilizer broadcast. Early dressings worked deeply into the soil gave slightly higher yields than dressings broadcast on the seedbed. In 1949 a phosphate-potash fertilizer (15% P<sub>2</sub>O<sub>5</sub>, 13% K<sub>2</sub>O) applied three inches below the soil surface and two inches to the side of the seed gave consistently higher yields than the same quantity of broadcast fertilizer. The average *extra* yields of threshed peas from placing as compared with broadcasting 4.5 cwt. of fertilizer per acre in experiments over three years were

						extra yield of peas cwt. per acre
1947	3 experiments	..	..	..	..	2.8
1948	5 experiments	..	..	..	..	2.2
1949	6 experiments	..	..	..	..	1.5

One experiment in 1949 on peas picked green for canning gave higher yields from placing than from broadcasting fertilizer. Placement was also superior to broadcasting in three experiments on spring beans.

#### RADIOACTIVE TRACERS

During 1949 apparatus was assembled and standardized for using radiotracers in soil and fertilizer investigations. Work elsewhere on the uptake of nutrients from soils and added fertilizers had revealed some uncertainties in the interpretation of results of experiments with radiotracers as indicators through possible damage to plants by radiation and also through isotopic exchange between soil phosphate and added phosphate. It was therefore decided to begin by examining isotopic exchange phenomena in simpler systems before proceeding to experiments on soils and plants. With anion exchange resins and preparations of basic calcium phosphate exchange with added phosphate proceeded very rapidly, equilibria being attained within a day or so. With coarsely crystalline fluorapatite the exchange, though much slower, was still appreciable. Estimates of the apparent surface for exchange were about ten times that calculated from the size of the crystals. Measurements of the speed and extent of isotopic exchange distinguish sharply between coarsely and finely crystallized materials, and thus offer means for comparing the surface activities of preparations of calcium phosphates and other materials likely to be involved in the behaviour of fertilizer products in soils.

#### SOIL ORGANIC MATTER

Earlier work on the extraction of organic matter from soils and the nature of the organic nitrogen in soils was prepared for publication. It had been shown that at least one-third of the organic nitrogen of soils was in the form of protein. The amino-acid composition of soil hydrolysates has been studied by the paper chromatography technique and the following amino-acids identified; aspartic and glutamic acids, serine, threonine, glycine, alanine, valine, leucine, isoleucine, proline, hydroxyproline, arginine, histidine, lysine, phenylalanine, tyrosine, β-alanine, α-amino-n-butyric acid and γ-aminobutyric acid. In addition, glucosamine and an

unidentified substance giving a purple colour with ninhydrin have been detected. Preliminary investigations suggest that the latter is  $\alpha\epsilon$ -diaminopimelic acid. Results so far obtained indicate that the amino-acid composition of the protein material in different soils is substantially the same. No free amino-acids have been detected in any of the soils studied.

The paper chromatography technique has also been employed in preliminary work on the nitrogen metabolism of soil and in a comparison of the amino-acid composition of fresh and rotted straws.

#### MANGANESE AND COPPER IN SOILS

In pot experiments on a fen soil low in total manganese the addition of small amounts of molybdate to the soil gave a considerable proportion of peas showing "Marsh Spot" under conditions in which untreated soil gave healthy peas. In a later experiment on a mineral soil low in total manganese healthy peas were obtained whether or not molybdate was added. It is possible that the effect of molybdate on the fen soil involved an increase in the ratio of soluble nitrogen to manganese in the plant, as earlier experiments had shown that "Marsh Spot" could be made more severe by injecting simple nitrogen compounds into plants. In pot experiments copper and manganese added on the surface of fen soils were held almost completely in the top centimetre or so of the soil. These results illustrate the firmness with which copper and manganese are retained in organic soils.

Neutral pyrophosphate extracts of organic soils when diluted with additional neutral pyrophosphate dissolve relatively large quantities of manganese when treated with manganese dioxide. In one case the neutral pyrophosphate extract corresponding to 1 g. of a fen soil dissolved 0.1 g. of manganese.

#### SOIL REACTION

In an experiment on different amounts of chalk on a very acid light sandy soil at Tunstall, East Sussex, quite small dressings (1 ton  $\text{CaCO}_3$  per acre) sufficed to give good crops of sugar beet so long as the nitrogen dressings were in the form of sodium nitrate. From 1941 onwards the sodium nitrate was replaced by ammonium sulphate and the yields of sugar beet and the pH values of the surface soils rapidly fell. Over the whole period of the experiment good yields were obtained on plots with surface pH values of 5.5 and over. In the early years the sugar beet failed when the surface soil had pH values around 5.0 but towards the end of the experiment there were moderate crops on plots with these very low pH values. The difference is due to the circumstances that in the early years the pH values of subsoils were low but in the later years the subsoils on the limed plots had relatively high pH values and exchangeable calcium contents through the leaching of calcium from the added chalk.

For some purposes, *e.g.* for growing lime-sensitive crops or for increasing the availability of certain micronutrients, it may be necessary to acidify field soils. A number of experiments have been made with such materials as sulphuric acid, aluminium sulphate, sulphur and ammonium sulphate. For the first year or so after treatment there is a risk of damage to certain sensitive species from the residues of some of these materials, especially in dry seasons.

Experiments are in progress to discover what interval must be allowed for safety under various conditions.

#### GENERAL

Papers and reports dealing with the results of field experiments on crop rotations and manuring were prepared for two international conferences and for other discussions on fertilizer policy.

#### ANALYTICAL

A large amount of time was devoted during the year to transferring the vast collection of samples of soils and crops built up over a century from the old sample house near the laboratory to a new one in the outbuildings to the Rothamsted Manor.

As the first crops were cut in the new arable-ley rotation experiments at Rothamsted much time was devoted to devising satisfactory methods for handling and analysing the samples. Complications frequently arise in newly established leys and under some conditions in old permanent grass through the inclusion of appreciable quantities of soil in samples cut by a rotary scythe.

For periodic analyses of field and pot soils satisfactory results were obtained by rapid methods of analysis for nitrate by a brucine colorimetric test and for ammonia by nesslerising the ammonia collected in a Conway diffusion unit.

In the colorimetric determination of phosphorus by the stannous chloride-ammonium molybdate method, the solution containing phosphorus as orthophosphate must be free from iron. The tedious separation of iron by precipitating and filtering may be avoided by using Zeokarb 216, a cation exchange resin. Ferric iron is retained by the exchange material whilst the phosphate passes through completely and may be determined colorimetrically in the leachate without further treatment.

Low results in the micro-determination of fluorine by titrating with thorium nitrate may be caused by some of the fluorine being present as fluosilicate ion,  $\text{SiF}_6$ , after separation of fluorine from interfering ions by distillation from sulphuric or perchloric acid. The fluosilicate ion does not form an unionized compound with thorium as fluoride does. It was found that this error could be avoided by carrying out the titration in a 50 per cent. alcoholic system buffered at pH 5.3 using gallocyanine indicator.