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## Chemistry Department

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E. M. Crowther (1953) *Chemistry Department* ; Report For 1952, pp 39 - 50 - DOI:  
<https://doi.org/10.23637/ERADOC-1-74>

## CHEMISTRY DEPARTMENT

E. M. CROWTHER

### FERTILIZER AND OTHER FIELD INVESTIGATIONS

The supply position for sulphuric acid from sulphur, pyrites or anhydrite has eased, at least temporarily, and the reintroduction of subsidies on inorganic nitrogen and phosphorus fertilizers has restored the balance between prices of fertilizers and crops. The need for increasing the output of British farms and, at the same time, of keeping down imports of raw materials requires continued work on improved methods for making and using fertilizers. Some of the new processes under consideration yield products containing little water-soluble phosphorus, and it is therefore necessary, before these processes are adopted on a large scale, to ascertain the agricultural value of the products under a variety of conditions. For some crops considerable economy can be obtained by placing fertilizer close, but not too close, to the seed. Superphosphate, alone or in mixtures, is now commonly drilled with cereals, but for other crops drilling fertilizer with the seed or sets may be unsafe. For some crops controlled placement in bands at a safe distance from the seed has marked advantages but for other crops broadcasting remains an excellent method. Until the rules are worked out in detail there is little prospect of manufacturers producing the kinds of machines which will allow farmers and market gardeners to obtain the benefits of controlled placement of fertilizers.

#### *Fertilizer placement*

In extending earlier work G. W. Cooke, with M. V. Jackson and F. V. Widdowson, carried out in 1952 nineteen further field experiments comparing broadcast and placed fertilizers for potatoes planted by machines. The planter was used on flat land, planting the potatoes and covering them with a ridge of soil after applying the fertilizer. Early dressings of broadcast fertilizer cultivated deeply into the seedbed were compared with late dressings broadcast on the surface, immediately before planting, and with dressings placed either in contact with the seed or in a sideband below the level of the seed. National Compound No. 1A (8 per cent. N., 6 per cent  $P_2O_5$ , 10.5 per cent  $K_2O$ ) was tested at 7.5 and 15 cwt. per acre by each of these four methods.

On the average of all the experiments, placed fertilizer gave much higher yields than broadcast fertilizer. There was no advantage from early broadcasting, before cultivating to prepare the seedbed, over late broadcasting. At the lower rate fertilizer placed in contact with the seed gave slightly higher mean yields than fertilizer in a band at the side of the seed; at the higher rate contact placement was slightly inferior to sideband placement.

The mean yields of 14 experiments in 1951 and of 19 experiments in 1952, averaging rates of application, were :

*Mean yields, tons per acre*

	1951	1952
Broadcast early .. ..	—	8.8
Broadcast late .. ..	10.1	8.9
Placed in contact .. ..	11.1	9.8
Placed in sideband .. ..	11.0	9.8
No fertilizer .. ..	7.4	5.7

In both years placed fertilizer gave about one ton per acre more potatoes than the same amount of fertilizer broadcast. The relative efficiencies of the various methods of application, obtained by graphical interpolation from a smooth curve, taking sideband placement as the standard, were :

*Relative efficiencies of methods of applying fertilizer*

Method	1951		1952	
	Low rate	High rate	Low rate	High rate
Broadcast early .. ..	—	—	57	63
Broadcast late .. ..	50	68	61	67
Placed in contact .. ..	Over 100	Over 100	113	87
Placed in sideband .. ..	100	100	100	100

In each season fertilizer broadcast on the seedbed was inferior to placed fertilizer, two parts of placed fertilizer giving about the same yield as three parts of broadcast fertilizer. In both years placement was superior to broadcasting in more than three-quarters of the experiments, the differences being significant at about half of the centres.

In both years emergence and early growth of potatoes were depressed at most centres by the heavier dressings placed in contact with the seed, but, later, the crops recovered from the early check. At both rates in 1951 and at the lower rate in 1952, placement in contact with the sets gave higher yields than placement in sidebands. In 1952 the higher dressing placed in contact with the sets gave slightly lower yields on light soils than when placed in sidebands, but there was little difference between the two methods of placement on heavy land. With heavy dressings there is some risk of lower yields from contact placement on light land and in dry summers. There is need for a planting shoe with double walls to serve as fertilizer coulters on each side of the shoe. Such an arrangement might allow heavy dressings of fertilizer to be applied with safety even on light soils and, through economy in fertilizers, should prove worthwhile, even for farmers with only moderate acreages of potatoes.

G. W. Cooke with M. V. Jackson carried out preliminary experiments on fertilizer placement for horticultural crops at Rothamsted and at Luddington Experimental Horticulture Station (in collaboration with H. Fairbank and N. D. Goodway). Several of the crops suffered from drought. At Luddington, where both broadcast and placed fertilizer (National Compound No. 1A) increased yields of onions, placed fertilizers gave the higher yield. At Rothamsted a granular fertilizer containing 14 per cent P<sub>2</sub>O<sub>5</sub> and 14 per cent K<sub>2</sub>O gave much higher yields of broad beans when placed than when broadcast. At both centres National Compound No. 1A gave higher yields and earlier crops of lettuce when placed than when broadcast.

In an experiment on spring beans at Rothamsted superphosphate had little effect whether broadcast or placed: potassium sulphate gave a small increase when broadcast and a large one when placed. In a lucerne experiment at Rothamsted, P, K and PK fertilizers were tested as dressings broadcast before and after the final ploughing in preparing the seedbed. The effect of a "starter-dose" of superphosphate drilled directly below the seed was tested in conjunction with all the other treatments. The "starter-dose" gave much better early growth and yields than the broadcast dressings. The ploughed-in dressings gave slightly higher yields than the seedbed dressings in the first but not in the second cutting.

#### *Alternatives to superphosphate*

One alternative to using sulphuric acid for making superphosphate is to dissolve the phosphate rock in nitric acid and then to add ammonia to form a mixture containing mainly ammonium nitrate and dicalcium phosphate. To improve the condition of the mixture it is necessary, in addition, either to remove excess calcium nitrate, to add ammonium sulphate or to use a mixture of sulphuric and nitric acids in place of nitric acid alone. Materials prepared in these ways are now known as "Nitrophosphates." Various kinds of product need to be tested under many agricultural conditions before their agricultural value can be adequately assessed and the best conditions determined for their preparation.

In three experiments on spring-sown barley in 1952, G. W. Cooke with M. V. Jackson and F. V. Widdowson compared a "Nitrophosphate" (prepared with addition of ammonium sulphate) against an equivalent mixture of granular superphosphate and "Nitro-Chalk", the fertilizers being applied broadcast and also by combine-drill. On the average, the broadcast superphosphate mixture was superior to the broadcast "Nitrophosphate," but when combine-drilled both kinds of fertilizer gave similar yields. From these preliminary experiments it would appear that a "Nitrophosphate" with equal proportions of N and  $P_2O_5$  would be suitable for drilling with spring cereals.

Two series of co-operative field experiments, initiated by the Fertilizer Conference of the Agricultural Research Council and planned and co-ordinated from Rothamsted, were continued in 1952. The field work was carried out under the direction of Soil Chemists of the National Agricultural Advisory Service and the staffs of the Northern Ireland Ministry of Agriculture, the Macaulay Institute for Soil Research and Rothamsted Experimental Station.

In the first series, on the average of nine potato experiments, yields decreased in the order superphosphate, dicalcium phosphate, silicophosphate and Gafsa rock phosphate.

The second series of experiments tested three kinds of "Nitrophosphate," prepared in three countries. All plots received equal amounts of N and K and the tests were therefore concerned with the availability of the P. On the average of nine experiments on grass cut for hay or silage, a "Nitrophosphate" made with addition of ammonium sulphate gave yields rather better than those from equivalent superphosphate; a "Nitrophosphate" made with mixed nitric and sulphuric acids was about two-thirds as effective as

equivalent superphosphate; a "Nitrophosphate" made by removing surplus calcium nitrate was much inferior to the other forms and gave very little response. Closely similar results were obtained in ten experiments on potatoes.

It is not by any means certain that these results depend on essential features of the processes by which the various "Nitrophosphates" were made. We noticed that there were marked differences in the physical properties of the granules and that these did not remain constant from year to year in products from a single factory. In some of the preparations the granules slaked rapidly, whilst in others the granules remained hard and compact. It is possible that the rate at which dicalcium phosphate enters or moves within the soil may be influenced by the speed with which the granules break down in contact with moisture. This property may depend on details in the drying or granulating processes rather than on the general method of preparation. Investigations on new kinds of fertilizers are inevitably complicated by the circumstance that the methods of preparation have not been stabilized. Indeed, the agricultural investigations sometimes reveal possible improvements in production methods, at the cost to the experimenter of having different kinds of material in successive years of what may originally have been intended to be a uniform series of repeated experiments.

#### *By-product ammonium sulphate*

G. W. Cooke and J. K. Gasser made preliminary observational tests on a sample of ammonium sulphate prepared at a gasworks by a new process in which 69 per cent of the S was as sulphate, 12 per cent as sulphite and 18 per cent as thiosulphate. The product, which was in poor mechanical condition, was applied in heavy dressings to grass, cereals, potatoes and market garden crops to test possible toxic effects in comparison with ordinary commercial ammonium sulphate. In one experiment on wheat early growth was poor with the by-product and in one experiment on grass the foliage was slightly burnt but in many other experiments there were no signs of damage or reduced growth. If by-product fertilizers, difficult to apply or containing materials likely to be harmful, are to be used in agriculture, they must be offered at greatly reduced prices.

#### *Nutrition problems in forest nurseries*

Investigations in collaboration with the Research Branch of the Forestry Commission were continued. The background of the work and some of the main findings were reviewed in the Rothamsted Report for 1949. Annual summaries are published in the Forestry Commission's "Reports on Forest Research." B. Benzian was in charge of the experiments in several nurseries and forests and R. G. Warren, H. A. Smith and J. E. A. Ogborn of associated laboratory work. The Soil Microbiology and the Nematology Departments made special investigations on biological aspects of certain problems arising in the course of the work.

In experiments at several nurseries in each of seven seasons we have had marked improvements from treating the soil with formalin

solutions at least three weeks before sowing Sitka spruce or other conifers. The results have improved as we gained experience on the best times and methods of applying the formalin. A successful treatment has been to apply 250 ml. of formalin per square yard, after diluting to such a volume, often 5 l., as the soil can take up quickly. It was found in three nurseries that formalin applications in December 1951 were even better than those given in February 1952. It would be difficult to apply the formalin treatment on a commercial scale, on account of the large volumes of water needed. We have continued our search for alternative materials, partly in the hope of finding something more convenient on a large scale and partly because materials with more specific effects than formalin might throw light on some of the major factors involved in the effects of soil disinfection under various conditions. In 1952 injection of neat formalin at 9 inch centres gave only very small improvements at two nurseries, with fair results at a third. Paraformaldehyde was ineffective in 1952. From past failures with a variety of fungicides in field and pot experiments it seemed likely that a major difficulty was to secure intimate incorporation of the active material throughout the whole mass of surface soil. It was therefore decided to test a number of volatile fumigants. Chlorpicrin, injected in February in about 2 ml. doses at 9 inch centres, gave significantly better results than formalin solutions in each of three nurseries in which it was tested. Chlorpicrin also gave good results in pot experiments on soils from three nurseries. Ethylene dibromide failed in the pots and in two of the three nurseries, but it gave marked improvements in Ringwood nursery, which is known to carry a much heavier population of nematodes than the other nurseries in which we have made experiments. J. B. Goodey's examination of plants from experiments in the Ringwood nursery showed that formalin, chlorpicrin and ethylene dibromide greatly reduced the numbers of the nematode *Hoplolaimus uniformis* on first-year Sitka spruce seedlings. There were also differences associated with manurial treatments. In another experiment in the same nursery transplants growing on untreated plots carried a heavy infestation of the same nematode, whilst those on plots previously treated with formalin were completely free of it.

D.D., a chlorinated propane and propylene, checked "damping-off" and improved growth of Sitka spruce seedlings in pots. It will be tested in field experiments against other fumigants and formalin, at various intervals before sowing.

Formalin solutions applied two months before lining-out markedly improved the growth of Sitka spruce transplants in several nurseries. In one nursery the formalin treatment of transplant beds was deliberately postponed until a month before lining-out to avoid chemical reactions with another factorial soil treatment in the experiment. The results were disastrous: most of the plants on the formalin plots were killed. Although the disinfection or fumigation of transplant beds has great promise and some theoretical interest in confirming that the benefits from formalin treatment do not depend primarily on checking early "damping-off," the technical details must be worked out more fully before the method can be used safely for transplants.

Seedlings raised on formalin treated plots have behaved very well in transplant beds and in forest plantings. Each year representative plants from experiments in several nurseries have been examined for mycorrhiza by Dr. I. Levisohn of Bedford College, but no clear relationships have so far been found between nursery treatments and the occurrence of mycorrhiza. A large number of representative plants are examined each year at Rothamsted for gross morphological features. It is common to find that poor plants from plots without disinfectants show signs of damage to the tap root and laterals. They also often have long black roots, presumably infected by pathological fungi. Sometimes it appears that fine fibrous roots arise through repeated damage and are not necessarily a sign of favourable conditions and vigour.

Sowing was unavoidably late at all nurseries in 1952 and this may have introduced some abnormal features. A number of visual symptoms were either different from or occurred much later than in most of the preceding years. An acute general yellowing of transplants on plots known to be potassium-deficient was observed at Wareham for the first time since 1946. The yellowing and hardening of the younger needles, shown by responses to manurial treatments to be a symptom of magnesium deficiency, did not appear in 1952 until late in October and were much less marked than in earlier years. The usual purplings from potassium deficiency were general on plots lacking this element in certain compost and fertilizer treatments.

An experiment started on very acid soil in Sugar Hill Nursery, Wareham in 1948 received eight kinds of seed-covers for four successive crops of one-year Sitka spruce seedlings. The fifth crop in 1952 received a uniform quartz cover to measure the residual effects of the earlier treatments. The residues from four covers containing considerable amounts of calcium carbonate as limestone or shell fragments gave much poorer growth of Sitka spruce seedlings than covers free from calcium carbonate. In this experiment we reproduced a set of conditions which in the past had led to serious losses of productivity in many nurseries. Calcareous seed-covers were used quite frequently before the autumn of 1947 when, on our recommendation, they were banned from Forestry Commission's Nurseries.

Many experiments indicate, without completely establishing, that the benefits from keeping conifer nurseries very acid and from using soil disinfectants in the old nurseries depend in part on maintaining a supply of ammonium nitrogen in place of nitrate nitrogen. In one experiment continued for four seasons in an old neutral nursery, repeated dressings of ammonium sulphate gave better Sitka spruce seedlings than equivalent dressings of "Nitro-Chalk." In new experiments in 1952 in two old nurseries the heights decreased in the order ammonium sulphate, "Nitro-Chalk," calcium nitrate—for equivalent top-dressings; the differences were small and irregular in newer acid nurseries.

In an experiment at Wareham, which has run for four seasons with two years' grass ley followed by two successive crops of one-year Sitka spruce seedlings, the first crops of Sitka spruce have been much poorer than the second crops. Observations on irregularities

in other experiments in this nursery, on a site which had carried ley two years previously, suggest that the grass root residues decompose very slowly and, in some way, interfere with the normal growth of Sitka spruce seedlings. In a large rotation experiment started in Kennington nursery in 1951 the Sitka spruce seedlings of 1952 were poorer after green crops in 1951 than after the Sitka spruce in that year. A parallel experiment at Wareham showed only small differences. In two earlier series of rotation experiments there was little benefit from resting conifer seedbeds under green crops or leys.

In an experiment continued for five seasons on very acid poor soil at Bagley Wood, plots with fertilizers gave rather better average mean heights than plots with a standard compost of bracken and hopwaste, but the fertilizers were slightly inferior to the compost in one season of prolonged drought. The best growth over all seasons was from special composts prepared by loading either straw or bracken with heavy dressings of fertilizers. The progressive improvement of the plots with time decreased in the order: composts made with fertilizers, heavy fertilizer, ordinary composts, light fertilizer, raw organic wastes with fertilizers, unmanured. This series suggests that most of the observed differences can be ascribed to the nutrients in the composts and fertilizers with little additional benefit from the organic matter as such.

#### *Soil conditioners*

G. W. Cooke and his colleagues carried out small-scale trials on thirteen farms in Eastern England to test the effects of a soil conditioner (the sodium salt of a hydrolyzed polyacrylonitrile, supplied as "Krilium CRD-189") on potatoes. The tests, which adjoined other fertilizer experiments, consisted of four very small plots, each of two rows of potatoes six feet long. One diagonally opposite pair of plots received the conditioner, which was carefully forked in at the rate of 600 lb. per acre, no filler being used. No differences in soil structure or in crop growth were observed in repeated inspections during the season but, when the potatoes were lifted, the soil at two centres appeared to have better structure on the treated plots. The yields from such small plots are inevitably uncertain but the over-all average yields of 11.6 tons per acre with soil conditioner and 11.2 tons per acre without soil conditioner give little indication of any general benefit.

B. Benzian carried out three small-scale experiments in forest nurseries, in association with the Research Branch of the Forestry Commission, to test the soil conditioner at the rate of 3 cwt. per acre, carefully incorporated into the surface by forking, raked into the surface inch after forking, and applied in both ways. The soils were fine sands or sandy loams. No visible effects on soil structure or crop growth were observed at any stage, apart from some inferiority in growth following the surface application in one nursery.

The above experiments were made with direct applications of the active material without diluent or filler. Its hygroscopic nature may have interfered with intimate incorporation. It would appear that improved methods of preparation and application must be devised before synthetic soil conditioners can be expected to improve crop growth under normal agricultural or horticultural conditions.



### *Liming materials*

E. M. Crowther and T. W. Walker published a summary of several series of field experiments carried out by soil chemists of the National Agricultural Advisory Service on the relative values of alternative liming materials. The standard rate of application was generally determined by the Hutchinson-McLennan "lime requirement" method. On the average of large numbers of experiments, crop yields were doubled by liming materials applied at the standard rate, but lower rates of application were highly effective. On the average, dressings at half of the standard rate gave 85 per cent of the crop increases obtained from the standard rate. Although the full rate of dressing may sometimes prove profitable, especially as a long-term investment, there must be large areas of land which would give a very high return from quite modest applications of liming materials. On many farms with acid soils it would be a better investment to work round most of the fields quickly with light dressings than to proceed piecemeal with heavy ones.

Experiments with specially prepared size-fractions of limestone showed that materials passing a sieve with 40 meshes per inch gave yields close to those from equivalent amounts of burnt lime. Even coarse fractions (with only 9 per cent passing a 40-mesh sieve) were better than half the equivalent amounts of burnt lime. There is no need in practice to grind limestones more finely than is required to give 40 per cent through a 100-mesh sieve. Such limestones gave, on the average, rather higher yields than equivalent amounts of burnt lime, presumably because the limestones can be spread more evenly and incorporated more uniformly throughout the soil. In a few experiments on magnesian lime and limestones there was some evidence of greater benefit from the magnesian than from the high-calcium materials for sugar beet grown on recently reclaimed acid sands. Provided burnt lime or limestone are used at something approaching "lime requirement" rate, the form chosen and the precise rate of application are of little, if any, importance. After taking into account the cost of transport and spreading, the ease and uniformity of incorporation and allowing for the subsidy, farmers should select the form which supplies the desired neutralizing value (expressed as equivalent calcium oxide) at the lowest cost.

## SOIL INVESTIGATIONS

### *Soil organic matter*

In continuing earlier work on the nitrogen complexes of soil organic matter, J. M. Bremner has studied the amino-acid composition of the protein material in various fractions and given some attention to the more chemically resistant fraction of the soil nitrogen. The main subject of investigation has, however, been the amino-sugar fraction, the presence of which was established by colour tests and chromatographic techniques. Six soils with nitrogen contents ranging from 0.17 per cent to 2.82 per cent were subjected to detailed examination for amino-sugars by various methods of analysis and it was found that from 6 per cent to 10 per cent of the total nitrogen was in the form of 2-amino sugars. K. Shaw investigated the decomposition of amino-sugars in the soil

by determining the amounts of ammonia-N and nitrate-N after incubating glucosamine and chitin with soil for various periods of time. After a slow start these materials nitrified readily, though less rapidly than casein or a nucleic acid preparation. After incubation for 35 days, 42 per cent and 54 per cent of the nitrogen added as chitin and glucosamine, respectively, were recovered as nitrate.

In earlier work J. M. Bremner could find no free amino-acids in cold aqueous extracts of several neutral clay loams and fen soils after concentrating the extracts at low temperature *in vacuo* and examining them by paper partition chromatography. More recently this technique revealed the presence of several amino compounds in aqueous extracts of acid peats, and serine, glycine, alanine, aspartic and glutamic acids could be identified. The amounts of free amino-acids detected were however very small and it does not appear likely that free amino-acids occur as more than traces in normal agricultural soils.

In conjunction with P. W. Arnold, of the School of Agriculture, Cambridge, and formerly of this department, J. M. Bremner investigated the possibility of applying paper chromatographic techniques to the separation, identification and estimation of various inositol phosphates, materials believed from work elsewhere to form a considerable fraction of the organic phosphorus in soils. The results so far obtained indicate that these techniques would be of limited value. Other methods of fractionating and characterizing inositol phosphates are being explored.

In continuing investigations, summarized on page 44 of the Rothamsted Report for 1951, on the reaction between lignin and nitrous acid, a need arose for a satisfactory method of separating and identifying small amounts of hydroxylamine. J. M. Bremner succeeded in devising a reliable method based on paper chromatography with acidic solvents and detection by specific reagents.

As a preliminary to a projected investigation on the rates of nitrification of various nitrogenous materials and on factors influencing the decomposition of plant residues in grassland soils, K. Shaw tested, and, in some cases, improved methods commonly employed in nitrification studies. Ammonia nitrogen in soil extracts prepared by a modification of Olsen's method, was determined by distillation with a buffer at pH 8.8, which did not appreciably decompose urea, glutamine, allantoin, asparagine and other labile compounds. Later work showed that distillation with magnesium oxide in a Conway microdiffusion unit at room temperature gave closely similar results to the buffer-distillation method. Glucosamine-nitrogen was recovered almost quantitatively as ammonia by the buffer-distillation method but no significant amount of ammonia was liberated from glucosamine by the magnesia-microdiffusion method. Amino-sugar nitrogen in soil hydrolysates could be estimated by the difference between these two methods.

Nitrates are being determined by the phenoldisulphonic acid method on an extract made with calcium sulphate solution. The determination of ammonia and nitrate nitrogen together by reducing with iron in acid solution at room temperature is being investigated but the results, so far, are not satisfactory.

*Soil phosphorus*

G. E. G. Mattingly carried out a number of pot and field experiments to gain experience of various techniques for using radio-phosphorus as a tracer in studying the availability to plants of the phosphorus present in soils and fertilizers. In this kind of work it is necessary to establish that plant growth is not appreciably influenced by the radioactive tracer itself. If special precautions are taken to ensure that the  $^{31}\text{P}$  and  $^{32}\text{P}$  are uniformly distributed throughout an experimental batch of fertilizer, determinations of the radioactive form in any plant grown with this fertilizer will show how much of the  $^{31}\text{P}$  as well as the  $^{32}\text{P}$  came from the fertilizer. Plants will also take  $^{31}\text{P}$  but not  $^{32}\text{P}$  from the soil and it is thus possible to calculate for any prescribed set of conditions how far the fertilizer phosphorus has been diluted by soil phosphorus. This amount of soil phosphorus may be taken as an estimate of "available" soil phosphorus and, following an American suggestion, is known as the "A value." It should be noted that the technique determines only an end-result and records only the historical fact that a certain proportion of the phosphorus in the plant had at one time been in the fertilizer, even though it may have reacted or exchanged with other phosphorus compounds in the soil and become "soil phosphorus" before it was taken up by the plant. In experiments on this subject the results obtained depend on the form of the test-fertilizer, the way in which it is applied to and incorporated with the soil, the pattern of root growth and many other factors, many of which must be examined experimentally.

Series of experiments were carried out with radishes and ryegrass on soils from three plots in the Exhaustion Land of Hoosfield, which had received no phosphorus in fertilizers or manures since differential manuring was discontinued in 1901. The radish experiment gave irregular results through poor germination. The ryegrass was cut three times. In the first cut superphosphate added after the soil had been crumbed gave slightly higher yields than superphosphate incorporated before the soil was crumbed, but this difference disappeared in the later cuts. Neither experiment showed any effect from varying the amounts of  $^{32}\text{P}$  in the added superphosphate.

The results of the pot experiments, averaging several rates of added superphosphate, are given below together with typical recent results from a barley crop on the same plots.

Field treatment to 1901	Field results Barley 1950 cwt. grain per acre	Pot experiments g. dry matter per pot			
		Radishes		Ryegrass	
		no P	+ P	no P	+ P
no P .. ..	11.0	0.8	1.4	0.8	3.9
Farmyard manure ..	22.2	2.0	2.2	4.8	5.3
Superphosphate ..	20.9	1.6	1.9	4.4	5.1

The residues from superphosphate or farmyard manure applied over fifty years ago in the field gave somewhat higher yields in the pots than the average of the various rates of superphosphate added to the soil without manurial residues. The estimates of "available phosphorus" (A values) were 3 mg. P per 100 g. soil for the unmanured plot and 11 mg. P per 100 g. soil for the plots with residues

from superphosphate or farmyard manure applied last century. The radish and the ryegrass experiments gave closely concordant estimates of "A values."

Preliminary field experiments were carried out by G. E. G. Mattingly and G. W. Cooke to test the responses of beans, potatoes, fodder beet and swedes to four phosphate fertilizers, broadcast in advance of sowing, with a small dressing of radioactive superphosphate drilled with the seed on all plots. Determinations of total phosphorus and of the proportion derived from the placed superphosphate were made on several occasions throughout the season. On the average of three crops—potatoes, beet and swedes—at final harvest, the percentage of the plant phosphorus derived from the placed fertilizer were 8.5, 7.5 and 6.6 for superphosphate broadcast at the rates of 0, 0.3 and 0.6 cwt.  $P_2O_5$  per acre. The "A values" derived from these data agreed satisfactorily with the amounts of superphosphate broadcast but the agreement may be fortuitous since some of the other fertilizers gave discordant results. The standard errors were high through the inevitable difficulties of working on small plots of isolated crops and using a very small experimental drill for placing the radioactive fertilizer and sowing the seeds. Radioactive fertilizers are much too expensive at present for full-scale experiments in the field and it will be necessary to refine the small-scale technique before tracers can be used to attack many problems of both theoretical and practical importance in crop nutrition and manuring. In this kind of work it is not sufficient to use radiotracers merely to demonstrate that water-soluble fertilizers placed near seeds are taken up by plants more rapidly than less soluble fertilizers in the same position or than broadcast fertilizers distributed throughout the whole mass of soil. Much detailed and exacting work will be needed before radiotracers can be used to resolve old problems and throw new light on mechanisms.

O. Talibudeen has used radiotracer techniques in studying the nature of the precipitated calcium phosphates which lie between dicalcium phosphate and hydroxyapatite. Suitable techniques were developed for measuring  $^{45}Ca$  as oxalate and  $^{32}P$  by the direct evaporation of aliquots. Attempts are being made to differentiate in precipitated calcium phosphates between primary nucleation, recrystallization and secondary nucleation of a heterogeneous phase from an apparently saturated solution. Using a light acid soil from Woburn and a heavy calcareous soil from Rothamsted, isotopic equilibrium measurements are being made to determine the percentage of the total phosphorus in equilibrium with the phosphorus extracted by acetate buffer solutions of different hydrogen ion concentrations and ionic strengths.

F. S. C. P. Kalpagé commenced an investigation into factors influencing the apparent solubility of phosphate rock and other fertilizers in the conventional citric acid and ammonium citrate tests for "available phosphoric acid."

#### *Soil manganese*

S. G. Heintze continued her investigations on the reduction and extraction of synthetic higher oxides of manganese added to alkaline soils, using various reducing agents. Hydroquinone followed by

calcium nitrate extracted little manganese from soils incubated with hausmannite or  $\gamma$  manganite and large proportions from soils treated with colloidal manganese dioxide, manganese sulphate or  $\gamma$  manganese dioxide. From a fen soil the recoveries were about three-quarters of those from mineral soil. Hydrosulphite in ammonium acetate extracted about one-half of the manganese added in any form to the mineral soil and about one-third of that added to the fen soil, apart from  $\gamma$  manganite which gave much lower recoveries from the fen soil. The proportions of the total manganese extracted from the untreated soils were roughly similar for the various extractants to those obtained from soils treated with colloidal manganese dioxide or manganese sulphate but were markedly different from those treated with hausmannite or  $\gamma$  manganite. From fen soil treated with colloidal manganese dioxide the proportion of added manganese extracted with alkaline pyrophosphate was low relative to that from the mineral soil or to the proportion of the total manganese extracted from untreated fen soil. It appears from this work that the inert manganese in some fen soils is not present in forms resembling hausmannite or  $\gamma$  manganite.

In a pot experiment with mineral soil treated with various manganese compounds, the manganese contents of the repeatedly cut Timothy grass fell off in the order: manganese sulphate (as crystals), synthetic  $\gamma$  manganese dioxide, synthetic hausmannite, synthetic  $\gamma$  manganite, natural pyrolusite and potassium permanganate (as crystals). The order for oxides reflects that obtained in reduction-extraction experiments.

#### GENERAL

E. M. Crowther, R. G. Warren, G. E. G. Mattingly and K. Shaw attended the Soil Fertility Meeting held in Dublin in July 1952 and organized by the Irish Department of Agriculture and Commissions II and IV of the International Society of Soil Science.

G. W. Cooke visited France, Belgium and the Netherlands with an Agricultural Research Council Travelling Grant to study recent developments in the production and testing of fertilizers based on dicalcium phosphate.

M. V. Jackson returned to the National Agricultural Advisory Service after secondment to this department for two years to gain experience in field experimentation. His place was taken by J. C. Wilcox. C. P. Kirkland of the Forestry Commission was seconded for a further year to assist in forest nursery investigations. J. K. R. Gasser, a Colonial Office Scholar spent part of the year in the Chemistry Department and part in the Pedology Department. W. B. Haines joined the department.

E. M. Crowther acted as Director of Studies for a week's course at Rothamsted on field experimentation, organized by the British Council and including lectures and demonstrations by members of the Botany, Chemistry and Statistics Departments, and the Field Experiments Section.