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Chemistry Department

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CHEMISTRY DEPARTMENT

R. K. SCHOFIELD

The grievous loss which the Station sustained through the sudden death of E. M. Crowther on 17 March particularly affected the Chemistry Department of which he had been the Head since 1927. R. G. Warren, G. W. Cooke and B. Benzian immediately shouldered additional responsibilities, and thus ensured the effective continuation of the work. R. K. Schofield became Head on 1 October.

FERTILIZER PLACEMENT

Horticultural crops

G. W. Cooke, F. V. Widdowson and J. C. Wilcox continued their field experiments on horticultural crops in which the effects of placed and broadcast fertilizers have been compared. National Compound Fertilizer No. 1 (7 per cent N, 7 per cent P_2O_5 , 10.5 per cent K_2O) was used for all crops. Placing fertilizer in one band beside the seed gave higher yields than broadcasting in experiments on cabbage, lettuce, broad beans, runner beans, maize and onions. The differences in favour of placement were significant in the experiments on broad beans, runner beans, maize and onions.

Thirty experiments on horticultural crops have been carried out from 1952 to 1954, the results are summarized below by averaging all experiments on each crop. There have been worthwhile gains from placing as compared with broadcasting for all crops except beetroot and French beans. Placed fertilizer gave higher yields than broadcast fertilizer in twenty-two experiments, in ten of these experiments placing was significantly better than broadcasting. There were no experiments where placing was significantly inferior to broadcasting.

TABLE 1

Experiments on horticultural crops 1952-54

| Crop | No. of experiments | Unmanured yield | Response to | Gain from |
|------------------------|--------------------|-----------------|----------------------|---------------------------|
| | | | broadcast fertilizer | placing over broadcasting |
| Mean yields, cwt./acre | | | | |
| Cabbage | 4 | 97 | 47 | 23 |
| Lettuce | 6 | 124 | 18 | 23 |
| Beetroot | 3 | 58 | 5 | 4 |
| Onions | 2 | 209 | 24 | 28 |
| Maize | 2 | 103 | 7 | 14 |
| Broad beans .. | 5 | 64 | 2 | 12 |
| French beans .. | 3 | 72 | -5 | 5 |
| Runner beans .. | 5 | 96 | 7 | 7 |

Placement has two advantages for horticultural crops. First, the amounts of fertilizer needed to produce a given yield are often smaller when the dressing is placed than when it is broadcast; for broad beans, placed fertilizer has increased yields in experiments

where broadcast dressings have had little effect. Secondly, many of the crops grown with placed fertilizer were ready to harvest before those grown with broadcast fertilizer. These advantages may be very profitable where high-value cash crops are grown, and will speedily repay the cost of special placement drills. The experiments have been carried out on ordinary arable land carrying rotations of farm crops with occasional horticultural crops. No experiments have been carried out on intensively-cultivated, long-established market-garden land. Where such soils have received heavy dressings of manures it is not likely that fertilizers will markedly increase crop yields, and the advantages of placement are likely to be smaller.

In a subsidiary series of experiments, comparisons have been made of mid-season top-dressings of nitrogen fertilizers applied for brassica crops. Dressings localized near to the base of each plant have had little advantage over dressings applied by the usual method of broadcasting over all the surface of the soil.

Cereals

Four experiments on spring cereals tested a nitrophosphate (made with addition of ammonium sulphate) against an equivalent mixture of granular superphosphate with "Nitro-Chalk". The fertilizers were applied both broadcast and combine-drilled. Superphosphate plus "Nitro-Chalk" again gave higher yields than equivalent dressings of nitrophosphate, but the differences were smaller than in previous years. Thirteen experiments on wheat and barley were made from 1952 to 1954 to compare superphosphate (plus equivalent nitrogen) with nitrophosphate. The results are summarized in Table 2 by averaging all experiments.

TABLE 2
Experiment with cereals 1952-54

| | Yield of grain, cwt./acre |
|--|------------------------------|
| Mean yield with nitrogen only | 22.1 |
| <i>Increase from superphosphate plus "Nitro-Chalk"</i> | |
| Broadcast | 2.8 |
| Combine-drilled | 4.7 |
| <i>Increase from nitrophosphate</i> | |
| Broadcast | 1.8 |
| Combine-drilled | 4.0 |
| <i>Increase from drilling over broadcasting</i> | |
| for superphosphate | 1.6 |
| for nitrophosphate | 2.1 |

Both nitrophosphate and superphosphate increased yields significantly at seven of the thirteen centres when the fertilizers were drilled with the seed. When the fertilizers were broadcast there were significant increases from superphosphate at seven centres, but nitrophosphate increased yields significantly at only three of the centres. In all years phosphate drilled with the seed improved establishment and early growth. Generally water-soluble phosphate gave better growth in the early stages than insoluble phosphates. Where a quick start is important for cereals, water-soluble phos-

phates are to be preferred; but if nitrophosphates are used, they should be drilled with the seed.

In two experiments on barley grown on medium-textured soils there were good responses to nitrogen, and combine-drilling of ammonium sulphate gave higher yields than broadcasting the dressings on the seedbed. Top-dressings of "Nitro-Chalk" applied in May gave large increases in yields, even where ammonium sulphate had been applied in the seedbed. In two experiments on wheat grown on heavy, badly-drained soils the effects of nitrogen were much smaller. Combine-drilling gave higher yields than broadcasting in one of the experiments, but top-dressing did not increase the yields.

Potatoes

In one experiment on potatoes placing of both nitrogen and potash fertilizers gave higher yields than broadcasting the dressings on the seedbed before planting. In another experiment placing nitrogen and potash was superior to broadcasting when low rates of dressing were used, but at high rates broadcasting gave higher yields.

In seven experiments on main-crop potatoes 1.0 cwt. N/acre was sufficient for maximum yields. When this amount of nitrogen was split, half being applied (as ammonium sulphate) at planting and half broadcast (as "Nitro-Chalk") when the potatoes were earthed-up, the top-dressing did not increase yields. When the full dressing of nitrogen was applied at planting, later top-dressings decreased yields. Similar results were obtained from experiments carried out in 1953. There is no justification for applying mid-season top-dressings of nitrogen for potatoes.

In three of the experiments on main-crop potatoes nitrogen fertilizers did not give worth-while increases in yield. Of four cereal experiments, there were no benefits from nitrogen at two of the centres. These results emphasize the difficulty of making practical recommendations for using nitrogen. There are no satisfactory soil tests for "available nitrogen" to provide guidance on manuring. British farmers spend about £20 million annually on nitrogen fertilizers. Although this investment yields a handsome return on average, it is difficult to forecast the likely gains on individual fields. Any excess of inorganic nitrogen may be lost during winter before another crop is grown. There are large potential gains in fertilizer efficiency, and savings to the farmers, from any improvements in practical advice on manuring which current research can provide.

RADIO-TRACERS IN SOIL AND FERTILIZER RESEARCH

G. E. G. Mattingly and F. V. Widdowson have conducted four experiments near the same sites and with the same crops as in 1953; there were only minor alterations of the designs used previously. Results are given below for the grain yield of barley at one site in both years, together with the estimates of uptake of placed radioactive superphosphate, broadcast inactive phosphate fertilizers and A-value increase due to the broadcast fertilizer. The uptake of

placed active fertilizer, which was drilled with the seed, was estimated from radiochemical assay of plant samples; the apparent uptake of broadcast fertilizers was estimated by difference.

TABLE 3

Experiments on barley 1953 and 1954

| Unlabelled fertilizer broadcast, cwt. P ₂ O ₅ /acre | Year | Radioactive superphosphate 0.1 cwt. P ₂ O ₅ /acre, placed | | | | Rock phos- phate 0.45 | S.E. |
|--|------|---|----------------|-------|--|--------------------------------|---------|
| | | nil | Superphosphate | | Di- calcium phos- phate 0.45 | | |
| Yield, dry grain, cwt./acre | 1953 | 20.5 | 22.2 | 24.0 | 23.0 | 21.7 | ±0.477 |
| | 1954 | 12.3 | 19.8 | 20.1 | 19.3 | 12.8 | ±0.595 |
| Uptake of placed radioactive super- phosphate, cwt. P ₂ O ₅ /acre | 1953 | 0.015 | 0.015 | 0.013 | 0.015 | 0.015 | ±0.0012 |
| | 1954 | 0.014 | 0.016 | 0.012 | 0.013 | 0.016 | ±0.0014 |
| Apparent uptake of broadcast phosphate, cwt. P ₂ O ₅ /acre | 1953 | — | 0.016 | 0.033 | 0.023 | 0.006 | ±0.014 |
| | 1954 | — | 0.074 | 0.082 | 0.067 | 0.021 | ±0.012 |
| Increase in A-value due to broad- cast fertilizer, cwt. P ₂ O ₅ /acre | 1953 | — | 0.030 | 0.360 | 0.156 | -0.030 | ±0.100 |
| | 1954 | — | 0.319 | 0.664 | 0.556 | 0.008 | ±0.133 |

There were significant responses to the broadcast phosphate fertilizers, except rock phosphate, in the presence of 0.1 cwt. P₂O₅ drilled with the seed in both years on this site; responses were much greater in 1954, when a cold, wet summer resulted in slow growth, particularly of late-sown crops.

In both years the crop took up about 15 per cent of the phosphorus drilled with the seed, and this quantity was almost independent of the presence of the broadcast fertilizer. The most interesting result, however, is the markedly different utilization of the broadcast fertilizers in the two years. In 1953 the apparent uptake of broadcast superphosphate was about 5 per cent of that applied, that is about one-third of the uptake of the combine-drilled fertilizer. In 1954, however, about 17 per cent of the broadcast fertilizer was apparently used (average of 0.3 and 0.6 cwt. P₂O₅ broadcast), a figure which is slightly higher than the uptake from combine-drilled phosphate.

The increase in A-values due to the broadcast fertilizers in the two years are markedly different. In 1953 broadcast superphosphate was only one-third as effective as placed fertilizer, while in 1954 they appear to have been equally effective. Substantially similar results have been obtained from the other field experiments, the results of which are not, however, yet completed. These experiments illustrate one use of fertilizers labelled with ³²P in determining in one experiment the relative efficiency of a placed and broadcast fertilizer. This information can be obtained if necessary by analysis of only small unweighed crop samples taken before harvest.

G. E. G. Mattingly has completed the pot experiment on ryegrass made to test the residual effects of superphosphate and Gafsa mineral phosphate to which reference was made in the 1953 report. There was a steady decline in the yield and phosphorus uptake of three month's growth with the lapse of time up to three years since superphosphate had been applied to the soil. Lower and substantially constant yields and phosphorus uptakes were obtained from the soils which had received Gafsa mineral phosphate. A small known amount of radioactive phosphorus had been very evenly distributed through the soil in each pot, and measurements were

made of the radioactivity in the cut grass. The dilution of the tracer phosphate by soil phosphate, which is expressed by the A-values given in Table 4, was greatest for the grass grown in the soil which had most recently received the dressing of superphosphate, and declined with the lapse of time in the same way as the yields and phosphorus uptakes. If there were no loss, 1.2 cwt. P_2O_5 /acre applied as superphosphate to a depth of 6 inches would raise the A-value of the top soil by some 4 mg. P/100 g. The decline in three years is about three-quarters of this amount.

TABLE 4
Pot experiments on ryegrass
(400 g. soil per pot)

| Soil | Treatment | Years since last application | Yield, g./pot | Uptake, mg. P/pct 100 g. soil | "A-value", mg. P/100 g. soil |
|---|---|------------------------------|---------------|-------------------------------|------------------------------|
| Hoosfield Four-course rotation, 4% $CaCO_3$ | Superphosphate 1.2 cwt. P_2O_5 /acre every fifth year, total application 6 cwt. P_2O_5 /acre | 0 | 6.43 | 10.70 | 11.6 |
| | | 1 | 6.64 | 9.22 | 10.2 |
| | | 2 | 6.28 | 8.58 | 9.8 |
| | | 3 | 5.86 | 6.54 | 8.3 |
| | | 4 | 5.74 | 6.58 | 8.8 |
| Hoosfield Four-course rotation, 4% $CaCO_3$ | Gafsa mineral phosphate 1.2 cwt. P_2O_5 /acre every fifth year, total application 6 cwt. P_2O_5 /acre | 0 | 3.94 | 3.78 | 6.8 |
| | | 1 | 3.50 | 4.13 | 6.7 |
| | | 2 | 3.39 | 3.29 | 6.8 |
| | | 3 | 3.03 | 2.71 | 6.1 |
| | | 4 | 3.48 | 3.31 | 6.5 |
| | | S.E. | ±0.376 | ±0.659 | ±0.43 |
| Hoosfield Exhaustion land, 3% $CaCO_3$ | No phosphate Superphosphate total application, 28 cwt. P_2O_5 /acre | — | 1.63 | 1.62 | 3.4 |
| | | 53 | 5.83 | 8.56 | 9.4 |
| | | S.E. | ±0.103 | ±0.300 | ±0.13 |

Soils taken from two of the Hoosfield Exhaustion plots were included in this pot experiment. The values obtained for the plot which has had no phosphate since 1856 are lower than those for the Four-course plots, which have only had mineral phosphate since 1928 but occasional dressings of dung before that date. By contrast, the values for the plot which received annual dressings of superphosphate between 1856 and 1901 fall within the range of the values given by the Four-course plots, which have received superphosphate more recently but considerably less in total amount.

O. Talibudeen has made laboratory experiments with some of the same soils. Samples were continuously shaken in 0.001M-ammonium citrate solution to which a small known amount of radioactive phosphorus had been added. After different lengths of time measurements were made to determine: (a) how much soil phosphate had gone into the solution, and (b) what fraction of the radioactive phosphorus remained in the solution (the rest having been taken up by the soil particles). Values obtained by dividing (a) by (b) provide estimates of the amounts of labile orthophosphate in the different soils. Provisionally the values obtained after shaking 0.5 or 1 g. of soil in 100 ml. of the solution for 150 hours have been used because no increase was detected on prolonging the shaking to 200 hours.

In Table 5 the values so obtained are given under the heading P_e 0.001M, and may be compared with A-values obtained in pot experiments. The results indicate that essentially the same category of phosphate is estimated by both methods.

TABLE 5

Comparison of laboratory and pot experiments

| Soil | Treatment | mg. P/100 g. soil | | |
|---------------------------|-----------------------------|-------------------------|-----------------|---------------|
| | | A-value (pot expts.) | P_e 0.001M | P_e 0.1M |
| Hoosfield Exhaustion land | No phosphate | 3.4 | 4.8 | 6.5 |
| | Farmyard manure before 1901 | 10.0 | 11.2 | — |
| | Superphosphate before 1901 | 9.4 | 11.0 | 34.3 |
| Highfield | — | 16.0 | 17.0 | — |
| Sawyer's Field | — | 6.0 | 9.2 | 17.3 |

In further experiments increasing concentrations of ammonium citrate were used, and values for three of the soils obtained after 150 hours in 0.1M-ammonium citrate are recorded in Table 5 under the heading P_e 0.1M. With the more concentrated solution a much higher value was obtained for the soil of the Exhaustion plot, which still contains considerable residues from applications of superphosphate made before 1901, whereas there was very little increase in the value for the soil which has received no manure or phosphate fertilizer for over a century. These soils contain calcium carbonate, and it would appear that the stronger solution is capable of dissolving precipitated calcium phosphate. It also dissolved some phosphate from the acid soil of Sawyer's Field. Evidently the values obtained with the weaker solution more nearly reflect the field condition of the soils.

A procedure for the quantitative estimation of radioactive calcium (^{45}Ca) as the oxalate was worked out. The technique developed ensured reproducible precipitation, filtration and packing of samples with a mass density up to 70 mg. CaC_2O_4 /sq. cm. approximately. The reproducibility of the counting rate was within the error of the counting apparatus. From this it was possible to define the optimum conditions for the estimation of ^{45}Ca , to plot a correction curve for different weights of CaC_2O_4 and to give approximate figures for the self-absorption coefficient, the half thickness of absorption and the range of the weak-energy β -emission from ^{45}Ca . (R. C. Chen.)

SOLUBILITY RELATIONSHIP FOR FLUORAPATITE

F. S. C. P. Kalpagé continued his study of the solubility of finely divided Gafsa phosphate rock in acid and neutral solvents. He confirmed that when an excess of the phosphate rock remains undissolved, the resulting solution approaches a state of equilibrium with the residue of fluorapatite and fluorspa. The solutions obtained with 0.1M-citric acid, being better buffered, were less disturbed by the slow dissolution of calcium carbonate, and so got nearer to the state of equilibrium than the solutions obtained with 0.1M-hydrochloric acid. For all the solutions examined, the equilibrium state is characterized by the relationship

$$2\text{pH} - \frac{3}{2}\text{pCa} - \text{pH}_2\text{PO}_4 = 1.8$$

pCa and pH_2PO_4 are the negative logarithms of the activities of the calcium ions and the dihydrogen phosphate ions respectively. Both were computed without serious error from the observed concentra-

tions in dilute hydrochloric and citric acids with the aid of the well-known equation of Debye and Hückel. When ammonium citrate and sodium versenate are used, pCa cannot be obtained so simply, because calcium ions are sequestered in these solutions, and the results show very clearly that the solvent action of these neutral solutions is largely due to lowering of the activity of the calcium ions through complex formation.

The newly found relationship rules out the possibility which was previously entertained that dicalcium phosphate might have been precipitated as a coating on the residue not dissolved in 0.1M-hydrochloric acid. Brushite (dicalcium phosphate dihydrate) is the only form of dicalcium phosphate which could have been precipitated. Its solubility relationship is $\text{pH} - \text{pCa} - \text{pH}_2\text{PO}_4 = 0.6$. Thus brushite can be formed from fluorapatite in the presence of fluorspa only when $\text{pH} - \frac{1}{2}\text{pCa} < 1.2$ and $\frac{1}{2}\text{pCa} + \text{pH}_2\text{PO}_4 > 0.6$. For the second condition to hold, the concentration of dihydrogen phosphate ions must exceed 0.5M, and it is clearly impossible for this concentration to be produced starting with hydrochloric or citric acid as dilute as 0.1M. Much stronger hydrochloric acid is used in the manufacture of dicalcium phosphate from phosphate rock.

The finding of a quantitative solubility relationship for fluorapatite in the presence of fluorspa is an important step in the search for rational analytical procedure whereby the amount of dicalcium phosphate in a fertilizer can be determined without interference from any apatite that may be present. It also helps to define the soil conditions in which phosphate rock is an effective fertilizer.

NUTRITION PROBLEMS IN FOREST NURSERIES

B. Benzian and J. E. A. Ogborn, in collaboration with the Research Branch of the Forestry Commission, have continued work planned by E. M. Crowther. Five series of experiments in which rates of application of phosphate and potash had been tested over several years were concluded in 1954. Experiments which had received annual dressings of superphosphate showed remarkably constant responses to P from season to season and centre to centre (ranging from very acid to almost neutral soils). Averaging all nurseries and seasons, the response in mean height to 6 g. P/sq. yd. was very close to $\frac{1}{2}$ inch. Depending on the number of plants per square yard and the moisture content of the seedlings, a response of $\frac{1}{2}$ inch would be equivalent to between 5 and 10 cwt. dry matter/acre. Up to the highest rate of phosphate tested (6 g. P/sq. yd. or approximately 7 cwt. superphosphate/acre) the responses show no signs of falling off, and a new series of experiments has therefore been laid down to test higher rates. Responses to potash were smaller and varied more between centres.

A few years ago a bright yellow discoloration of Sitka spruce was identified as magnesium deficiency. Since 1951 magnesium has been tested annually in several nurseries. The intensity of the symptoms and the time of their appearance has varied from year to year, and 1954 was the first season in which several experiments showed a significant response in height.

In nurseries in which growth of Sitka spruce and other conifer seedlings is normally very poor, even on plots with ample manuring,

such treatments as steam, formalin and chlorpicrin have yielded excellent seedlings. These treatments have usually been applied either in December after the seedbeds had been cleared of the previous season's crop or in February, 3-4 weeks before sowing. As bad weather may prevent, or at least delay, application of treatments, and hence sowing, a series of experiments was started in which applications were made in the summer (June), autumn (October/November), early winter (December) and early spring (February).

Formalin was applied as a drench, containing either 167 or 333 ml. of formaldehyde, and chlorpicrin injected at rates of either 24 or 48 ml./sq. yd. The results, averaging rates of application, are given in Table 6.

TABLE 6
One-year seedlings of Sitka spruce 1954

| | Mean height, inches | | |
|--------------------|---------------------|------------------|------------------|
| | Kennington K 64 | Amphill Am 34 | Ringwood R 64 |
| Untreated | 1.7 | 2.1 | 1.5 |
| <i>Formalin</i> | | | |
| June | 2.0 | 2.3 | 2.0 |
| November | 3.1 | 2.9 | 2.4 |
| December | 3.0 | 3.3 | 2.5 |
| February | 2.7 | 3.3 | 2.4 |
| <i>Chlorpicrin</i> | | | |
| June | 2.4 | 2.7 | 2.4 |
| November | 2.8 | 2.7 | 2.3 |
| December | 2.9 | 2.8 | 2.3 |
| February | 2.7 | 3.1 | 2.2 |
| S.E. | ±0.11 | ±0.08 | ±0.08 |

Both formalin and chlorpicrin increased height at all three centres. In the case of formalin there were considerable differences between the dates of application, the June treatment being inferior to the remainder at all three centres. The responses to chlorpicrin appear to depend far less on the time of application, and at Amphill and Ringwood the June applications of chlorpicrin are similar to the November and December applications. There was no difference between the early November and the December applications of the two materials in five cases out of six.

At Amphill none of the treatments affected plant number, but at Ringwood the spring application of chlorpicrin caused a considerable reduction in stocking. Such a reduction in plant number has been noticed on previous occasions when treatments were applied only a few weeks before sowing, and this is another reason why it became necessary to test applications at other times of the year.

If the satisfactory results from summer applications of chlorpicrin and autumn applications of both formalin and chlorpicrin are confirmed, they may have considerable bearing on nursery practice. It is part of the Forestry Commission's policy to fallow annually one or more sections in many of the older nurseries. At present the fallow period is devoted mainly to the destruction of weeds and insect pests, but it may become possible to apply large-

scale treatments of formalin or chlorpicrin during the fallow period to some of the nurseries where these treatments are likely to be beneficial.

The search for safer and cheaper alternatives to formalin and chlorpicrin has continued. CBP 55 (chlorobromopropene) has given promising results, both injected and as a drench, in an experiment on 1-year Sitka spruce seedlings at Ampthill. The injection treatments of both chlorpicrin and CBP 55 were applied at rates of 12 and 24 ml./sq. yd. CBP 55 drench consisted of either 30 or 60 ml. of the emulsible concentrate in 4 l. water. The results averaging rates of application are given in Table 7.

TABLE 7

One-year seedlings of Sitka spruce 1954

| | | Ampthill (Am 47) | |
|----------------------------|-------|------------------------|------------------------------|
| | | Mean height, inches | No. of plants per sq. yd. |
| Untreated | | 2.4 | 1280 |
| | S.E. | ±0.10 | ±70.6 |
| <i>Applied in February</i> | | | |
| Chlorpicrin injected | | 3.3 | 1462 |
| CBP 55 injected | | 3.0 | 1516 |
| CBP 55 drench | | 3.3 | 1558 |
| | S.E. | ±0.15 | ±99.8 |

As the inhibition of nitrification may play some part in the benefit derived from such materials as formalin and chlorpicrin, a number of substances known to inhibit nitrification were tested in pot experiments. One of these materials, potassium dichromate, had shown some promise in pot experiments in 1952 and 1953, and was therefore tested in the field. In three experiments at Ampthill, Old Kennington and Ringwood 10 g./sq. yd of potassium dichromate dissolved in water were applied by power spray to the surface of the plots in December. Dichromate increased both height and plant number of Sitka spruce seedlings as shown in Table 8.

TABLE 8

One-year seedlings of Sitka spruce 1954

| | Mean height, inches | | | No. of plants per sq. yd. | | |
|-------------------------|---------------------|----------|---------------|---------------------------|----------|---------------|
| | Ken- nington | Ampthill | Ring- wood | Ken- nington | Ampthill | Ring- wood |
| | K 74 | Am 41 | R 69 | K 74 | Am 41 | R 69 |
| Untreated | 2.2 | 2.4 | 0.7 | 513 | 1558 | 771 |
| Potassium dichromate | 2.5 | 2.6 | 1.1 | 742 | 1585 | 902 |
| | S.E. ±0.05 | ±0.08 | ±0.05 | ±41.8 | ±46.3 | ±29.8 |

Eelworm examinations of seedlings and transplants at Ringwood Nursery were continued by J. B. Goodey. The infestations in 1954 were generally lower than they had been in previous years.

Mr. D. M. Griffin, working under Dr. Garrett, Director of the Sub-Department of Mycology, Botany School, Cambridge, has made mycological examinations of plants from many of the experiments with the aim of devising a suitable system of root disease rating,

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together with a method for identifying the particular fungal pathogens concerned.

SOIL ORGANIC MATTER

J. M. Bremner has further examined the view that the humic fraction of soil organic matter consists largely of lignin or lignin-derived material associated with protein. One of the most characteristic reactions of plant lignin is that it gives substantial yields (as much as 25 per cent) of phenolic aldehydes when oxidised with nitrobenzene in alkaline solution. Paper chromatographic analysis of the products formed by alkaline nitrobenzene oxidation of humic acid preparations from eight different soils did reveal the presence of vanillin, syringaldehyde and *p*-hydroxybenzaldehyde, but the amounts of phenolic aldehydes detected were very small, the highest yield, about 1 per cent, being obtained from a peat humic acid. Further evidence that plant lignins are drastically altered in the processes leading to the formation of soil organic matter has been obtained from a study of chemical changes during the biological decomposition of oat straw composted with ammonium carbonate. This showed that although decomposition of the straw was not accompanied by any substantial decrease in the total amount of lignin as estimated by the usual methods of plant analysis it was accompanied by a very marked decrease in the yield of phenolic aldehydes obtained by alkaline nitrobenzene oxidation.

Attempts to isolate protein from nitrogen-rich humic acid preparations, e.g., by removal of the non-protein material with mild oxidising agents such as chlorine dioxide, have not so far been successful, but substances with the properties of peptides have been detected by paper chromatographic analysis of the products liberated by partial hydrolysis of humic acid preparations with concentrated hydrochloric acid at 35° C.

Previous work on the alkaline decomposition of amino-acids (see the Report of Rothamsted Experimental Station for 1950, p. 42) was extended by a study of the effect of hot alkali on the following β -hydroxy- α -amino acids: glucosaminic acid, β -hydroxyaspartic acid, β -hydroxyglutamic acid, β -hydroxyvaline, β -hydroxynorvaline, β -hydroxyleucine, β -hydroxynorleucine, β -phenylserine, β -*p*-hydroxyphenylserine. The results showed that when a β -hydroxy- α -amino acid ($R \cdot CH(OH) \cdot CH(NH_2) \cdot COOH$) is heated with alkali it decomposes with the formation of glycine and, in some cases, the amino-acid $R \cdot CH_2 \cdot CH(NH_2) \cdot COOH$. Earlier work on nitrogen transformations during the biological decomposition of straw composted with inorganic nitrogen and on the chemical nature of the nitrogen in the humic fraction of soil organic matter was completed and prepared for publication.

P. W. Arnold has worked on the isolation and characterization of the principal organic phosphorus compounds which occur in soil. In British soils it is usual for about one-half of the total phosphorus to be present in organic combination, and information on the role of organic phosphorus in soil fertility problems is required.

Although a sodium hydroxide solution, usually preceded by a dilute acid leaching of the soil, is the most efficient organic phosphorus extractant, the unavoidable presence of the large amount

of organic matter in the sodium hydroxide extract greatly hinders attempts to proceed further with the characterization of the organic phosphorus compounds. It was found that cold concentrated hydrochloric acid extracted most of the organic phosphorus from soils without bringing about much hydrolysis; moreover, a comparatively small part of the total soil organic matter entered the extract. Practically all the phosphorus-containing organic matter extracted by concentrated hydrochloric acid is insoluble in 70 per cent ethanol, and inositol phosphate can be released from it by alkaline hypobromite oxidation. It is pertinent to record that additions of a few parts per million of inositol hexaphosphate to soils can be recovered quantitatively by a simple acid extraction without an alkaline hypobromite oxidation, but none of the soil's native inositol phosphate is isolated by such a procedure. It would appear that in soil the native inositol phosphate is linked to an organic nitrogenous moiety in an, as yet, unknown way.

In order that the inositol-bound phosphorus isolated from soil could be examined in detail a paper electrophoresis technique was employed. Microgram quantities of mono-, di-, tri- and tetraphosphorylated inositols have been separated from synthetic mixtures of the phosphates and from partially hydrolysed inositol hexaphosphate (phytic acid), but as the penta- and hexaphosphates migrate at the same speeds, no separation of these two latter phosphates has been possible by the electrophoretic technique. After cold alkaline hypobromination it has been found that the inositol phosphate isolated from soil contains at least five phosphorus atoms per inositol molecule, and minimal values for the inositol phosphate contents of a variety of British soils account for between one-third and two-thirds of the total organic phosphorus contents. It is possible that inositol mono-, di-, tri- and tetraphosphates are present in small concentrations in soils, but such compounds may also appear as artefacts when extraction conditions are too drastic.

As well as inositol-bound phosphorus, organic phosphorus occurs in soil in a form which has not yet been separated from the so-called humic fraction of soil. The only information available is that about 15 per cent of the total organic phosphorus is in this form in an acid peaty soil, but it is by no means certain that it constitutes a definite category of phosphorus. Only trace amounts of adenine and guanine have been isolated from the hydrolysates of well-humified soils, from which it has been calculated that not more than about 5 per cent of the total organic phosphorus of such soils can be present in nucleotide combination.

K. Shaw has continued to work on the decomposition of mat on old permanent pasture, using samples of mat separated from the underlying mineral soil on the unlimed sections of Park Grass Plots 1, 4₂ and 11₁. The rates of decomposition of the mat from plots 1 and 11₁, which have received annually 2 and 6 cwt./acre of ammonium sulphate respectively for almost 100 years, were followed by measuring the carbon dioxide and mineral nitrogen produced by incubation of the mat when mixed with its underlying mineral soil. Although the nitrogen contents of the mat from the two plots were appreciably different (plot 1, 1.51 per cent N; plot 11₁, 1.79 per cent N), the rates of decomposition as measured by production of

carbon dioxide or mineral nitrogen were very similar. The addition of sufficient calcium carbonate to bring the pH of the mixture of mat and mineral soil to about 7 did not affect the mineralization of the nitrogen in the mat, but did increase its decomposition to carbon dioxide. The production of carbon dioxide and mineral nitrogen by the mat from plot 1 was found to be substantially greater in the absence than in the presence of mineral soil.

Satisfactory micro-diffusion methods for the determination of ammonia and nitrate in soil extracts have now been developed. The ammonia is extracted by Olsen's method, and determined by distillation with magnesium oxide at 25° C. in a modified Conway micro-diffusion unit. Ammonia plus nitrate is determined on a separate sample of the same extract by reduction of the nitrate with titanous hydroxide and subsequent distillation with magnesium oxide, the reduction and distillation being carried out at 25° C. in a modified micro-diffusion unit. The methods are applicable to coloured extracts, and have the advantage that they require only a small volume of soil extract and permit the rapid analysis of a large number of samples.

S. G. Heintze has used neutral disodium monocalcium versenate to extract manganese from alkaline organic soils. The amounts obtained after 1 hour's shaking agree closely enough with those obtained in the same time with alkaline pyrophosphate to suggest that little if any reduction of tri- or tetravalent manganese has taken place. These values are therefore taken to represent divalent manganese complexed by the soil organic matter.

The nature of the organic complexes of manganese has been further studied with the aid of paper electrophoresis. Complexes which migrate to the cathode were made by the reaction of manganous sulphate with humic acid prepared from an alkaline fen soil and a sample of commercial lignin "Meadol" exhibited the same characteristic.

GENERAL

G. W. Cooke spent 6 weeks at the headquarters of the Food and Agriculture Organization of the United Nations in Rome and prepared the *Annual review of world production and consumption of fertilizers* for 1954. He was also invited to attend the General Assembly of the International Centre of Chemical Fertilizers held in Zürich in October. He read a paper on "The importance of organic matter in relation to crop nutrition".

J. M. Bremner worked for 3 months at the Institut für Biochemie des Bodens, Forschungsanstalt für Landwirtschaft, Völkenrode, Braunschweig, Germany, and then made a 1-month tour of other agricultural research centres in Western Germany. He also attended and contributed to the Conference on Soil Organic Matter held at Völkenrode. The visit to Völkenrode was at the invitation of Prof. W. Flaig, Director of the Institut für Biochemie des Bodens, and was supported by a grant from the German Ministry of Food, Agriculture and Forestry. His tour of agricultural research stations in Western Germany was made with the assistance of a travel grant from the Agricultural Research Council.

P. W. Arnold joined the staff at the beginning of the year. J. C.

Wilcox of the National Agricultural Advisory Service, J. Bolton of the Colonial Agricultural Research Service, and P. W. W. Daborn of the Forestry Commission were further seconded for field work. F. S. C. P. Kalpagé was awarded the Ph.D. degree of London University, and returned to Ceylon.