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DEPARTMENT OF CHEMISTRY

By E. M. CROWTHER

Several series of investigations involving related work in field, pot and laboratory experiments were continued. Many of these form parts of long-term enquiries under the aegis of committees or conferences of various Government Departments.

THE MANURING OF SUGAR BEET (Ministry of Agriculture Committee on Sugar Beet Research and Education)

This series has continued on comparable lines since 1933. The main set of experiments tests N, P, K, Na and B fertilisers on some twenty commercial farms annually, there being at least one in each of the sugar-beet factory areas. A supplementary series started in 1945 tested nitrate of soda against sulphate of ammonia both in the presence and absence of salt. The results in the first two seasons brought out a definite superiority of nitrate of soda over sulphate of ammonia. This could be ascribed in part to the nutrient value of the sodium, but there was also evidence that nitrate was better than ammonia as a source of available nitrogen, since sodium nitrate gave better results than the mixture of sulphate of ammonia and salt supplying equal amounts of sodium and nitrogen. Where nitrate of soda was used there was little or no further benefit from supplying additional sodium as agricultural salt. So far no clear evidence of improvement in sugar-beet yields by applying borax has been found in over 60 trials on representative soils, but boron effects are known to be markedly seasonal and the work will be continued to provide the opportunity for proper tests when weather conditions aggravate the effects of boron deficiency.

THE MANURING OF PEAS (Agricultural Improvement Council)

There is a singular lack of experimental evidence about the manurial requirements of peas and beans. Field experiments on beans have been in progress at Rothamsted for several years, and in 1946 a preliminary series of experiments on peas was designed in association with Mr. Shorrock of the Home Grown Threshed Peas Joint Committee and local agricultural officers. The experiments achieved a satisfactory standard of precision. Out of four experiments yields were significantly increased by phosphate in one and by potash in two experiments, but nitrogen, phosphate and potash fertilisers each caused one significant depression in yield. This preliminary series of experiments in which depressions were as frequent as responses suggests that current practice in the manuring of peas rests on an insecure basis. The manurial and cultural problems of any rapidly expanding crop need to be examined systematically by field experiments along lines similar to those employed since 1933 for sugar beet.

BULKY ORGANIC MANURES (Agricultural Research Council)

A series of field experiments at Rothamsted, Woburn and many commercial farms was continued to test a variety of bulky organic manures. The experiments were designed so as to bring out both the nutrient and the physical effects of the manures. The principal

materials tested were farmyard manures, sewage sludges, bracken, composts of straw with either sewage sludge or fertilisers, and straw ploughed in directly. Particular attention was given to experiments on horticultural crops and especially to keeping the experiments going over several seasons. In this way evidence has been obtained of physical effects of organic manures in the second or third season of experiments which had shown no such effect in the first year.

THE RESIDUAL MANURIAL VALUES OF FERTILISERS AND THE MANURIAL VALUE OF FEEDING STUFFS

The Director and Dr. Crowther served on a Conference constituted by the Ministry of Agriculture to revise the Voelcker and Hall Tables of residual manurial values. For the first time since this subject was raised by Sir John Lawes in 1870 it was possible to obtain an agreed report acceptable to the interested parties. The Report was published in the Ministry's Journal. The scientific background, including the results of Rothamsted and Woburn residual value experiments, has been summarised (17) in a paper, and the immediate practical problems considered in two lectures (14, 15) to the Central Association of Agricultural Valuers.

FOREST NURSERIES (Forestry Commission Committee on Nutrition Problems in Forest Nurseries)

The new programme of forest planting requires a rapid increase in the production of seedlings and transplants, especially of Sitka Spruce, Scots Pine and other conifers, but many acute problems remain to be solved in nursery practice. Sitka Spruce in particular grows very poorly in many nurseries. A series of manurial experiments was therefore started in 1945 to test fertilisers and composts, alone and in combination, on a range of nurseries, including an established nursery and new ones on old arable land, cleared forest, and cleared heathland. The preliminary results showed that on the sites known by their conditions and by soil analyses to be acutely deficient in nitrogen, phosphate and potash the seedlings and transplants responded strikingly to additions of these plant foods in suitable forms. The effects of various composts could be largely interpreted in terms of their contents of the three major plant foods. On the very poor soil of Wareham Heath there were particularly large responses to each of the elements nitrogen, phosphorus and potassium. Growth was unsatisfactory and visual symptoms of acute nutrient deficiencies were striking where only two of these three elements were added. Some of the past prejudice against the use of fertilisers in forest nurseries on such soils may well have been due to the aggravated symptoms of one nutrient deficiency produced by making good deficiencies in one or two other plant foods. With all three nutrients supplied as fertilisers large vigorous and well-furnished seedlings and transplants were produced in 1946 on what was intrinsically an extremely poor soil.

Some of the experiments were necessarily of complex statistical design because it was necessary to test different amounts and forms of each of the three major elements. Some of the differences between alternative forms of fertiliser have already been demonstrated. In an established nursery at Oxford it was shown that

the growth of Sitka Spruce could be greatly improved by acidifying the slightly calcareous soil on which this species has consistently failed for a number of years.

Plants from many of the experimental treatments in several nurseries will be planted out in experiments in three forests in 1947 and manurial experiments will also be made in these forests.

This work must be continued over a number of seasons and a variety of soils before a sound manurial policy for forest nurseries can be established. The results of the first two seasons are promising. Apart from their potential value for forestry practice they provide interesting material for studying problems of plant nutrition and soil chemistry at much lower levels of fertility than are obtained with agricultural crops.

FERTILISER PLACEMENT (Agricultural Research Council)

Experiments on potatoes in 1945 showed no differences between alternative methods of applying fertilisers. Through experience gained in the field in 1945 it was possible to suggest a number of improvements in the experimental drill built for this work by the National Institute for Agricultural Engineering (12). An improved drill was used in 1946 in 16 experiments on potatoes in the principal potato-growing areas of south and east England. The methods of fertiliser applications tested were, broadcasting before ridging, broadcasting after ridging, placement in contact with the seed and placement in two sidebands below seed level. There was very little difference in crop yield between broadcasting over ridges and placement in contact with the seed or in sidebands. The normal method of broadcasting over ridged land brings the fertiliser close to the sets and ensures the merits of controlled placement. Nothing is gained by any more elaborate method of applying the fertiliser. This result is at variance with the American experience that banded placement below and to the side of the sets is preferable. The explanation of the discrepancy is no doubt due to the common practice in America of using cut sets which are planted together with fertiliser by machines working on the plot. Broadcasting before ridging was clearly inefficient. Three parts of fertiliser applied before ridging gave about the same yields as two parts of fertiliser applied in any one of the three methods after ridging.

As the result of discussions during 1946 a new experimental drill for fertiliser placement tests on small seeds is being built by the National Institute of Agricultural Engineering. It is hoped to be able to use this in 1947.

PHOSPHATE FERTILISERS (Ministry of Supply)

Field experiments, mainly in collaboration with Advisory Chemists, were laid down to test a variety of forms of phosphate fertilisers, new and old. Yields were obtained from 29 experiments in 1945 and from about 25 in 1946. In the latter year the new fertiliser, silico phosphate, from the Ministry of Supply Experimental Plant at Strood was tested on a variety of soils and crops with promising results (13). Special attention was also given to dicalcium phosphate, both as a more or less pure commercial material and as a major ingredient of mixtures of superphosphate with basic materials. The fuller investigation of dicalcium phos-

phate is of great theoretical and practical importance. It may be possible in some soils to cut down the wastage of phosphate by rapid fixation. If it can be shown that a phosphate insoluble in water may be almost as active as superphosphate under appropriate conditions there will be good grounds for reviewing the whole position of the water-solubility test in the Regulations of the Fertiliser and Feeding Stuffs Act. At present many promising developments in the production and use of fertilisers are prevented by the commercial and legal customs of treating water-soluble phosphoric acid as having unique merit. This test, originally proposed by Sir John Lawes merely to distinguish between good and bad superphosphate, has outlived its usefulness and is now a serious obstacle to technical progress in many branches of science and technology.

BASIC CALCIUM PHOSPHATES

All consideration of the reactions and behaviour of phosphates in soils and fertilisers are rendered difficult by the lack of precise data on the equilibria and reactions between lime and phosphoric acid in aqueous systems. Equilibria are difficult to establish and the reactions are complicated by the low solubility, the ease of hydrolysis and the absorptive powers of the solid phases. As an index of the uncertainties it may be stated that there is still considerable doubt as to whether any such material as "tricalcium phosphate" can exist in contact with water, and yet the name and formula of this substance are used in almost all text books and discussions on soils, fertilisers and animal physiology. Until 1926 this hypothetical substance also served in expressing all phosphate analyses under the Fertiliser and Feeding Stuffs Act.

In re-examining the reaction between phosphoric acid and calcium hydroxide solutions evidence was obtained to suggest that some of the anomalies may be explained by the special properties of dicalcium phosphate, which may occur in some of the more alkaline as well as the more acid systems. A Russian method of precipitating basic calcium phosphates by very slow reactions in large volumes of water was found to give promising results.

With the object of finding a more adequate method of characterising available phosphates in fertilisers, studies have been commenced on the calcium citrate system and on the reaction between calcium phosphates and fluorides during extraction processes.

SOIL ORGANIC MATTER

In collaboration with the Biochemical Department an investigation is being carried out on certain aspects of soil organic matter. The usual methods of extraction with strongly alkaline solutions may produce artefacts and a search is being made for milder reagents. This led to the consideration of organo-metallic complexes in soil (21), and to a study of autoxidation of soil organic matter in alkaline solution.

Chromatographic analysis gave little success with the "humic acid" complex, but a useful resolution of the so-called "fulvic acid" fraction was achieved by using charcoal.

Some results suggest that mucopolysaccharides or mucoproteins

may be present in soil organic matter, but quantitative estimation of these materials and related chemical groups still present great difficulties. Thus no reliable method has yet been found for estimating uronides in soil.

IRON IN SOILS

Several methods of extracting iron from soils and soil colloids were studied with the object of finding better methods for characterising the forms of iron in soils and for studying the movement and deposition of iron compounds in soil formation. The work included a study of stability of iron-humus sols and the properties of complexes of iron and organic acids.

MANGANESE AND OTHER MINOR ELEMENTS

In collaboration with the Biochemical Department work was continued on the nature of the so-called "readily reducible" manganese of soils (22). It was found that polycarboxylic and hydroxyacids but not non-substituted acids formed complexes with manganic manganese which are soluble over a wide pH range. Extractants, such as pyrophosphate, polycarboxylic or hydroxyacids which dissolve polyvalent cations (e.g. manganese, iron and copper) from soil also extract organic matter (27). It was found that organic soils yielded more manganese in alkaline extracts than in neutral ones, and also that this manganese was present in the divalent form (26). Preliminary pot experiments were carried out to test the availability of manganic manganese. A fresh raw sphagnum peat, capable of fixing large amounts of added copper in a form which was soluble in pyrophosphate but not in the salt solutions used to determine "exchangeable" bases, also caused iron and copper chlorosis in oats.

SPECTROGRAPHIC ANALYSES

Sugar beet tops and roots from the standard series of fertiliser trials in 1945 were analysed for many elements, including boron. Many analyses were also made on samples of sugar beet taken in joint work with Mrs. Watson of the Plant Pathology Department and Dr. Hull of the Midland Agricultural College (24). Some of these experiments brought out interesting interactions in plant composition. Thus in one experiment addition of salt greatly reduced the calcium and magnesium contents, and nitrogen greatly increased the manganese contents of the leaves. Manganese sulphate applied ten weeks after sowing was far more effective in raising the manganese contents of the leaves than that applied at sowing.

A paper has been prepared for publication on the mineral composition of oil palms in Nigeria showing various deficiency symptoms and other pathological conditions. Analyses were also made on cotton leaves from South Africa and Sitka Spruce plants from the forest nursery investigations already mentioned.

In a survey of manganese-deficient soils in Hertfordshire in 1945 many samples of cereals and weeds were collected and analysed. Where oats were showing symptoms of manganese deficiency and wheat was free, the wheat nevertheless had lower manganese concentrations in its leaves. Vetches and cleavers both had higher concentrations than the two cereals. It was also found

in this survey that chickweed belonged to the "high-sodium" class of plants, with 2.0 per cent. of Na_2O on the dry matter as compared with less than 0.1 per cent. for many other species.

Spectrographic methods for boron and nickel were developed.

Dr. J. B. Hale worked for six months in 1946 with Professor Lundegardh at Uppsala and Professor Goldschmidt of Oslo.

An investigation on the mineral composition of Broadbalk straws over a term of years was completed. The results were examined in relation to manurial treatments and weather conditions. A number of the analytical data were found to be significantly related to the distribution of rain, when examined by Fisher's method of analysis.

ROTHAMSTED CLASSICAL PLOTS

Steady progress has been made in preparing for analysis the large mass of soil samples taken from Broadbalk in 1945. A similar set was taken from Hoosfield in 1946. Preliminary work has been done in building up apparatus and checking appropriate methods for the critical analyses required in analysing these soil samples.

ANALYTICAL AND OTHER METHODS OF INVESTIGATION

Work on rapid and micro-methods of analysis of soil and plants has been continued by several members of the staff. By using a mixture of selenium, copper sulphate and a large amount of potassium sulphate and digesting for one hour the recovery of nitrogen from guanidine was raised to 99 per cent. The micro-Kjeldahl method was developed to deal with from 20 to 30 mg. of dried ground plant material. It was found that the needles of Sitka seedlings have much the same nitrogen, phosphorus and potassium content as the average of the whole plant. It may therefore become possible in future work to judge the nitrogen status of experimental plants by needle samples which are easily collected and analysed.

It was found that moderate amounts of nitrate could be included in the total nitrogen by both micro- and macro-Kjeldahl analyses with salicylic acid even in the presence of appreciable amounts of water.

In extending an earlier method of examining bulky organic manures by measuring the production of carbon dioxide under standard conditions, it was found possible to reduce the labour involved in ensuring good aeration, by designing an apparatus in which hydrogen peroxide automatically supplied additional oxygen as required.

The Ter Meulen-Spithost method for organic carbon in soils has been modified to a compact unit with volumetric determination of the carbon dioxide.

APPARATUS

Mr. Nixon and Dr. Lees of the Biochemistry Department have designed and constructed a simple and robust pH meter which incorporates all the normal features of commercially made instruments but has the additional advantages of being driven entirely

from dry batteries and of being ready for use a few seconds after switching on. Work has been started on the design of a different type of direct reading pH meter which will be accurate to 0.1 pH and sufficiently stable, light and robust to be used in the field for survey and advisory work or in the laboratory where the more refined instrument is not required.

TECHNIQUE FOR GRASSLAND EXPERIMENTS

In collaboration with the Statistics Department some 800 samples of pasture grass were taken in 1946 from random points in the High Field Experiment at Rothamsted and in a trial at Biggleswade. Similar samples from High Field in 1945 were bulked and analysed. The purpose of the work is to discover a suitable technique for grassland experiments, especially on the relative production of leys and permanent grass. The High Field experiment provides the opportunity of comparing the starch and protein equivalents of the herbage on a number of plots with the actual live weight increases of the grazing animals.

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