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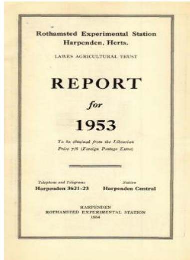
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CHEMISTRY DEPARTMENT

E. M. Crowther

Alternative phosphate fertilizers

The phosphates in most British compound fertilizers are derived from superphosphate or ammonium phosphate and are valued in terms of a water-solubility test, but in many other countries phosphates insoluble in water are classed with water-soluble compounds as " available phosphoric acid " in assessing fertilizer values. In the United Kingdom the citric acid test is used for basic slags, and it is known to distinguish fairly sharply between the active silicophosphates and the almost inactive fluorapatite in Open Hearth basic slags. The citric acid test is of little, if any, use in characterizing ground phosphate rocks, because the amounts dissolved vary markedly with the conditions of extraction.

A universally applicable method for evaluating phosphate fertilizers would be of great assistance to farmers and their advisers, and especially to manufacturers conducting pilot-plant investigations on new processes, but there is a serious risk of error if the analytical method chosen should prove to be inappropriate for any important type of soil or class of product. The availability of phosphate fertilizers to crops involves so many complex factors that laboratory methods should be checked and standardized by the results of direct comparisons of fertilizers in field experiments under a wide range of conditions. This is of special importance at the present time, when attempts are being made in several countries to effect economies in sulphuric acid by using new processes which give products with high proportions of their phosphate insoluble in water. Before such materials are produced and sold on a large scale it is important to know how they compare in the field with superphosphate supplying equal amounts of phosphorus, for the newer processes are not likely to succeed unless the products prove to be at least as economical as superphosphate.

In order to obtain basic data on these general questions, several series of co-operative field experiments have been conducted with associated laboratory work. E. M. Crowther, R. G. Warren and G. W. Cooke have published a detailed account (21) of field experiments on materials of special interest during the war and the following years. Since 1951 two new series of field experiments, initiated by the Fertiliser Conference of the Agricultural Research Council and planned and co-ordinated from Rothamsted, have been conducted annually by the soil chemists of the National Agricultural Advisory Service and the staffs at the Northern Ireland Ministry of Agriculture, the Macaulay Institute for Soil Research and the Rothamsted Experimental Station. G. W. Cooke has prepared the following interim summary of the results so far to hand. Both series of experiments were in 6×6 Latin Squares with superphosphates at rates of 0, 1, 2 units of P_2O_5 and three other phosphates equivalent to 1·5 units. All plots received equal amounts of nitrogen and potassium.

The results are summarized below as crop yields and as " percentage superphosphate equivalents ", the latter figures giving the amounts of superphosphate found graphically to give the same mean yields as one hundred parts of the fertilizer tested.

TABLE 1

Experiments on potatoes (1951–53) *and swedes* (1951–52)

Cwt. P_2O_5 per acre	No. of experiments :	Potatoes on very acid soils (pH 5·5 and less) 10	Potatoes on acid soils (pH 5·6–6·5) 15	Potatoes on neutral soils (pH over 6·5) 9	Swedes 24
	Yields in tons per acre				
—	No phosphate	9·2	9·8	9·1	11·6
0·33	Superphosphate	10·9	10·9	9·9	17·2
0·66	Superphosphate	11·6	11·2	10·3	19·7
0·5	Dicalcium phosphate	11·5	10·9	10·0	18·3
0·5	Silicophosphate	11·2	10·8	9·6	18·1
0·5	Gafsa phosphate	10·3	10·6	9·2	18·1
	Percentage superphosphate equivalents				
	Dicalcium phosphate	122	62	88	90
	Silicophosphate	92	56	30	87
	Gafsa phosphate	34	37	4	87

The results of the first series of experiments on potatoes and swedes are given in Table 1, the potato experiments being grouped by soil reaction. Most of the swede experiments were on soils with pH values between 5·5 and 6·0. Dicalcium phosphate, which is highly soluble in citric acid or neutral ammonium citrate but not in water, was used in a finely divided form, and gave results only slightly inferior to those from equivalent superphosphate for both crops on all classes of soils. Silicophosphate, prepared by heating phosphate rock with sodium carbonate and also without water-soluble phosphate, gave almost as good results as superphosphate for potatoes on very acid soils and for swedes, but was markedly less active than superphosphate for potatoes on moderately acid or neutral soils. Ground Gafsa mineral phosphate gave very good results on swedes but poor ones on potatoes, even on very acid soils. This material is not expected to work on neutral soils. With current subsidies unit phosphate in ground Gafsa mineral phosphate costs only about one-third as much as that in granular superphosphate, and there would therefore seem to be a good case for using mineral phosphate much more extensively on the large areas of acid soils which remain in the hill lands of the wetter areas. Ground mineral phosphate could serve as the only source of phosphate for swedes and established grass, but for other crops, including the seeds for leys, it would need to be supplemented by a moderate dressing of a soluble phosphate as a " starter-dose ".

In several countries compound fertilizers—" Nitrophosphates " —are being made by using nitric acid in place of sulphuric acid to attack the phosphate rock; ammonia is added to neutralize the excess acid and form dicalcium phosphate and ammonium nitrate, but it is also necessary to reduce the content of soluble calcium salts still further. In one process excess calcium nitrate is removed before adding the ammonia. In others calcium sulphate is formed by using a mixture of sulphuric acid and nitric acids or by adding ammonium sulphate. As the products are granular, the important question arises whether the insoluble dicalcium phosphate can act quickly enough where early establishment and growth are important.

TABLE 2

Experiments on potatoes and grass (1952–53)

Cwt. P_2O_5 per acre	No. of experiments :	Potatoes on acid soils (pH 6·5 and less) 11	Potatoes on neutral soils (pH 6·6 and over) 7	Grass 20
	Yield in tons per acre			
—	No phosphate	9·7	10·7	2·33
0·3	Superphosphate	10·7	11·3	2·51
0·6	Superphosphate	11·6	12·1	2·52
	Nitrophosphate made by :			
0·45	Adding ammonium sulphate	11·0	11·2	2·50
0·45	Using nitric and sulphuric acids	10·7	11·2	2·47
0·45	Removing calcium nitrate	10·2	11·0	2·46
	Percentage superphosphate equivalents			
	Nitrophosphate made by :			
—	Adding ammonium sulphate	88	51	—
	Using nitric and sulphuric acids	66	52	—
	Removing calcium nitrate	34	20	—

Three kinds of Nitrophosphate were compared in the co-operative trials of 1952 and 1953, with results set out in Table 2. All three Nitrophosphates proved to be inferior to superphosphate for potatoes, especially on neutral soils. There were also marked differences between the three kinds of Nitrophosphate, the one made by removing calcium nitrate being inferior to the other two. The grassland experiments were very insensitive, with negligible benefits from increasing the superphosphate dressing. Although the differences were very small, the order of the Nitrophosphates was the same as for the average of the potato experiments. These results suggest that producers of Nitrophosphate or similar fertilizers should not value the phosphate at more than about three-quarters of water-soluble phosphate. Further, it may be misleading in pilot-plant developments to rely on the citric acid tests. The product made by adding ammonium sulphate had 28 per cent of its phosphorus in a water-soluble form, and the other two had almost none, but only 89 per cent of its phosphorus was soluble in citric acid, as compared with 100 and 96 per cent in the two products which behaved less well in the field. The behaviour of dicalcium phosphate in granular fertilizers needs much more detailed investigation in the laboratory and the field in relation to the precise form of the crystals, the physical conditions of the granules and the nature of the other salts present before it would be safe to rely on laboratory methods to characterize the products. The necessary field work, laborious and expensive as it is, should be regarded as part of the developmental costs to be incurred before a new kind of phosphate fertilizer is introduced. For farmers and their advisers it would appear that the phosphate in Nitrophosphate behaves in much the same way as that in high-soluble basic slags. These

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two classes of fertilizer have not been compared directly, since they are normally used in different ways.

The general results of both series of experiments emphasize the outstanding merits of water-soluble phosphate on most, if not all, classes of land. Although other tests are needed for certain special classes of phosphate fertilizer, formal simplicity should not be secured at the cost of sacrificing the water-solubility test for superphosphate, ammonium phosphate and mixtures based on them.

Fertilizer placement

G. W. Cooke with F. V. Widdowson and J. C. Wilcox tested a Nitrophosphate (made with the addition of ammonium sulphate) against an equivalent mixture of granular superphosphate and " Nitro-Chalk ", both lots being applied broadcast and combine-drilled. On the average of five experiments on spring cereals, Nitrophosphate was of little value when broadcast and better, though still inferior to the superphosphate and " Nitro-Chalk ", when combine-drilled. The mixture with soluble phosphate gave much better early growth than Nitrophosphate. On very many soils cereals require phosphate only to ensure quick establishment, and for this purpose water-soluble phosphates are much to be preferred.

In extending earlier work on methods of placement for PK and NPK fertilizers, experiments were made to test individual fertilizers. On the average of seven experiments on potatoes, ammonium sulphate at a light rate (0·5 cwt. N per acre) was better placed, whilst double this amount was better broadcast. Placing potassium sulphate (3 cwt. per acre) gave slightly higher yields than broadcasting in five of seven experiments.

There was no worth-while advantage from splitting the nitrogen dressing, applying half at planting and half in the summer, over giving all of it at planting. In another series of experiments additional nitrogen as a top dressing gave only trivial increases in yield, even in areas where potatoes are regarded as maturing too early in the autumn.

In further experiments on horticultural crops placed fertilizers gave better results than broadcast fertilizers on lettuce, cabbage, beetroot, broad beans and runner beans. The benefit showed particularly well in the first cuttings of lettuce, French or runner beans and cabbage.

Much of the work on fertilizer placement has now reached the stage at which it should be extended to other areas not easily reached from Rothamsted. A useful beginning has been made in this direction in the Eastern Province of the National Agricultural Advisory Service in trials on threshed peas and also on peas picked green for market, canning, or freezing.

Experiments on several crops have shown the advantage of placing moderate amounts of PK fertilizers near the seed. In a recent experiment on lucerne a " starter-dose " of superphosphate placed directly beneath the seed improved establishment and early growth. Many experiments on old arable soils have shown only small responses to normal dressings of phosphate fertilizers, and considerable economy could often be made by broadcasting a fertilizer rich in nitrogen and potassium and placing a small amount of water-soluble phosphate near the seed to promote early growth and to act as an insurance against an unsuspected deficiency of soil phosphate. Heavy manuring of potatoes and other more responsive crops often supplies unnecessarily large amounts of phosphate, and there is now a need for an additional National Compound Fertilizer with high N, low P and high K or even for an NK fertilizer. For cereals P and K should always be applied by combine-drill, with nitrogen broadcast at rates limited only by the risk of lodging. Kale and similar forage crops require only moderate quantities of phosphorus and potassium, which could be applied as a " starter-dose " close beneath the seed, with nitrogen broadcast at seeding time or later, at much heavier rates than are commonly given.

Long-term effects of fertilizer treatments

The conclusions drawn in the preceding paragraphs are based on single-year experiments. A number of the experiments were continued for a second or third year, but the residual benefits were generally small, and the comparisons of alternative materials after the first season were of low precision. Since the residual effects are generally small, there is little point in attaching much importance to them in comparing alternative fertilizers and in considering many other problems in practical manuring, with one important exception. There is no doubt that long-continued manuring at high rates builds up substantial reserves. Many farmers would justify their continued heavy use of phosphorus and potassium fertilizers as a long-term investment.

An extreme example of long-term residual effects is afforded by ten plots on the Exhaustion Land of Hoos Field, some of which received PK fertilizers or farmyard manure annually between 1856 and 1901 with none since. Nitrogen fertilizers have been applied to annual barley crops on these plots during the last dozen years, and the plots with manurial residues have given roughly twice the yields on the plots without. R. G. Warren, in continuing his analyses of soils and crops from the older Rothamsted experiments, has obtained results summarized in Table 3.

TABLE 3

Hoos Field Exhaustion Land

Plots	Annual manuring 1856–1901	Mean yields, P and K contents of barley in cwt. per acre per annum, 1949–51: Dry grain	Dry straw	P	K	Exchangeable K in soil, 1951, mg. K per 100 g.
1, 2, 5, 6	no P, no K	10·1	11·6	0·033	0·137	6·1
9	P (with K to 1875)	19·7	19·0	0·071	0·226	7·0
7, 8, 10	P, K	21·1	20·7	0·077	0·337	11·2
3, 4	F. Y. M	21·3	22·0	0·082	0·289	9·3

The plots with PK or farmyard manure last century gave crops with over twice as much phosphorus and potassium as those not receiving these manures. It is not easy to decide whether the P and K act independently or whether the large crops grown by the P residues are able to explore the soil more thoroughly for K. It was shown in the 1950 Report that the readily soluble P in the soil was higher on the plots with P residues, and the difference has been brought out vividly in several recent pot experiments on soils from these plots. Although the residues of P and K are sufficient to double the yields of barley, it may be noted that the amounts of these elements recovered each year in the crops represent only very small fractions (around 0·5 per cent) of the total amounts applied to the plots last century. This experiment gives a good example of the long duration of manurial residues and the very low rates of recovery. Although the exchangeable potassium contents reflect past treatments, they account for only a small part of the residues, the bulk of which must remain in other, as yet, ill-defined forms.

W. E. Chambers has recently published (12, 13) two parts of an investigation on the soils and crops of the Broadbalk wheat experiment. One paper follows changes over long periods, and the other through a single season. On plots which had received no added potassium, the crops over eighty years extracted three or four times as much potassium as was found in the exchangeable form. Large changes in the amounts of potassium added to or removed from the soil were associated with only small changes in the amounts of potassium extractable by a neutral salt solution or by dilute acids. It was also shown that sodium and magnesium sulphates increased the uptake of potassium by the crops, presumably by liberating potassium from some non-exchangeable form. It would appear from investigations on the Hoos Exhaustion Land and on Broadbalk that the amounts of exchangeable or readily soluble potassium are only loosely and indirectly related to the amounts likely to be taken up by crops, though they provide convenient empirical methods for comparing soils.

Radiotracers in soil and fertilizer research

G. E. G. Mattingly carried out pot experiments using labelled monocalcium phosphate as a tracer. One series paralleled the series of field experiments already summarized in Table 1, but included five soils, four neutral and one acid. It is convenient to express the results as "A values" (i.e., estimates of amounts of soil phosphorus bearing the same ratios to the added labelled phosphates as are found for the soil and fertilizer phosphorus in plant samples). The purpose of several of the pot and field experiments was to see how far the estimated "A values" were altered by adding other unlabelled phosphorus fertilizers to the soils. Table 4 shows satisfactory agreement between the changes in "A values" and the amounts of unlabelled fertilizer added. (P labelled with 10 μ C activity was added at the rate of 2 mg. P per pot with

TABLE 4

Pot experiment on ryegrass

P in mg. per pot added as unlabelled fertilizer	Increase in "A values", mg. P per pot: Mean of four neutral soils	One acid soil
5·0 as superphosphate	5·3	6·6
10·0 as superphosphate	10·9	11·2
7·5 as dicalcium phosphate	8·3	8·4
7·5 as silicophosphate	7·0	8·2
7·5 as Gafsa rock phosphate	−0·3	10·6

400 g. soil. The estimates are for the second cut of perennial ryegrass.)

The estimates made from plant analyses agreed fairly well with the amounts of fertilizer added, with the expected exception that Gafsa mineral phosphate was inactive on the neutral soils. Experiments of this kind can be used to provide estimates of the relative availabilities of phosphate fertilizers, even where the yield responses are small.

A second pot experiment tested soils from the Hoos Four-course experiment on the residual effects of superphosphate and Gafsa mineral phosphate over five-year periods. The results are not fully worked out. They showed the expected differences between the two forms of fertilizer, and that increasing the specific activity of the labelled phosphorus five-fold reduced the uptake of fertilizer phosphorus by about 10 per cent, but did not affect the yields or uptake of soil phosphorus.

G. E. G. Mattingly with G. W. Cooke also carried out several field experiments. In one series (Table 5) labelled phosphorus fertilizers containing 0·1 cwt. P_2O_5 per acre were placed below the seed on plots which provided contrasts between various unlabelled fertilizers applied broadcast.

TABLE 5

Field experiments on labelled fertilizers

Unlabelled fertilizer broadcast, cwt. P_2O_5 per acre	Increase in "A values", cwt. P_2O_5 per acre: Barley straw, Highfield	Barley straw, Sawyers	Fodder-beet tops, Highfield
0·3 as superphosphate . .	0·12	0·03	0·32
0·6 as superphosphate . .	0·35	0·31	0·70
0·45 as dicalcium phosphate . .	0·27	0·14	0·44
0·45 Gafsa mineral phosphate	−0·04	−0·04	0·25

The barley straw gave increase in "A values" markedly below those expected from the amounts of phosphate fertilizers broadcast, but the agreement was satisfactory for fodder beet in Highfield.

In a second kind of experiment on barley with 0·1 cwt. P_2O_5 per acre of labelled superphosphate placed near the seed, broadcasting 0·2 cwt. P_2O_5 per acre as unlabelled superphosphate increased the A value by about 0·04 cwt. P_2O_5 per acre. With 0·2 cwt. P_2O_5 per acre of labelled superphosphate broadcast, the placing of 0·1 cwt. P_2O_5 per acre as unlabelled superphosphate increased the A value by 0·30 cwt. P_2O_5 per acre. This experiment indicates by measurements from both directions that the placed fertilizer was from three to five times as effective as an equal weight of broadcast fertilizer, but the results are provisional, as the main purpose of the experiment was to test and develop a technique for field experiments using labelled fertilizers.

O. Talibudeen used some of the soils from the above pot and field experiments for evaluating the rate and extent of isotopic exchange of phosphorus under laboratory conditions.

Solubility tests on Gafsa rock phosphate

F. S. C. P. Kalpagé studied the approximate equilibria established between excess finely ground Gafsa phosphate rock and various dilute acids and chelating agents. When increasing amounts of Gafsa phosphate rock (in excess of those required for full solution) are added to fixed quantities of dilute hydrochloric acid, the amount of carbon dioxide liberated steadily increases and the amount of phosphate in solution decreases. The apparent solubility of phosphate rock can be increased at will to any value by selecting the ratio of acid to rock. Extrapolation indicates that about 20 per cent of the total calcium carbonate present is dissolved independently of the rest. If this is regarded as " free calcium carbonate ", it might be supposed that the attack on the remaining complex is arrested when it becomes coated with dicalcium phosphate. An alternative interpretation is that the phosphoric acid and monocalcium phosphate formed by the initial attack on the rock react with the " free carbonate " exposed by the undissolved complex and are precipitated as dicalcium phosphate. Attempts are being made to distinguish between these two views. The final equilibria do not agree sufficiently well with the solubility product for dicalcium phosphate to support the view that the solutions are saturated with this substance. O. Talibudeen found that from 4 to 6 per cent of the phosphorus in the undissolved residue equilibrated with added radio-phosphorus. This is of the same order as would be expected if dissolved phosphate was precipitated in an active form by reaction with " free calcium carbonate ". F. S. C. P. Kalpagé also studied the equilibria with citric acid, alone and partially neutralized, and with sodium versenate, which around pH 7·5 extracts more Ca and P from excess phosphate rock than 0·1*N*.-HCl does at pH 3·0.

Nutrition problems in forest nurseries

Investigations were continued in conjunction with the Research Branch of the Forestry Commission, B. Benzian being in charge of the field work, and R. G. Warren, assisted by H. A. Smith and J. E. A. Ogborn, of the analytical work. Members of the Soil Microbiology and Nematology Departments investigated special aspects of some of the field experiments. Summaries are published in the Forestry Commission's annual *Reports on Forest Research* (20).

Most of the experiments in six nurseries are planned to run for several years with repeated annual crops of Sitka spruce or other conifer seedlings or transplants. As seasonal fluctuations are inevitably large, summaries are postponed until a series of experiments is completed. In 1953 two large rotation experiments at Sugar Hill Nursery, Wareham, and Kennington Nursery, Oxford, completed their preliminary years to give all phases of a three-course rotation testing fallow, various green crops, seedlings and transplants in the second phase and seedlings in the third phase, with additional comparisons between compost and fertilizers, repeated every year. There are supplementary experiments on manuring continuous seedbeds and continuous transplant beds and on testing as transplants seedlings raised in the second and third phases of the main experiment. The sites had not before been used for nurseries and, as special precautions have been taken to isolate the plots, it is hoped that the experiment may produce evidence on the vexed question of whether composts and other

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methods of supplying organic matter are essential for maintaining productivity over long periods.

During the last few seasons new plots on a very acid sandy soil at Sugar Hill Nursery have shown a characteristic needle tip-burn on many of the plants with fertilizers but on very few of those with a standardized compost made from bracken and hop waste. The symptoms have not been recognized in any other nursery, and no explanation can yet be offered, apart from the possibilities of lack of calcium or some minor element.

In 1953 early sowing and a moist season allowed very good growth in most experiments, with marked responses to major nutrients, especially nitrogen. Deficiency symptoms showed earlier, but seemed more complicated than usual. Sitka spruce seedlings provide sensitive material for studying the interrelationships of N, K and Mg, and the effects of these and other elements are being tested in plots as well as in the field.

TABLE 6

One-year seedlings of Sitka spruce 1953

	Mean height in inches		
	Four neutral or moderately acid soils		Two very acid soils
	Without formalin	With formalin	Without formalin
No nitrogen	0·9	1·6	1·6
Calcium nitrate	1·2	2·3	2·6
"Nitro-Chalk"	1·4	2·5	2·5
Ammonium sulphate ..	1·6	2·3	2·4
Formalized casein ..	1·6	2·6	2·9

In past years some of the benefits from formalin treatment, especially in the older nurseries and on neutral soils, have been ascribed in part to the inhibition of nitrification and the consequent accumulation of ammonia. Additional evidence on this point was obtained in 1953 from experiments at six nurseries testing four alternative forms of nitrogen fertilizer supplying 9 g. N per square yard: formalized casein applied a month before sowing and three inorganic nitrogen fertilizers applied to two summer top-dressings. Table 6 shows mean heights of one-year Sitka spruce seedlings in experiments with treatments in both 1952 and 1953. The data for four nurseries on neutral and moderately acid soils are given for plots with and without previous treatment with formalin. Where no formalin was given, growth was poor throughout, particularly on plots with calcium nitrate; the superiority of ammonium sulphate over calcium nitrate was significant in three of the four experiments, and "Nitro-Chalk" gave intermediate results in all four. Formalin greatly increased growth for all treatments, and at the poor established nurseries gave crops resembling those grown in very acid newer nurseries. Further, on formalin plots at old nurseries and on plots without formalin on very acid soils there were only small differences between the three kinds of inorganic fertilizer. The superiority in 1953 of the slowly acting organic fertilizer applied in the seedbeds may be due to its supplying nitrogen in a wet season before the inorganic fertilizers were given as top-dressings.

The series of experiments added support to the view that conifers profit from receiving their nitrogen as ammonia.

In several experiments chlorpicrin injected in January or February 1953 gave improvements similar to those from formalin applied as a drench. Series A in Table 7 shows that earlier application was sometimes better for formalin, but that the time of application had no effect for chlorpicrin.

TABLE 7

One-year seedlings of Sitka spruce 1953

	Mean heights in inches			Eelworms per plant
	Kennington K 68	Ampthill Am 30	Ringwood R 59	Ringwood R 59
Series A				
Untreated	1·8	1·8	1·4	100
Chlorpicrin—January	2·5	2·9	2·7	2
Chlorpicrin—February	2·5	2·9	2·8	4
Formalin—January ..	3·1	2·7	2·8	17
Formalin—February ..	2·5	2·7	2·0	89
S.E.	±0·10	±0·15	±0·12	—
	K 69	Am 31	R 58	R 58
Series B (January treatments)				
Untreated	1·7	1·8	1·3	156
Paraformaldehyde ..	2·1	1·9	1·5	111
DD	2·1	2·7	2·8	4
Ethylene dibromide ..	2·2	2·5	2·8	2
Formalin..	3·1	2·7	2·9	8
S.E.	±0·08	±0·09	±0·07	—

In Series B ethylene dibromide and DD applied in January gave very good results at two of the nurseries but much poorer ones at the third (Kennington). At all three nurseries paraformaldehyde gave little improvement in 1953.

J. B. Goodey continued his examination of plants from several experiments in the Ringwood nursery, making counts of the numbers of the nematode *Hoplolaimus uniformis* in seedlings and transplants. At this nursery January applications of formalin, chlorpicrin, ethylene dibromide and DD greatly increased growth and markedly reduced infestation with nematodes, paraformaldehyde in January and formalin in February being much less effective on growth and against nematodes. Similar results were obtained in other seedbed experiments at Ringwood. Formalin treatment of transplants beds at Ringwood reduced the mean numbers of eelworm from 1,680 to 120 per plant. Although this is presumptive evidence that part of the benefits from fumigants is through control of eelworms, it may be noted that in the Ampthill nursery, where plant and soil examinations have revealed very few eelworms, the effects of various fumigants on plant growth were generally similar to those at Ringwood. The Ringwood eelworm data thus add one more class of organisms to the lengthy list already known to be affected by soil fumigation in our forest nursery experiments.

Six species of conifers showed closely similar responses to fumigation with formalin and chlorpicrin and also to other manurial and remedial treatments. The 1953 plots and stockbeds of Sitka spruce in each of the older nurseries (now no longer used for raising

D

conifer seedlings) gave, after formalin treatment, outturns of usable seedlings approaching those from the best new nurseries in the country. If techniques for soil fumigation can be interpreted, standardized and mechanized they may prove to have applications not only in forest nurseries but in some intensive branches of horticulture in the open as well as under glass.

The nature of soil organic matter (J. M. Bremner)

Previous work on the estimation and decomposition of amino sugars in soil and on the identification of hydroxylamine and hydrazine by paper chromatography was completed and prepared for publication.

Earlier work on the chemical nature of the nitrogen in the humic (i.e., acid-insoluble) fraction of soil extracts was extended by comparing the properties of humic fractions isolated from $0{\cdot}5N$-sodium hydroxide and $0{\cdot}1N$-sodium pyrophosphate (pH 7·0) extracts of mineral and organic soils. This investigation showed that alkali- and pyrophosphate-extracted humic acids differed markedly in nitrogen content, nitrogen distribution and other properties. For example, the proportion of the total nitrogen liberated in the form of amino-acids by acid hydrolysis of the alkali-extracted humic acids (31–48 per cent) was considerably greater than that liberated by hydrolysis of the pyrophosphate-extracted acids (20–35 per cent). Estimation of the amino-sugar contents of the preparations by an alkaline decomposition technique showed that only 3–8 per cent of their total nitrogen was in the form of amino-sugars. No marked differences in the amino-acid compositions of the alkali- and pyrophosphate-extracted humic acids could be detected by paper chromatographic examination of their acid hydrolysates. The nitrogen in both types of humic acids was practically non-dialysable through Cellophane.

Previous work on the effect of nitrous acid on humic acid preparations has been extended by a detailed investigation of the behaviour of various alkali- and pyrophosphate-extracted humic acids under the conditions used in the Van Slyke nitrous acid method of estimating amino-nitrogen. The results showed that 10–20 per cent of the nitrogen in the humic preparations examined could be accounted for as free amino-nitrogen by this method using a reaction period of 15 minutes. The amount of gas evolved under the conditions of the Van Slyke method was found to increase steadily with time of reaction. The reaction was not affected by light, and the results were not significantly different when the preparations were dialysed against distilled water or extracted thoroughly with ether, alcohol, benzene or dilute acid before analysis. The mechanism of the reaction between humic acid and nitrous acid is still obscure, but analysis of the products has shown that the reaction leads to an increase in the nitrogen content. Tests with straw and wood lignins showed that treatment of lignin with cold nitrous acid also led to an increase in the nitrogen content and that methoxyl groups were destroyed in the reaction. Whatever the nature of the reaction between humic acid and nitrous acid, it does not appear to involve free amino-groups, since no free amino-groups could be detected when the preparations were examined by the fluorodinitrobenzene technique developed by Sanger.

Previous work on nitrogen transformations during the biological decomposition of straw composted with ammonium carbonate has been completed, and a paper giving the results is being prepared for publication. The transformations were studied by following changes in the amounts of inorganic and organic nitrogen present and in the amounts of ammonia-, volatile base-α-amino- and amino-sugar-nitrogen liberated by acid hydrolysis. Changes in the amino-acid composition of the composts were also studied by paper chromatographic examination of their acid hydrolysates. The results showed that synthesis of organic nitrogen during the biological decomposition of straw composted with ammonium carbonate is not accompanied by any gross change in the distribution of the organic nitrogen in the compost. A large fraction of the organic nitrogen synthesized is in the form of protein; a smaller fraction is in the form of amino-sugars. The amino-acid compositions of acid hydrolysates of the rotted and unrotted straws were not greatly different. The rotted, but not the unrotted, straw hydrolysates contained β-alanine and a substance provisionally identified as $\alpha\varepsilon$-diaminopimelic acid. Tests with an oat straw compost containing 3·94 per cent nitrogen showed that it nitrified extremely slowly when incubated with soil under conditions known to produce rapid nitrification of casein and ammonium sulphate.

The search for methods of fractionating and characterizing inositol phosphates has been continued, and promising results have been obtained using the method of paper electrophoresis. An attempt is now being made to use this technique to identify inositol phosphates in soil.

The decomposition of organic materials in soil (K. Shaw)

The rates of decomposition of various commercial nitrogenous materials and of nitrogenous materials prepared in the laboratory have been studied by estimating the mineral nitrogen (ammonia + nitrate nitrogen) produced on incubation of the samples with soil under standard conditions. A product containing 11·7 per cent *N* prepared by the nitration of sawdust was found to produce only about 10 p.p.m. of mineral nitrogen in eighty days. Two commercial nitrogenous materials, hoof and casein, were formalized in the laboratory. The formalization had only a temporary depressing effect on the rate of mineralization of the nitrogen, and after seventy days the production of mineral nitrogen was approximately equal in the formalized and normal products. A material prepared by the deamination of casein decomposed at nearly the same rate as the untreated protein.

Work was started on the formation and decomposition of " mat " on old permanent pasture, using initially samples of " mat " separated from the underlying mineral soil on some of the Park Grass Plots (plots 1, 4_2 and 11_1). A preliminary fractionation of this organic material shows decreasing amounts of cellulose and hemicelluloses and an increasing amount of lignin on passing down through the " mat ". The rate of decomposition of the material when mixed with its underlying mineral soil, with two added levels of nitrogen and calcium, is being followed by measuring the carbon dioxide and mineral nitrogen produced during incubation. The results so far obtained with samples from the unlimed section of plot 1, which has received nitrogen annually for many years, indicate that added nitrogen has no effect on the rate of production of carbon dioxide from the " mat " material at any level of calcium.

The simultaneous determination of ammonia and nitrate nitrogen in Olsen extracts of soils by reduction with reduced iron in acid solution at room temperature was found to be unsatisfactory. Better results were obtained when titanous sulphate was used as a reducing agent in place of the reduced iron, and the ammonia formed estimated by distillation with magnesium oxide in Conway Units at room temperature, but the recovery of added nitrate was still incomplete. However, almost complete recovery of nitrate nitrogen as ammonia was obtained by carrying out the reduction with titanous sulphate and distilling with magnesium oxide in a larger plastic modification of the Conway Unit which permitted more satisfactory mixing of the contents of the outer chamber.

Soil Manganese (S. G. Heintze)

In a group of soils, mainly alkaline and with high organic matter, the occurrence of manganese deficiency symptoms in crops was associated with low values for several variables : total manganese, the absolute quantities and the fractions of the total manganese extracted by neutral ammonium acetate with hydroquinone or sodium hydrosulphite, calcium nitrate after reduction with hydroquinone, sodium pyrophosphate at pH 9·5. The mean of the two methods based on hydroquinone was somewhat better than either method separately. No single fraction of the soil manganese has been found to give an adequate estimate of availability to plants, but any of the above methods would merit further attention where it is necessary to classify soils in relation to field observations.

Neutral solutions of pyrophosphate do not extract much manganese, even in the presence of hydroquinone. Alkaline pyrophosphate removes much larger quantities, but dissolves large amounts of organic matter, which may reduce manganese in high states of oxidation. Sodium versenate behaves in the same way as alkaline pyrophosphate; solutions of sodium calcium versenate at pH 9·0 give only light-coloured extracts but remove more manganese from organic soils than neutral pyrophosphate. Neutral solutions of sodium calcium versenate dissolve less manganese than neutral pyrophosphate solutions, but the amounts of manganese dissolved by sodium calcium versenate are greatly increased by the presence of hydroquinone. These findings are consistent with, but do not establish, the view that in organic soils a considerable amount of the manganese present is held in high-valency forms by the organic matter.

General

Early in 1953 E. M. Crowther made an eleven weeks' tour in the Sudan and East Africa at the request of the Sudan Government, the Empire Cotton Growing Corporation and the Colonial Office Advisory Committee on Agricultural Research. In addition to visiting several research institutes and experiment farms, he attended a Specialist Conference on Fertilizers at the East African Agriculture and Forestry Research Organization and the Annual Research Meeting of the Sudan Ministry of Agriculture. J. M. Bremner attended the 17th Conference and 13th Congress (Physical Chemistry, Wood and Paper Chemistry) of the International Union of Pure and Applied Chemistry at Stockholm.

J. C. Wilcox, of the National Agricultural Advisory Service, J. Bolton, of the Colonial Agricultural Research Service, and A. Y. Kordofani, of the Sudan Ministry of Agriculture, were seconded to the Department for work on field experiments. P. W. W. Daborn of the Forestry Commission took the place of C. P. Kirkland on secondment for forest nursery work. A. E. Johnston was appointed for analytical work.