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CHEMISTRY DEPARTMENT

By E. M. CROWTHER

FERTILIZER INVESTIGATIONS

Phosphate fertilizers

For several years supplies of phosphate fertilizers in the United Kingdom have sufficed to meet a steadily increasing demand. Fertilizer prices were kept constant by subsidies as the prices of farm products and the cost of labour increased, and it was profitable to manure crops heavily. The prospects for continued expansion and intensification were, however, severely checked during 1950. The general fertilizer subsidies were reduced in 1950 and are to be removed in 1951, a subsidy on fertilizers for grassland taking their place. Severe cuts in the imports of sulphur and the likelihood of a continued world shortage of sulphur will require a critical re-examination of fertilizer policy, both nationally and on individual farms.

Restricted supplies of the standard fertilizers will have to be used more economically and efficiently by giving small quantities frequently in place of large ones occasionally. Ways must be found for making active phosphate fertilizers without using so much sulphuric acid. Wartime studies of the results of field experiments showed how individual crops and fields could be rationed to obtain the best returns. Under many common conditions rates of phosphate application on old arable land in fair condition, can be cut down without serious loss of crop. Several kinds of phosphate fertilizer without water-soluble phosphate can give results approaching those from superphosphate, at least on acid soil. On very acid soils in wet areas ground mineral phosphate often gives very good results, especially for swedes and grassland.

E. M. Crowther and G. W. Cooke have summarized, in a report to be published by the Ministry of Supply, the results of a series of field trials on silicophosphate, carried out in collaboration with the Advisory Chemists of the Ministry of Agriculture. The silicophosphate was prepared by the Building Research Station by heating phosphate rock with soda-ash, sand and steam in a rotary kiln furnace. Typical results are given below for the average of experiments in 1943 to 1946, mostly on acid soils chosen as likely to be deficient in readily available phosphate.

	Swedes tons/acre	Potatoes tons/acre	Growth of reseeded grass (visual scores)
Number of experiments	29	25	13
No phosphate	9.1	5.0	51
Superphosphate			
0.33 cwt. P ₂ O ₅ per acre	13.3	7.5	104
0.66 cwt. P ₂ O ₅ per acre	14.8	8.3	117
Silicophosphate			
0.5 cwt. P ₂ O ₅ per acre	13.8	7.6	112

The two rates of application of superphosphate (a little less than 2 and 4 cwt. per acre) were deliberately kept low in the hope of obtaining crops in the steep and sensitive portion of the response

curves. Where, as in so many earlier experiments, different kinds of fertilizers have been compared at the heavy rates commonly recommended in demonstrations, similar yields do not necessarily mean that the fertilizers were equally effective but merely that each was being used extravagantly. In the experiments summarized above, quite modest dressings sufficed to give good crops. On the average of 29 experiments on swedes and also of 25 experiments on potatoes, 2 cwt. superphosphate per acre increased yields by one half, and 4 cwt. superphosphate gave only small additional increases. Results of the same general pattern were obtained on reseeded grass. Even for sensitive crops there is little need for heavy dressings of phosphate fertilizer.

If halving the quantity of superphosphate makes only a small difference in the response of the crop, the relative values of two alternative forms of phosphate can be determined with confidence only from a large number of fairly precise experiments. The results of a few isolated experiments may be quite misleading.

In the above series of comparisons silicophosphate proved to be just as effective as superphosphate, on the basis of equal phosphorus, for swedes and reseeded grass but less efficient for potatoes. In a small number of experiments the silicophosphate appeared to be much less effective on cereals. Silicophosphate suitably used thus offers one possible way for economizing in sulphuric acid.

The results of field experiments on phosphate fertilizers are being summarized for publication, and new series of experiments are being planned in co-operation with the National Agricultural Advisory Service.

Fertilizer placement

Wartime experiments showed that superphosphate and compound fertilizers are used more efficiently by cereals when they are drilled with the seeds. The high initial concentration of plant nutrients near the roots favours early establishment and growth. Trials have been made with special experimental drills to see whether safe methods can be found for obtaining similar advantages for other crops, especially those in which the young seedlings are likely to be damaged by drilling the fertilizers in immediate contact with the seeds.

With potatoes planted in the furrows of ridged land side-band applications two inches from the sets had no advantage over the usual method of spreading fertilizer over the ridges before planting. Both of these methods were much superior to dressings broadcast before ridging. The rapidly increasing use of mechanical planters, working on the flat or planting into ridges, raises new questions, since these machines do not reproduce the relative positions of sets and fertilizers obtained by broadcasting fertilizer over ridged land. Discussions with the National Institute of Agricultural Engineering led to their developing a new experimental potato planter fitted with a fertilizer attachment, capable of applying known amounts of fertilizer in prescribed positions.

In continuing their investigations on fertilizer placement, G. W. Cooke and F. V. Widdowson obtained advantages from placing fertilizers in bands about two inches to the side of seeds of

several quickly growing and shallow-rooting crops, but there were no similar advantages for deeply-rooting crops with long growing seasons.

Ten experiments on sugar beet were carried out in 1949, a drought year. Granular PK fertilizer containing 16 per cent P_2O_5 and 13 per cent K_2O was applied by several methods, nitrogen fertilizer being broadcast uniformly over all plots. Germination and plant establishment was not damaged by PK fertilizer placed two inches to the side of the seed. Broadcast PK fertilizer increased yields of sugar significantly at three centres. There were no significant differences between the yields given by placed and broadcast fertilizer.

The results of the 1949 experiments on sugar beet confirm those of earlier years; there is no advantage from placing a full dressing of fertilizer beside the seed in districts where the crop is normally grown, except that labour is saved in applying the fertilizer. The results of experiments over three years, of which two were very dry, are summarized below:

				1947	1948	1949
No. of experiments	8	13	10
<i>Fertilizer tested</i>						
Per cent N	9.0	9.0	0.0
Per cent P_2O_5	7.5	7.5	16.0
Per cent K_2O	4.5	4.5	13.4
Amount, cwt./acre	6.8	7.5	5.2
<i>Mean unmanured yields</i>						
Sugar cwt./acre	44.3	39.6	37.0
Tops tons/acre	7.7	9.9	12.6
<i>Mean increases in yield from broadcast fertilizer</i>						
Sugar cwt./acre	2.0	4.8	1.1
Tops tons/acre	1.1	2.8	0.9
<i>Mean increase in yield from placing over broadcasting</i>						
Sugar cwt./acre	-1.0	0.4	0.0
Tops tons/acre	0.5	0.1	-0.2

Experiments were carried out in 1950 on winter beans, spring beans, threshed peas and on peas picked when green. Granular fertilizer containing 14 per cent P_2O_5 and 14 per cent K_2O was applied by several methods. Broadcast fertilizer was applied at two stages in the preparation of the seedbed. Early dressings on the ploughed land were worked in deeply by the cultivations given to prepare the seedbed. Late dressings were applied to the seedbed and harrowed in shallowly. Placed fertilizer was applied in a single band two inches to the side of the seed and three inches below the soil surface. Tests were also made of half the fertilizer placed beside the seed and half broadcast (either early or late).

For winter and spring beans and for green peas early broadcasting gave higher yields than late dressings. For all of these

crops placed fertilizer gave higher average yields than broadcast fertilizer. For both types of beans and for green peas approximately 2.5 cwt. per acre of fertilizer placed beside the seed gave maximum yields which were higher than the yields given by double the quantity of broadcast fertilizer. There was no advantage for any crop from broadcasting half the dressing and placing the remainder beside the seed. Results over several seasons will be summarized when the 1951 experiments are completed.

Experiments on carrots, kale and red beet compared broadcast dressings of a granular phosphate-potash fertilizer with the same fertilizer placed two inches to the side of the seed and three inches below the soil surface. Nitrogen fertilizer was broadcast uniformly over all the plots.

In two experiments on carrots broadcast fertilizer increased yields significantly while placed fertilizer had no effect. The responses to fertilizer were small and irregular in two other experiments on carrots.

In a single experiment on kale placing fertilizer gave higher yields than broadcasting. Both methods of applying fertilizer for red beet gave similar increases in yield.

National Compound Fertilizer No. 2 (9 per cent N, 7 per cent P_2O_5 , 7 per cent K_2O), was tested in one experiment on spinach. Placing fertilizer two inches to the side of the seed increased yields significantly; broadcast fertilizer gave only a small increase in yield.

Rates of action of nitrogen fertilizer

Investigations briefly described in the 1949 Report were extended in 1950, R. G. Warren being responsible for preparing special materials and analysing the crops, E. H. Cooke for carrying out pot experiments on repeatedly cut perennial rye grass and B. Benzián for the trials in forest nurseries and forests. In the pot experiments factorial combinations of graded dressings of urea applied at appropriate times throughout the season served as standards, together with coarse (5-6 mm.) and fine (1-2 mm.) fractions of crushed hoof. Formalized casein, a plastic waste, again gave outstanding results, acting fairly rapidly and maintaining good growth throughout the season and well on into the winter, when the effects of many other materials had been exhausted. Some of a series of urea-formaldehyde condensation products prepared in industrial research laboratories acted much more rapidly, giving results closely akin to those from fine hoof. Attempts to slow down the action of hoof by inactivating it with formaldehyde, copper salts or nitrous acid were so successful that the experiments will have to be continued into 1951 to decide whether the very slow liberation of available nitrogen will continue long enough to allow a high total recovery. Further work on these lines may make it possible to develop, for experimental purposes at least, a set of nitrogen fertilizers of known rates of action. A danger in relying on organic wastes for slowly available nitrogen was illustrated in this experiment by a commercial sample of meat meal which gave only a very small proportion of rapidly available nitrogen with negligible amounts of slowly available nitrogen.

The rates of action of fragments of organic materials were appreciably reduced by coating them with aminoplastics but similar trials with granular and other inorganic fertilizers were less successful. It appeared that the salts diffused out rapidly or, alternatively, that the coated granules soon absorbed water and burst.

NUTRITION PROBLEMS IN FOREST NURSERIES

Investigations in collaboration with the Forestry Commission, reviewed over the period 1945 to 1949 in the Rothamsted Report for 1949, were continued by E. M. Crowther, R. G. Warren and B. Benjian. In the wet season of 1950 there were much more striking contrasts and responses to treatments than had been obtained in the three preceding years.

Sitka spruce seedlings showed large responses to each of the major nutrients in experiments on very acid soils, but in some of these experiments composts well supplied with nitrogen, phosphorus and potassium gave better results than inorganic fertilizers. It appeared that the fertilizer nitrogen applied in the seedbeds in spring and in an early summer top-dressing had been leached out of the surface soil during the very wet summer and autumn before the period of most active growth.

In the neutral or slightly acid soils of old nurseries Sitka spruce seedlings generally make very poor growth, even when well manured with compost or fertilizers. In 1950 at several nurseries there were very striking responses on such soils to acidification in previous years by ammonium sulphate or sulphur. By contrast, the residual effects of aluminum sulphate were small. In one experiment with repeated dressings of nitrogen fertilizers on the same plots for seeds sown in 1949 and again in 1950, there were only moderate gains in 1950 from "Nitrochalk" but very good ones from equivalent amounts of ammonium sulphate. In the drought of 1949, when nitrogen fertilizers were generally ineffective, neither material did any harm. The repeated dressings of ammonium sulphate appear to provide a safe method of supplying available nitrogen and at the same time acidifying the soil. If this kind of result can be repeated under other conditions it may offer a simple practical remedy for an acute example of "soil sickness."

Steam and formalin treatments of the soil some weeks before sowing again gave dramatic improvements, the boundaries between plots showing very sharp contrasts. At four nurseries experiments on different amounts of formalin gave response curves closely akin to those for plant nutrients on highly deficient soils. It is not yet possible to offer an adequate interpretation of "partial sterilization" by steam and formalin. In addition to killing many classes of microorganisms both treatments greatly increase the supply of available energy, as is shown by a rapid increase in the production of carbon dioxide and ammonia in incubated soils. On the treated plots the ammonia contents of the soils remained higher throughout the season and nitrification in incubated soils was checked.

The hypothesis that partial sterilization depends on the elimination of soil fungi harmful to or competing with the roots of the conifer seedlings was examined in several nurseries and in series of

pot experiments by E. H. Cooke. A wide variety of fungicides and two antibiotics were added to the soil or applied as seed-dressings. Several of these materials reduced early deaths by "damping-off" in the pot experiments, and others damaged the seedlings, especially at high rates of application. None of them, however, approached steam or formalin in their general effects on growth. Such results in a good growing season indicate that the control of soil fungi may be a relatively unimportant factor in the effects of steam, formalin and acidification in improving the growth of Sitka spruce seedlings on the so-called "Sitka-sick soils." Many of the observations already made could be interpreted on the hypothesis that conifer seedlings utilize ammonia in the soil more efficiently than nitrate, but the results of further investigations in the Microbiology and Chemistry departments must be awaited before this hypothesis can be adequately tested.

In several experiments on neutral or slightly acid nurseries Sitka spruce responded well to superphosphate on plots which had received formalin but not on plots without formalin. An indication of the complexity of formalin effects was given in two experiments on very acid nurseries, one on heathland and the other in a clearing in a conifer forest. On plots without formalin inorganic fertilizers gave better plants than compost. Previous treatment with formalin greatly improved growth on the compost plots and had no effect on the fertilizer plots. The appearance of the plants suggested that those with formalin and compost received large quantities of available nitrogen late in the season. Presumably the formalin retarded the breakdown of proteins from the compost in much the same way as in the pot experiment on hoof described in the previous section of this report.

SOIL INVESTIGATIONS

Soil Organic matter

J. M. Bremner's earlier work on the amino-acid composition of the protein material in soil was completed and prepared for publication. Ten soil samples, differing greatly in pH value, organic matter content and cultural history, were examined, the amino-acid composition of their acid hydrolysates being studied by paper partition chromatography. The following twenty amino-acids were found in every hydrolysate: phenylalanine, leucine, isoleucine, valine, alanine, glycine, threonine, serine, aspartic acid, glutamic acid, lysine, arginine, histidine, proline, hydroxyproline, α -diaminopimelic acid, α -amino-n-butyric acid, β -alanine, γ -aminobutyric acid and tyrosine. Methionine sulphoxide and glucosamine were found in most of the hydrolysates, but cystine, methionine and tryptophan could not be detected. D-amino-acids were detected in the hydrolysates but the small amounts found could have arisen by racemization during hydrolysis. No free amino-acids could be detected in any of the soils studied. The detection of glucosamine, serine and threonine in the hydrolysates confirmed previous evidence that 2-amino sugars and hydroxy-amino-acids occur in soil.

Comparison of the strengths of the spots on the chromatograms indicated that the protein materials in the ten soils examined were similar in amino-acid composition.

During the course of the work described above it was noted that alkaline hydrolysates of soil contained greater amounts of glycine, alanine and α -amino-n-butyric acid than did acid hydrolysates. This observation led to an investigation of the effect of hot alkali (NaOH and Ba(OH)₂) on various amino-acids. Results so far obtained show that under the conditions commonly employed for the hydrolysis of proteins with alkali cystine and cysteine yield alanine ; serine yields glycine and alanine ; threonine yields glycine and α -amino-n-butyric acid. An attempt is now being made to determine the extent of these dismutation reactions under various conditions.

A review of recent work on the organic phosphorus and nitrogen of soil and on the uronic fraction of soil organic matter was prepared for publication.

Studies in conjunction with R. H. Kenten of the Biochemistry department on the amino-acid metabolism of soil using the perfusion technique were temporarily abandoned owing to the practical difficulties encountered. The experience gained, however, made it obvious that there was need of a rapid method of identifying small amounts of amines formed by decarboxylation of amino-acids, and some progress has been achieved in the application of paper partition chromatography to this problem. The chromatographic behaviour of a large number of biologically important amines in various solvents has been studied and many useful separations have been achieved.

Soil phosphorus

J. B. Rickson has used the radioactive tracer technique in studying the behaviour of soil and other phosphates. When a solution of a phosphate labelled with radioactive phosphorus is added to soil the changes in the amounts of P³¹ and P³² can be used to estimate what fraction of the total phosphorus of the soil is capable of undergoing exchange. Soils with contrasted manuring for over a century in Broadbalk field were compared. In one with superphosphate annually about one-fifth of the total phosphorus was exchangeable. In one without added phosphate for the same period the amount of exchangeable phosphorus was negligible.

In similar experiments on ground crystalline fluorapatite the exchangeable phosphorus varied from 0.05 to 0.4 per cent of the total phosphorus according to the size of the particles. For laboratory preparations the following values were obtained: dicalcium phosphate 1.7 per cent, aged hydroxyapatite 1.5 per cent, freshly prepared hydroxyapatite 8.1 per cent. The "exchangeable" phosphorus determined in this way depends to some extent on the particle size but also, to a lesser degree, on the time allowed for the exchange. There is evidence that the "exchangeable" phosphorus is not confined to the surface of the particles.

In a number of experiments covering a range of concentrations of P³¹ and P³², it was shown that all the phosphate adsorbed on a synthetic anion exchange resin was readily exchangeable.

Fluorine in soils

Work briefly summarized in the Annual Report for 1948 has been continued by J. B. Rickson. Only about 20-40 per cent of the

fluorine added in superphosphate over a long period of years is retained in the soil. The increase by manuring is small in comparison with the amounts naturally present in soils. For soils with from 14 to 24 parts fluorine per million the increases by manuring for about 50 years were from 3 to 8 parts fluorine per million.

Soil manganese

In continuing her work on factors influencing the availability of manganese in soils, S. G. Heintze tested in pot experiments the effects of a number of different ways of adding manganese to a skirtland fen soil before sowing oats. The soil was acutely deficient in available manganese and no treatment prevented the appearance of grey-speck symptoms. Copper deficiency was also visible in the young leaves of tillers for most of the treatments.

All additions of manganese significantly increased yields of grain. Although few of the differences between alternative forms were significant the best grain yields from manganese compounds were from permanganate solution, manganese dioxide and manganese sulphate crystals coated with an aminoplastic.

ANALYTICAL

Exhaustion Land, Hoosfield

An account was given in the Rothamsted Report for 1949 of the history of plots which showed in the barley crop of that year most striking residual benefits from farmyard manure and superphosphate applied before 1901. The site had been used from 1856 to 1874 for a manurial experiment on continuous wheat and from 1876 to 1901 for one on continuous potatoes. Since then the land has been cropped mostly with cereals, without fertilizers until 1939 and subsequently with cereals receiving a liberal dressing of ammonium sulphate on all plots. The 1949 yields of barley grain and straw are given below together with analytical data by R. G. Warren for the crops and soils. Several plots have been averaged to give groups with no added phosphorus from 1856 to 1901, with superphosphate from 1856 to 1901, and with farmyard manure from 1876 to 1901 (superphosphate was given with the farmyard manure from 1876 to 1882).

Plots	Manuring to 1901	1949 Barley crop (cwt./acre)		
		Grain	Straw	P ₂ O ₅ in total crop
1, 2	None	8.8	10.4	0.047
5, 6	Nitrogen only ..	10.8	13.9	0.056
7, 8, 9, 10	Superphosphate ..	25.3	24.8	0.155
3, 4	Farmyard manure ..	26.4	24.8	0.165

Plots	Manuring to 1901	1949 soil analyses		
		pH	nitrogen per cent total	P ₂ O ₅ , mg/100g Readily soluble
1, 2	None	7.2	0.110	1
5, 6	Nitrogen only ..	6.8	0.112	1
7, 8, 9, 10	Superphosphate ..	7.2	0.112	6
3, 4	Farmyard manure..	7.2	0.138	6

Plots which had received phosphorus before 1901 in farmyard manure or in superphosphate gave nearly three times as much grain and twice as much straw as plots without any added phosphorus. The crops on plots with farmyard manure or superphosphate residues contained over three times as much phosphoric acid as those without added phosphorus before 1901.

The manurial residues were clearly shown by soil analyses. The contrasts were relatively great for readily soluble phosphoric acid (extracted by leaching with 0.5 M acetic acid). The residues of farmyard manure increased the soil nitrogen and organic matter by one quarter. The prolonged residual effect of heavy dressings of farmyard manure is also illustrated in the continuous barley plots in the same field.

Plot	Manure	Nitrogen per cent of soil
1-0	Unmanured since 1852	0.100
7-1	Farmyard manure 1852-1871, then unmanured	0.147
7-2	Farmyard manure annually since 1852 ..	0.266

Soil analyses on unreplicated plots are always subject to uncertainties through the risk of inherent irregularities, but the consistency of these two sets of plots gives support to the conclusion drawn from other investigations that farmyard manure leaves some very inert organic residues. The fact that superphosphate and farmyard manure have similar residual effects on crops and also on readily soluble soil phosphorus suggests that much of the residual benefit from farmyard manure is to be ascribed to its inorganic constituents. These results suggest that the conventional low estimates of the residual value of phosphate fertilizers and the emphasis placed on phosphate fixation may derive in part from the failure of ordinary field experiments to measure small benefits maintained over long periods.

Spectrographic analyses

In the Lundegårdh flame method of spectrographic analysis using a medium quartz spectrograph, H. A. Smith is attempting to replace the usual photographic record by direct photometry. An exit slit in the focal plane of the camera lens isolates the required line, the intensity of which is measured by a photo-multiplier tube with a suitable amplifier. This method may have advantages over direct flame photometry in that it allows measurements to be made in the ultraviolet, which is particularly convenient for manganese and magnesium. The sensitivity so far attained promises to compare favourably with the photographic method.

GENERAL

E. M. Crowther, S. G. Heintze, J. M. Bremner, and J. B. Rickson attended the Fourth International Congress of Soil Science at Amsterdam in July, 1950. E. M. Crowther was Chairman of the Soil Fertility Section.