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Full Table of Content

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DEPARTMENT OF CHEMISTRY

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Several series of investigations involve related work in field, pot and laboratory experiments. A number of investigations on the manuring of sugar beet and peas, the use of various kinds of bulky organic manures and phosphate fertilisers were continued on similar lines to those described in the 1946 report and are not discussed here. A good deal of time was devoted to tests on new or local forms of fertiliser and to the design and analysis of results of experiments on soil fertility questions carried out by Ministry of Agriculture and the Colonial services. Much of the work was carried out as team work by several members of the Chemistry Department, often in collaboration with members of other Departments.

Fertiliser placement

Field experiments on potatoes in the United States have shown that fertiliser placed in bands beside the sets is more effective than the same quantity of fertiliser broadcast and worked into the soil before planting. It would not, however, be safe to apply the results of the American work directly to British practice because there are many important differences between the methods of planting potatoes in the two countries. Many of the American experiments were on cut sets planted mechanically but in Britain it is customary to broadcast fertiliser over drawn-out ridges before planting whole sets. The British method automatically ensures good "fertiliser placement" and there may be little advantage in using special machines to place the fertiliser in definite positions.

In 1945 an investigation was commenced under the aegis of a Conference of the Agricultural Research Council to test alternative methods of applying fertiliser to potatoes grown in ridges.

Fertiliser dispensing mechanisms used on commercial drills are not accurate enough for experimental work on alternative methods of applying prescribed amounts of fertiliser; the delivery rate for a given setting varies with the condition of the fertiliser and the atmospheric humidity. The National Institute of Agricultural Engineering, therefore, built a special experimental fertiliser placement machine to overcome this difficulty by using a positive displacement mechanism. Fertiliser is contained in a cylinder fitted with a rising piston which pushes the fertiliser out of the top of the cylinder where it is dispensed to tubes feeding adjustable coulters in the soil. Studies of this machine over two seasons showed that it could be relied upon to deliver a definite volume of fertiliser for a given distance travelled. Changes in the density of the fertiliser caused by alterations in atmospheric humidity did not cause sufficiently great changes in delivery rates to affect the accuracy of the field experiments.

In four preliminary experiments in Hertfordshire in 1945 there were only small differences between broadcasting a compound potato fertiliser over the ridges or placing it in contact with the seed, in a single band 2 in. below the seed or in two bands, 2 in. below and 2 in. on either side of the seed. At one centre very deficient in phosphate there was some advantage at low rates of manuring from placing the fertiliser in contact with the seed.

During 1946 and 1947 25 experiments were carried out in some of the important potato-growing areas of Eastern England to test two methods of broadcasting—(a) on the plot before ridging (b) after ridging but before planting—against two methods of placement—(c) in contact with the sets (d) in two side bands 2 in. below and 2 in. to the side of the sets. A National Compound Fertiliser (7% N, 8% P_2O_5, 10·5% K_2O) was used at three rates, 5, 10 and 15 cwt. per acre, by each method. The mean increases calculated for the average dressing of 10 cwt. fertiliser per acre were:

Increase in yield of potatoes, tons per acre

	Experiments	*Broadcast* Before ridging	*Broadcast* After ridging	*Placement* Contact	*Placement* Side-bands	
1946	15	2·5	3·3	3·4	3·2	±0·17
1947	10	1·7	2·1	1·9	2·1	±0·15
1946 & 1947	25	2·2	2·8	2·8	2·8	±0·11

On the average of both seasons broadcasting after ridging and before planting was significantly better than broadcasting before ridging. The two methods of controlled placement by the experimental machine gave results very similar to those by broadcasting after ridging. From the response curves for increasing amounts of fertiliser the general conclusion can be drawn that 7 cwt. of compound fertiliser applied after ridging will give the same average yield as 10 cwt. of the fertiliser broadcast before ridging. Farmers who still apply their fertiliser before ridging would be well advised to follow the practice more common among specialist growers of applying fertilisers after ridging. So long as ridges are drawn there is little need for special machines to provide controlled placement; if mechanical planters working on the flat are to be used, broadcasting fertiliser before planting may be inefficient and some attachment will be needed to place fertilisers near the sets but not so close as to risk damage in dry seasons.

In 1945 and 1946 there were no checks to early development from heavy dressings of fertiliser in contact with the sets; in the long dry spell from mid-May to the end of June, 1947, 15 cwt. of fertiliser per acre in contact with the seed retarded early development at several centres, though the crops recovered after heavy rain at the end of June.

During 1947 preliminary experiments on fertiliser placement for row crops—sugar beet, mangolds, swedes and peas—were carried out with a special experimental drill built by the National Institute of Agricultural Engineering again using a top-delivery fertiliser mechanism. At a number of centres fertilisers placed in bands below the seed, either immediately below or a little to the side, gave much better yields than fertilisers broadcast. During the extremely dry season of 1947 much of the broadcast fertiliser must have remained uselessly in the top inch or so of dry soil. The experiments showed the danger of placing fertilisers with a high proportion of soluble salts close to the seeds of root crops, as e.g. by drilling fertiliser with the seed. In several experiments 4·5 cwt.

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of National Compound No. 2 per acre placed in contact with the seed killed the plants, but the same amount placed to the side of the seed gave a good stand.

Sugar beet manuring and soil analysis

The standard series of manuring experiments testing N, P, K, Na and B fertilisers was carried out again in 1947 with at least one experiment in each factory area and there was also a smaller series on forms of nitrogen fertiliser.

The responses of sugar beet to superphosphate on 216 non-calcareous mineral soils and to potash on 248 mineral soils over the years 1936 to 1946 were examined in relation to the results of a number of analytical methods for soil samples taken from the experimental sites immediately before the fertilisers were applied in the standard series of experiments. The value of the analytical methods was assessed by evaluating the average profit (at 1946 prices) that would have accrued over the whole area represented by the experiments if certain centres had been selected for manuring by means of each analytical method in turn—the other centres being unmanured—and comparing this profit with what would have been obtained if the same total quantity of superphosphate or muriate of potash had been divided evenly over all the centres.

Only about one-quarter of the soils gave highly profitable responses to superphosphate. If one-quarter had been picked by the citric acid method as the most phosphate-deficient and given superphosphate at the rate of 1·0 cwt. P_2O_5 per acre the average profit over the whole series would have been equivalent to 0·62 cwt. of sugar per acre as compared with 0·39 cwt. of sugar per acre if the same total quantities of superphosphate had been spread over the whole of the centres at the rate of 0·25 cwt. P_2O_5 per acre. The immediate profit from superphosphate would have been increase by over one-half by using soil analysis.

The responses to potash were more general and there was therefore less opportunity for economy by omitting potash. If five-eighths of the centres chosen by the citric acid method had received 0·6 cwt. K_2O per acre, the average profit over the whole series would have been 1·57 cwt. sugar per acre as compared with 1·23 cwt. sugar per acre from distributing the same total amount of potash evenly over all centres.

There were only small differences in value between the principal recognised methods of analysis. It was possible from such investigations to improve analytical methods by prescribing the conditions under which they should be used and by changing the limits in accordance with other soil characters. Thus the citric acid method for phosphate may fail on very acid soils. For potash it gives better results if lower limits are used for heavy soils.

Salt for sugar beet

During 1944–6, 30 experiments were carried out on commercial farms to test different times and methods of applying agricultural salt. The results show that nothing would be lost by spreading the salt at a less busy time in winter. It is just as good to distribute the salt on firm land before the winter ploughing as to apply it

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broadcast to the ploughed land either in winter or in spring. Salt should be used in such a way and at such a time as will get it well down into the soil.

Mean increase in sugar, cwt. per acre

		Mean of 3 and 6 cwt. salt per acre			Mean of times	
	No. of trials	Winter ploughed in	Winter broadcast	Spring broadcast	3 cwt. salt	6 cwt. salt
1944	14	3·4	3·4	3·9	3·5	3·5
1945	9	4·6	3·9	4·3	4·1	4·5
1946	7	3·5	4·1	2·0	2·2	4·3
All years	30	3·8	3·7	3·2	3·2	3·9

NUTRITION PROBLEMS IN FOREST NURSERIES

First year seedlings of Sitka spruce and Scots pine raised in 1946 at Wareham, Dorset, on heathland soil carrying its first crop of conifer seedlings and treated with fertilisers gave good establishment and growth when tested in 1947 as transplants in several nurseries or when planted directly into three forests. The extremely dry conditions of 1947 restricted growth in many experiments and provided a good test for possible damage to seedlings from fertiliser salts; none was found. Although responses to nitrogen fertilisers were frequently poor, ammonium sulphate gave excellent results at two nurseries when used as top-dressings on watered plots; on several plots at each nursery the mean heights of Sitka spruce exceeded 3·0 in. Neither watering alone nor nitrogen fertiliser alone gave much improvement.

In several nurseries on heathland or forest sites there were very large benefits from superphosphate, which sometimes proved markedly better than basic slag or mineral phosphate. Superphosphate does not appear to have been tested previously in forest nurseries in this country, and recent demonstrations of its special value may prepare the way for a more general application in forest nurseries of methods of manuring developed in agriculture and horticulture. Seedlings or transplants grown with either composts, fertilisers or both gave no evidence in size and subsequent growth that the composts exerted any effect beyond supplying available nutrients. There have been several cases in which individual kinds of compost have been relatively deficient in one or other of the major plant nutrients. Many experiments are being made to test whether there are any long-term differences in the subsequent behaviour of the trees when planted in forests.

Several nurseries with neutral or calcareous soils gave particularly poor Sitka spruce and Scots pine seedlings in 1947. Treating the soil with either acid or formalin gave some improvement, but the treated soils failed to produce large plants. The precise cause of the failure has still to be determined, but some indication of a "lime-induced chlorosis" was obtained when it was found in 1947 that a local failure of conifers in a calcareous corner of an otherwise acid nursery was matched by a parallel failure of yellow lupins with equally good growth of both conifers and lupins in the acid parts of the nursery. It was found during 1947 that a number of established nurseries in which conifer seedlings grow badly had high pH values as the result of lime, limestone or other basic materials used in manures for green crops, in composts or in calcareous seed covers. The characteristic failure of conifers on some of these soils was reproduced in pot experiments on Sitka spruce grown in mixtures of soil and acid-washed flint.

Spectrographic analysis

In the course of a large number of plant analyses by the Lundegardh flame spectrographic method, a series of crop samples was examined from an old liming experiment at Oaklands, St. Albans. This experiment was laid down in 1933 as a 5×5 Latin Square with increasing dressings of chalk. In 1946 the pH values ranged from 4·3 to 6·5. Samples of wheat taken on five occasions during 1946 showed that liming had very little effect on the concentration of calcium within the plant, but that liming had increased the concentration of magnesium and decreased that of manganese. Analyses of peas, beans, oats and barley grown on the same plots in 1945 led to the same conclusions. Rye grass and clover hay in 1947 had high calcium contents on the limed plots, but the increase in calcium was due to the higher proportions of clovers which are rich in calcium. The individual species, like the wheat and the other crops examined in previous years, showed very little effect of liming on the actual concentration of calcium within the plant.

Analyses on plants from cereal variety trials in Hertfordshire showed a higher concentration of manganese in the roots than in the tops of the plants, but the possibility of soil contamination renders the conclusion somewhat uncertain.

A number of Broadbalk soils have been analysed and a method developed for studying the ion-concentration of the soil solution.

The basic calcium phosphates

In a study of precipitated calcium phosphates over the range between the well-known materials dicalcium phosphate and hydroxyapatite $Ca_5OH(PO_4)_3$, there was no evidence of the formation of tricalcium phosphate $Ca_3(PO_4)_2$ as a definite compound. In a continuous series of solid solutions this particular composition merely marks the stage at which further uptake of calcium must be accompanied by the entry of OH (or F) ions. Precipitates of a composition represented by $Ca_4H(PO_4)_3$ were repeatedly encountered in the course of the work. They were shown to have an apatite-like structure but they also had X-ray diffraction lines indicating a sheet-like structure. Similar precipitates were described long ago by R. Warington, under the name "octo-phosphate" but they have rarely been mentioned in later work. It appears that "octo-phosphate" forms a continuous series of solid solutions with increasing amounts of calcium up to hydroxyapatite.

Some of the anomalies in the potentiometric titration curve of phosphoric acid and calcium hydroxide, the apparent weakness of dicalcium phosphate as an electrolyte, and discrepancies between experimental pH values and those calculated from the concentrations of calcium and phosphate and the dissociation constants of phosphoric acid, could be reconciled by the assumption that some such complex ion as $CaPO_4$ is present.

Soil manganese

Work on the various forms of manganese in soils was continued in collaboration with the Biochemistry Department with special reference to organic soils. Earlier work by Dion and Mann had shown that neutral pyrophosphate extracts of mineral soils contain mainly trivalent manganese. It was found that alkaline (pH 9·3) extracts of mineral soils and both neutral and alkaline extracts of fen soils contain divalent manganese. When mineral soils poor in organic matter and rich in the higher oxides of manganese are extracted with neutral pyrophosphate containing manganous sulphate, the added manganese reacts with the higher oxides to yield more soluble manganese (reverse dismutation). Under similar conditions fen soils retained large amounts of the added manganese in a form which within a few hours ceased to be readily exchangeable with ammonium acetate, but could be recovered by extraction with alkaline pyrophosphate solution. Manganese salts added to fen soils either alone or with ammonium acetate behaved in the same way as those added in neutral pyrophosphate solutions. In experiments on a number of salts it was found that Cd^{++}, Ni^{++}, and Cu^{++} were particularly effective in preventing the uptake of added manganese and in recovering the manganese held in other than readily exchangeable forms by fen soils. The same cations also increased the amount of manganese extracted from neutral organic soils containing little exchangeable manganese, though the high values obtained with ammonium acetate containing copper may have been due in part to a reduction of higher oxides of manganese in the presence of copper salts and organic matter.

Some fractionation of the complexes between metal and organic matter could be obtained by pretreating the soil with sodium chloride and then, in turn, with water, pyrophosphate solution and 2 per cent. sodium hydroxide. Manganese and copper retained by soils in forms not exchangeable for sodium could be recovered subsequently in the water or pyrophosphate extracts. It appeared that the manganese and copper in the water extracts remained combined with organic matter as in the soil itself.

Soil iron

Iron compounds appear to react with soil organic matter in two ways. The iron may enter the exchange position to form a material which may be described as a "basic ferric humate". Such iron can be extracted only by acids or salts capable of forming complex ions with iron. Iron may also react with amino and hydroxy or similar groups in soil organic matter to form a complex which can be extracted when soil, previously washed with a hydroxyacid, is saturated with sodium and then extracted with water. Iron present in organic complexes is left behind when sodium pyrophosphate extracts of soils are dialysed against running water.

Soil organic matter

As soil organic matter is oxidised and degraded when treated with caustic alkali, an attempt was made to find alternative extractants less likely to alter the physiochemical properties of the organic complexes. The solubility of soil organic matter is largely determined by the nature and extent of its association with metals. The efficiency of neutral salt extractants appears to depend on the ability of the anion to remove interfering metals either as insoluble precipitates or as soluble coordination complexes. It is well known that cations other than sodium, potassium and ammonium precipitate organic matter, and that calcium interferes with the extraction of organic matter. Neutral sodium pyrophosphate was found to be particularly effective for extracting organic matter from soils; the optimal conditions for this extraction were worked out.

An attempt was made to determine the forms in which organic nitrogen occurs in soils and, in particular, to establish whether or not the major part of soil nitrogen is present in the form of protein. Proteins as such could not be isolated from soil, but a considerable fraction of the nitrogen in soil hydrolysates was found to be present as α amino-acids. By determining the α amino-acid contents of various soil hydrolysates it has been shown that at least 30 to 40 per cent. of the total nitrogen in the soils examined was in some form of protein-like combination. There was some evidence that some of the organic nitrogen of soils occurs as amino-sugars.

Nitrogen contents of Broadbalk soils

A systematic survey of the chemical changes in the soils from the long-continued cropping and manuring experiments at Rothamsted is in progress. The following summary of changes over 80 years of almost continuous wheat growing is given for some of the principal plots in Broadbalk field. The plots were fallowed every fifth year from 1925.

Nitrogen percentages of Broadbalk soils, first 9 inches, passing 2mm. sieve

Annual Manuring	3 None	5 PK	7 NPK	2A Farmyard manure from 1885	2B Farmyard manure from 1843
1865	0·105	0·106	0·117	—	0·175
1881	0·101	0·107	0·121	—	0·184
1893	0·094	0·101	0·115	0·136	0·213
1914	0·093	0·103	0·115	0·191	0·251
1936	0·103	0·105	0·120	0·186	0·226
1945	0·105	0·106	0·123	0·194	0·236

The 1945 samples were taken from a large number of holes on each plot, the earlier ones from only a few holes often dug to considerable depth. There can be little doubt that the high value for plot 2B in 1914 was fortuitous, as the two samples concerned were highly discordant, probably through the inclusion of manure in one of the samples (0·266 and 0·236 per cent.).

Plots without farmyard manure appear to have reached substantial equilibrium within 20 years of the beginning of the experiment. The slight fall on the unmanured plot up to 1914 was made good more recently. On the plots with farmyard manure annually the nitrogen percentages rose steadily for about 50 years and then changed but slowly. It would be expected that fallowing every fifth year would check the accumulation of soil organic matter, because no organic matter is added in the fallow year either as manure or plant roots, and residues from recent applications would be rapidly oxidised. On the plots without farmyard manure the nitrogen contents increased slightly after fallowing was introduced, probably as the result of the much better crops grown in the year immediately following the fallows.

Analytical methods

Particular attention was given to the development of rapid methods in analysing soils for readily soluble plant nutrients, the determination of fluorine in soils and of nitrates in soils and composts. A paper on a semi-micro method for determining carbon in soils was read to the Society of Public Analysts and other Analytical Chemists.

Methods for fertiliser experiments

For the guidance of agricultural workers in the colonies a memorandum was prepared describing some of the methods of field experimentation which had proved their value in recent manurial and soil fertility investigations in Britain.