ROTHAMSTED RESEARCH

Report for 1956

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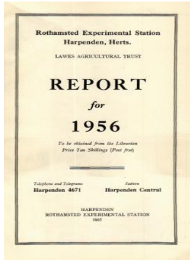

Chemistry Department

G. W. Cooke

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CHEMISTRY DEPARTMENT

G. W. Cooke

R. K. Schofield resigned on 14 January to take up the appointment of Reader in Soil Science at the University of Oxford. G. W. Cooke was appointed to succeed him on 1 March 1956.

A. W. Taylor resigned at the end of July to take up an appointment at Pennsylvania State University; W. F. Roue resigned in March and A. Stephens resigned at the end of the year.

J. K. R. Gasser joined the staff in October; J. M. d'Arifat, G. H. Owen and R. J. B. Williams were appointed to carry out analytical work.

P. W. W. Daborn of the Forestry Commission was seconded for a further year for work on nutrition problems in forest nurseries. Several members of the Colonial Agricultural Research Service were trained in the Department in soil-fertility work and field experimentation. J. C. Chisnall worked in the Department in the spring before going to British Guiana; R. K. Cunningham left in September to take up an appointment at the West African Cocoa Research Institute; A. Pinkerton completed his training at the end of the year and was appointed to the Department of Agriculture, Kenya; R. Webster joined the Department in November.

Dr. T. Harada from The National Institute of Agricultural Sciences, Japan, worked with J. M. Bremner on soil-nitrogen problems for six months. Professor S. W. Melsted from the University of Illinois came in September to spend a period of sabbatic leave. Mr. P. Kivinen of the University of Helsinki, Mr. L. Overrein of the Agricultural College of Norway and Mr. C. Bishop of Reading University all worked in the Department for several weeks.

P. W. Arnold was seconded to work at the West African Cocoa Research Institute for a year. S. G. Heintze was granted a year's leave of absence to work at the Galloway Laboratory, Hamilton, New Zealand.

G. W. Cooke, S. G. Heintze, G. E. G. Mattingly, K. Shaw and R. G. Warren attended the Sixth Congress of the International Society of Soil Science held in Paris.

Fertilizer Placement

(G. W. Cooke, F. V. Widdowson and A. Penny)

A small series of field experiments which compared broadcasting and placing of separate nutrients for a number of crops has now been concluded.

In twelve experiments on potatoes carried out since 1953 gains from placing ammonium sulphate and potassium sulphate beside the seed, as compared with broadcasting these fertilizers on flat land before planting by machine, have been examined. In each year there have been marked and consistent increases in yield from placing over broadcasting for each nutrient at the lower rates of application used (0·5 cwt. N and 0·75 cwt. K_2O/acre). Gains from placing the higher rates (1·0 cwt. N and 1·5 cwt. K_2O/acre) of both nutrients were smaller and less consistent. The results of the experiments emphasize the special value of placement when fertilizer dressings are restricted. There is no case for separating the components of a mixed fertilizer and applying part placed and part broadcast.

Further experiments on broad beans and peas were carried out in 1956, both crops being picked green for market. Superphosphate and muriate of potash and a mixture of the two fertilizers were broadcast and worked into the seedbed and compared with dressings placed in a single band beside the seed. The effects of broadcasting P, K and PK fertilizers on yields of broad beans were small and irregular. When the dressings were placed there were large increases in yields of beans from phosphate and potash applied separately and together. The experiments also tested a complete NPK fertilizer; there was no worthwhile gain from the addition of nitrogen. These results confirm those of a similar experiment on broad beans carried out in 1955. In the 1956 experiment on peas there were no gains from the fertilizer dressings, however applied. The two years' work suggests that benefits from placing a PK fertilizer beside the seed, demonstrated in earlier experiments on peas and beans, were due to both the phosphorus and potassium components of the mixture. The work also emphasizes that tests of broadcast fertilizers for peas and beans may give misleading impressions, since much larger yield increases are obtained by placing the fertilizers beside the seed.

Combine-drilling potassium fertilizers for cereals

Comparisons of combine-drilling and broadcasting of potassium fertilizers for spring-sown barley were continued in 1956. Four experiments compared fertilizers broadcast and harrowed into the seedbed with combine-drilled dressings. At each centre a single dose of potash (0·25 cwt. K_2O/acre) when combine-drilled gave higher yields than twice as much potash broadcast. At three of the four centres combine-drilling the double dressing gave higher yields than drilling the single dressing.

Methods of Application and Rates of Nitrogen Fertilizer for Cereals

Winter wheat (F. V. Widdowson)

Four experiments were carried out on three varieties of stiff-strawed winter wheat to compare two rates of "Nitro-Chalk" applied as a spring top-dressing. There were good responses to nitrogen in each experiment, at two centres 4 cwt./acre of "Nitro-Chalk" was sufficient for maximum yields, at the other two centres the highest yields were given by 8 cwt./acre. There were no gains at any centre from splitting the nitrogen dressing and applying 1 cwt. of "Nitro-Chalk" in autumn, the remainder being applied in spring. On average of all the centres Hybrid 46 gave the largest

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response to nitrogen, at the high rate of dressing Heine 7 was inferior to Hybrid 46. The unmanured yield of the third variety, Minister, was higher than those of the other two varieties, but it gave much smaller responses to " Nitro-Chalk " at both rates of application.

Spring cereals (F. V. Widdowson, A. Penny and G. W. Cooke)

Fourteen field experiments on spring cereals have been carried out since 1954 to compare combine-drilling and broadcasting of ammonium sulphate and to measure the additional effects of top-dressings of " Nitro-Chalk " applied in May. The results are summarized in Table 1. There were ten experiments on barley and four on wheat. Generally barley gave much larger responses to nitrogen than wheat, but in this summary results on the two crops have been averaged. In three-quarters of the experiments combine-drilling gave a higher yield than broadcasting the dressing either on the seedbed or as a May top-dressing. The average gain from combine-drilling the heavy dressing was nearly 2 cwt. of grain/acre.

TABLE 1

Unmanured yields of grain (in cwt./acre) and the increases given by nitrogen fertilizers applied in different ways in experiments on spring-sown wheat and barley

Approximate dressing per acre :	1954	1955	1956	Mean: Yield	Mean: No. of positive effects
No. of experiments	4	3	7	14	14
Yield without nitrogen ...	*24·8*	*25·5*	*15·8*	*20·4*	—
Increase from 0·25 cwt. N/acre :					
Broadcast	2·6	5·7	6·4	5·2	13
Drilled	3·8	4·6	7·9	6·0	12
Top-dressed *	(2·0)	4·7	6·5	(4·8)	13
Increase from 0·5 cwt. N/acre :					
Broadcast	5·0	7·3	9·4	7·7	13
Drilled	6·8	9·6	11·0	9·5	14
Top-dressed *	(4·1)	9·8	7·8	(7·2)	13
Gain from drilling over broadcasting :					
At low rate	1·2	−1·1	1·5	0·8	10
At high rate	1·8	2·2	1·7	1·8	11
Increase from top-dressing plus seedbed dressing of :					
0·25 cwt. N broadcast ...	7·1	11·9	10·6	9·9	13
0·25 cwt. N drilled	8·0	11·1	11·4	10·3	14
0·5 cwt. N broadcast ...	7·8	12·7	10·8	10·4	12
0·5 cwt. N drilled	7·4	10·7	11·6	10·2	13

* In 1954 top-dressings were tested by applying 4 cwt./acre of " Nitro-Chalk " to split plots; the increases in yield given by top-dressing alone in 1954 have been determined by graphical interpolation of yields on plots with no seedbed dressing, and are therefore approximate.

There was a good average gain (2·7 cwt./acre of grain) from top-dressing given in addition to the heavy broadcast seedbed dressing, but in the presence of the drilled seedbed dressing, top-dressing

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gave only a small additional yield (0·7 cwt./acre of grain) which would not be sufficient to pay for the extra fertilizer used. The effects of top-dressing varied. In the wet years of 1954 and 1956 top-dressings alone gave smaller average increases in yield than either broadcasting or drilling the same amount of nitrogen. In 1955, when the summer was dry, top-dressings and seedbed dressings gave similar increases in yield. In 1956 nitrogen top-dressings were much inferior to seedbed dressings in all experiments on barley. Crops on plots receiving top-dressings made very soft growth and produced much more straw than barley grown with seedbed dressings only. At harvest practically all top-dressed plots were badly lodged; on these plots the crop was much less mature and more uneven, and the quality of the grain was markedly inferior to that grown with seedbed dressings alone. These experiments suggest that top-dressing with nitrogen in May cannot be recommended for spring barley. Full yields have been produced by combine-drilling adequate amounts of ammonium sulphate with the seed, while top-dressings given in addition to drilled seedbed dressings have not produced worthwhile average increases in yield, and in wet years have made harvesting difficult and late and have reduced the quality of the grain. This work has been carried out in a restricted area of the Eastern Counties, and it needs to be extended to other corn-growing areas so that firm recommendations may be made.

Comparisons of Forms of Nitrogen Fertilizers

(F. V. Widdowson, A. Penny and G. W. Cooke)

Spring cereals

In two experiments on barley and one on wheat, combine-drilling and broadcasting of both ammonium sulphate and calcium nitrate were compared. Calcium nitrate gave slightly higher yields than ammonium sulphate when the fertilizers were broadcast; there was little difference between yields given by the two fertilizers when they were drilled. In the two barley experiments combine-drilling gave consistently higher yields than broadcasting when ammonium sulphate was used; with calcium nitrate broadcasting was slightly superior. In the wheat experiment broadcasting of both fertilizers gave higher yields than combine-drilling.

Potatoes

Eight experiments on main-crop potatoes tested 0·5, 1·0 and 1·5 cwt. N/acre applied as ammonium sulphate, calcium nitrate and urea. Average responses to nitrogen were smaller than have been obtained in recent years, and 1·0 cwt. N/acre was sufficient for maximum yields. At the low rate of dressing ammonium sulphate and calcium nitrate gave similar yields; at the medium rate (1·0 cwt. N/acre) calcium nitrate was slightly inferior. The heavy dressing of ammonium sulphate gave the same average yield as the medium dressing, but the high rate of calcium nitrate reduced yields markedly. At the light and medium rates of dressing urea was markedly inferior to the other forms of nitrogen, and at the highest rate it gave lower yields than were obtained on plots receiving no

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nitrogen. At three of the centres fertilizers were broadcast over the furrows before planting by hand; at all rates of dressing urea checked emergence and early growth at these three centres, the effect being particularly serious at the high rate, where emergence was delayed by about a month and many plants were killed. The high rate of calcium nitrate also caused a check to growth, although the effect was less serious. Ammonium sulphate was quite safe. At the other five centres fertilizers were broadcast over the flat land before planting by machine, and early growth was not checked by urea or calcium nitrate; urea gave consistently lower yields than ammonium sulphate even at centres where there was no check to growth.

Kale

Two experiments on kale also compared ammonium sulphate, calcium nitrate and urea each applied at 1·0 and 2·0 cwt. N/acre. At one centre where the crop was grown on wide rows practically no plants germinated on plots dressed with urea, the heavy dressing of calcium nitrate also damaged germination, but ammonium sulphate was quite safe; the damaged plots were resown. At the other centre the kale was grown in rows 14 inches apart and the plants were not thinned; urea damaged germination, but sufficient plants emerged to give a satisfactory though thinner plant. At both centres ammonium sulphate gave higher yields than calcium nitrate at the low rate of dressing, but calcium nitrate was superior at the high rate; urea gave much lower yields than ammonium sulphate at both rates. These experiments also tested the effect of splitting the dressings of nitrogen fertilizers, part being applied before sowing and part as a top-dressing of "Nitro-Chalk" in summer. Split applications gave higher yields than dressings applied wholly to the seedbed when ammonium sulphate was applied at planting, but not when calcium nitrate was used.

The urea used in the experiments on potatoes and kale was an imported granulated fertilizer-grade material having excellent physical condition. It contained approximately 4 per cent of biuret, and it is thought that this constituent was responsible for damage to early growth and subsequent poor yields. Less-severe checks to early growth were also caused by calcium nitrate in the dry and cold spring of 1956, and it is possible that a part at least of the damage caused by urea was due to high salt concentrations which developed as this material decomposed. Damage to germination and early growth caused by urea was also observed in experiments on ryegrass; the crops recovered to give satisfactory takes of grass. In future work on urea samples free from biuret will be used.

Formalized casein for grass (K. Shaw and F. V. Widdowson)

Laboratory incubation experiments showed that formalized casein produced inorganic nitrogen at a slow and uniform rate, confirming the results of earlier work with this material in pot experiments (*Rep. Rothamst. exp. Sta. for* **1950**, 39, and **1951**, 39). Formalized casein was tested as a slowly-acting nitrogen fertilizer in a field experiment on newly-sown Italian ryegrass from which three cuts were taken in 1956. The availability of the nitrogen in the formalized casein, as measured by the response, was compared with responses produced by three equal dressings of ammonium sulphate supplying the same total quantity of nitrogen. There was little benefit from the formalized casein at the first cutting, but at the second and third cuttings, yields compared favourably with those given by repeated dressings of ammonium sulphate. The experiment also compared single dressings of casein and ammonium sulphate with repeated dressings of ammonium sulphate, calcium nitrate and urea. Repeated dressings produced slightly higher aggregate yields than single dressings.

Field Experiments with ^{32}P-labelled Superphosphate

(G. E. G. Mattingly)

The results of a series of field experiments using labelled superphosphate which were carried out in collaboration with F. V. Widdowson over several years have now been summarized.

Radiation effects

Two field experiments were carried out on barley in 1954 and 1955 in which the initial specific activities were 0·62 mC and 0·36 mC/g. respectively. At an early sampling both yield and total phosphorus uptake were slightly lower on the plots receiving ^{32}P-labelled superphosphate than on plots where ordinary superphosphate was used. In 1955 (but not in 1954) these differences persisted at harvest. None of the effects which could be attributed to radiation were significant, although for both yield and phosphorus uptake at the early sampling they were greater than the appropriate standard error. In a 1954 pot experiment yield and total phosphorus uptakes by grain and roots were slightly greater where ^{32}P was applied than where ^{31}P was used, but none of the effects were significant. These results suggest that while effects due to the active isotope may occur in experiments using ^{32}P-labelled fertilizers, they are generally very small compared with the increases in yield and phosphorus uptake given by the main treatments. These conclusions are in general agreement with those of American workers.

Comparison of drilling and broadcasting phosphate

Four experiments on barley and five experiments on root crops (fodder beet, swedes and potatoes) were carried out from 1952 onwards. The effects were measured of broadcast dressings of ordinary superphosphate and other phosphate fertilizers containing ^{31}P on the uptake from a light, uniform dressing of ^{32}P-labelled superphosphate (applied at 0·1 cwt. P_2O_5/acre for barley and 0·2 cwt. P_2O_5/acre for roots). The active superphosphate was applied to all plots of the experiments. For both barley and for roots the broadcast inactive fertilizers increased yields and the *total* uptake of phosphate in the presence of the drilled active dressing. Measurements of the phosphorus taken up from labelled superphosphate showed that the amounts were reduced slightly by the presence of

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the much larger broadcast dressings. These reductions amounted on average of all the experiments to only 7 per cent of the uptake of placed active phosphate for barley and 13 per cent for roots. Their magnitude suggests that moderate dressings of broadcast phosphate fertilizers have rather little effect on the uptake of phosphorus from a small dressing drilled close to the seed.

This point was further investigated in three other experiments on barley carried out from 1953 to 1955. The uptake of ^{32}P from broadcast dressings of labelled superphosphate applied at 0·2 cwt. P_2O_5/acre was measured in the presence and absence of 0·1 cwt. P_2O_5 as ordinary superphosphate drilled with the seed. On average of the three experiments there were only small increases due to phosphate, the mean recovery from broadcast superphosphate being only 8 per cent. Drilling the dressing of ordinary superphosphate had very little effect on the uptake from broadcast active superphosphate. These results all suggest that the uptake of phosphorus by barley from broadcast superphosphate is largely independent of the uptake from a simultaneous drilled dressing when low rates of application are used.

Residual effects of phosphates

An experiment previously described (*Rep. Rothamst. exp. Sta. for* **1955**, p. 46) was continued to measure the effects of residues of fertilizers applied in 1954 and 1955 on the uptake by ryegrass of phosphorus from a broadcast dressing of 0·5 cwt. P_2O_5/acre as radioactive superphosphate applied in spring, 1956. The results of the 1956 work are summarized in Table 2.

TABLE 2

Residual effects of phosphate fertilizers on ryegrass

	Yield of dry matter, cwt./acre	Total P in crop from soil and residues of fertilizers, cwt. P_2O_5/acre	*Extra* P in crop from active superphosphate applied in 1956, cwt. P_2O_5/acre
Without phosphate in 1954–5	69·3	0·388	0·165
Increases due to residues of 3·0 *cwt.* P_2O_5 *per acre applied as :*			
Superphosphate 1954 ...	5·7	0·133	−0·023
Superphosphate 1955 ...	6·6	0·204	−0·050
Gafsa rock phosphate 1954	3·5	0·067	0·001
Gafsa rock phosphate 1955	5·2	0·164	−0·031

The residues from superphosphate and Gafsa rock phosphate applied in 1954 and 1955 increased yields and phosphorus uptakes of ryegrass grown in 1956. Residues from 1955 dressings were more effective than those from corresponding 1954 dressings. The uptake of phosphorus from ^{32}P-labelled superphosphate given in 1956 was significantly reduced by residues from both superphosphate and Gafsa rock phosphate given the year before; Gafsa applied in 1954 had no effect.

Recovery of applied phosphorus

In experiments with unlabelled phosphates estimates of the amounts of the applied dressing which are recovered are open to

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the criticism that the added phosphate so stimulates root growth that the crop takes up extra amounts of soil phosphate. These experiments with ^{32}P-labelled superphosphate have provided estimates of the percentages of the applied active phosphorus which have been recovered by crops grown on the Rothamsted Farm; they are not subject to errors due to extra uptake from soil phosphorus, and are therefore summarized in Table 3.

TABLE 3

Mean percentage recoveries of phosphorus from ^{32}P-labelled superphosphate in annual field experiments, 1952–56

Crop	Method of application	No. of experiments	Rate of application, cwt. P_2O_5/acre	Percentage recovery
Barley... ...	Drilled with seed	7	0·1	14
Barley... ...	Broadcast	3	0·2	8
Root crops ...	Placed near seed	5	0·2	21
Ryegrass ...	Broadcast	1	0·5	33

OIL-PALM EXPERIMENTS

(W. B. Haines)

Data from the oil-palm experiments discussed in last year's Report have been further examined. When manuring was stopped after many years there was an abrupt drop in the first year in bunch weight but not in bunch number, followed by a gradual decline of the potash effect at a rate similar to that at which it was built up. There were marked seasonal differences, the effect of P was to produce lower numbers of bunches in a dry season and an increased number in the early part of a wet season when yields were at their best. In contrast to this, K did not affect the bunch number in the early part of a wet season, but produced large effects in the remaining part of the year (i.e. the later wet season and the following dry season). Poaching between plots through root action was assisted where P had been given, due to the stimulating effect of this nutrient on root growth. It was necessary to correct potash deficiency before phosphate manuring gave good results.

Individual oil palms vary greatly in their yield capacity. Data have been examined to see whether fertilizer responses were related to palm classes in such a way that would make individual selective treatment desirable. The results show that all classes play their part in producing the return from manuring and that no class need be rejected in treating the data. Where high competition effects are suspected it might be economic to give increased dressings to the poorer classes of palm to help them withstand competition, rather than to concentrate manuring on the high yielders.

RESIDUES OF FERTILIZERS AND FARMYARD MANURE

(R. G. Warren)

An account of the changes in the total amount of soil organic matter in the Broadbalk and Hoosfield experiments and of the value

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to barley of P and K residues from fertilizers and farmyard manure applied last century on the Exhaustion Land Experiment was presented to the Fertiliser Society this year. A new scheme for the cropping of the Exhaustion Land, together with proposals for the addition of P and K fertilizers to parts of the experiment, are being prepared in order to measure the effects of the P and K residues on six different crops grown in the same year and to compare these effects with those from new applications of P and K.

The study of residues of organic matter has been extended to include the Deep Cultivation Experiment and the Ley–Arable Experiments. In the Deep Cultivation Experiment the addition of a total amount of 60 tons/acre of farmyard manure applied to the root crops grown during two cycles of the six-course rotation raised the organic-matter content of the top 12 inches of soil by 0·1 per cent organic carbon; these small increases in organic matter were similar for both depths of ploughing (6 inches and 12 inches). The deeper ploughing caused an overall reduction of 0·2 per cent organic carbon both on plots receiving farmyard manure and also where no manure was given. The combined effect of deep ploughing and applying farmyard manure was a reduction of 0·1 per cent organic carbon. In the Four-Course Rotation Experiment 80 tons/acre of farmyard manure applied over a period of twenty-five years raised the organic carbon by 0·1 per cent. Similar increases were given by straw and straw compost applied at the same rate of organic matter as the farmyard manure.

Soil Nitrogen

Denitrification (J. M. Bremner and K. Shaw)

Work on the factors affecting loss of nitrogen from soil by denitrification was continued. A critical examination of the methods available for following nitrogen changes in soil under conditions favourable for denitrification showed that the salicylic acid modification of the Kjeldahl method to include nitrate was not satisfactory for use with wet soil and that oven-drying of wet soil caused extensive loss of nitrate, nitrite and ammonia. A modification of a method of determining total nitrogen, including nitrate and nitrite, described by Olsen (*C.R. Lab. Carlsberg*, **17** (*1929*), *No. 3*) was found to give very accurate and consistent results, and this procedure was therefore adopted to follow total nitrogen changes in soil under various conditions. An investigation of the effect of various organic materials on the denitrification of nitrate in mineral soils showed that carbon in the form of readily decomposable substances, such as glucose, mannitol or cellulose, caused much more rapid and extensive denitrification than did carbon in the form of straw, lignin or sawdust. Water-extracted straw and decomposed straw had much less effect than untreated straw, and carbon added in the form of finely ground peat or fen soil had only a small effect compared with that produced by an equivalent amount of carbon as straw. The effect of adding different amounts of readily available carbon was studied. The total nitrogen loss decreased with increase in the amount of carbon added because

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carbon in excess of the amount required by denitrifying organisms for the reduction of nitrate to gaseous nitrogen stimulated the activity of nitrogen-fixing organisms. An investigation of the course of denitrification in soils treated with nitrate and different levels of glucose showed that the disappearance of nitrate was accompanied by the formation of considerable quantities of nitrite and small quantities of ammonia, and that the nitrite formed disappeared rapidly if the amount of carbon added as glucose was more than about twice the amount of nitrogen added as nitrate. Neither hydroxylamine nor hyponitrous acid could be detected at any stage in the denitrification process. Tests with hydroxylamine showed that it was immediately decomposed in Rothamsted soils by a reaction which appeared to be purely chemical. Experiments using $K^{15}NO_3$ showed that all of the nitrogen lost when nitrate and glucose were added to waterlogged soil was derived from the nitrate added. Further work on the effects of temperature and pH showed that the optimum temperature for denitrification is between 50° and 70° C. and that the low rate of denitrification in soils of low pH is not due to lack of calcium or molybdenum. Results so far obtained in experiments with soil at different moisture levels indicate that the degree of water saturation of the soil is of decisive importance in determining the rate and extent of denitrification. Below a certain moisture level no denitrification occurs; above this the rate of denitrification increases rapidly with increase in the amount of water present.

All the results so far obtained in this work support the view that denitrification occurs only under conditions when the supply of oxygen is limited. Claims that denitrification occurs even when the supply of oxygen is satisfactory could not be substantiated. For example, no loss of nitrogen could be detected when waterlogged soils containing nitrate and glucose were shaken in an atmosphere of oxygen or when moist soils containing nitrate and glucose were aerated continuously. From the practical aspect probably the most important conclusion reached is that no significant loss of nitrogen occurs if the water content of the soil is less than 60–70 per cent of the water-holding capacity, even if all other conditions are favourable for denitrification.

Mineralization of nitrogenous materials in soil (J. M. Bremner and K. Shaw)

The potentialities as slowly-acting nitrogenous fertilizers of various waste materials and of products prepared from such materials have been tested by determining the rate of mineralization of their nitrogen in soil under controlled conditions in the laboratory. Formalized casein and formalized hoof were found to release mineral nitrogen more slowly and uniformly than the unformalized materials. Deamination of casein had little effect on the rate of mineralization of its nitrogen. Products prepared by treating lignin with nitric acid and with nitrous acid released mineral nitrogen at similar rates and more rapidly than did lignin–ammonia complexes. Nitrated sawdust having a C/N ratio of 2·3 decomposed very slowly, and cellulose nitrate (C/N, 2·3) and amyl nitrate (C/N, 4·3) were resistant

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to decomposition. This work indicates that nitrogen in the form of nitrate ester is not mineralized by soil micro-organisms and provides further evidence that the carbon : nitrogen ratio of a material is not a reliable guide to its value as a nitrogenous fertilizer. Experiments with crushed hoof confirmed other evidence (*Rep. Rothamst. exp. Sta. for* **1949**, 32) that there is no justification for the traditional view that hoof is a slowly-acting nitrogenous fertilizer. The results with formalized casein and formalized hoof confirmed indications from pot experiments that such products may be useful as slowly-acting nitrogen fertilizers, and the value of waste formalized casein from the plastics industry is therefore being tested in field experiments.

Lignin-like material in soil (J. M. Bremner)

Further work was carried out to test the theory that a substantial fraction of soil organic matter consists of nitrogenous complexes formed by reaction of lignin or lignin-derived material with ammonia or protein. An investigation of the properties of lignin–ammonia complexes showed that the reaction of lignin with ammonia causes little destruction of methoxyl groups or of the units responsible for the formation of aromatic aldehydes on oxidation with alkaline nitrobenzene and that most of the nitrogen fixed by lignin in its reaction with ammonia is resistant to treatment with hot acid or alkali. Incubation tests showed that the nitrogen in a humic acid preparation was mineralized in soil at a rate intermediate between that of nitrogen in the form of lignin–ammonia and of lignin–protein complexes. Continuation of work previously reported showed that the reaction of humic acid with nitrous acid resembles the reaction of lignin with nitrous acid and indicated that lignin or lignin-derived material may be largely responsible for the high apparent amino-nitrogen values obtained when humic acids are analysed for amino groups by the nitrous acid method of Van Slyke. The reaction of lignin with nitrous acid was found to be similar in many respects to its reaction with nitric acid. Most of the nitrogen liberated by acid hydrolysis of lignin–nitrous acid reaction products was identified as ammonia and hydroxylamine. Examination of the products formed on nitration and alkali fusion of humic acid preparations showed that humic acids, like lignins, yield 3 : 5-dinitroguaiacol on treatment with nitric acid in ether and yield catechol and protocatechuic acid on fusion with potassium hydroxide.

These results, taken with the previous finding that humic acids yield aromatic aldehydes (vanillin, syringaldehyde and *p*-hydroxybenzaldehyde) on oxidation with alkaline nitrobenzene (*Rep. Rothamst. exp. Sta. for* **1954**, 50), leave little doubt that soil humic acids contain some lignin-like material, but no conclusions can yet be drawn regarding the amount of lignin-derived material they contain.

Effect of storage on the biological activity of soil (J. M. Bremner)

The biological activity of soil samples taken from Plots 3 and 7 of Broadbalk in 1881 and subsequently stored in an air-dried condition in sealed bottles has been investigated. The results showed that these stored soils were unable to nitrify ammonium sulphate but ammonified added organic nitrogen compounds and denitrified added nitrate more rapidly than did unstored soil taken from the same plots in 1956.

Acid-soluble (fulvic) fraction of soil organic matter (J. M. Bremner and T. Harada)

Earlier work on the amino-acid composition of the non-dialysable material in the acid-soluble (fulvic) fraction of 0·5*M*-sodium hydroxide and 0·1*M*-sodium pyrophosphate (pH 7·0) extracts of soil was extended. The results obtained confirmed the previous finding that this fraction is similar in amino-acid composition to the acid-insoluble (humic) fraction of soil extracts but contains relatively larger amounts of β-alanine and smaller amounts of the basic amino acids arginine and lysine.

Effect of treating soils with hydrofluoric acid (J. M. Bremner and T. Harada)

An investigation of the use of hydrofluoric acid for the separation of the organic and inorganic fractions of soil showed that pretreatment of mineral soils with hydrofluoric acid or with a mixture of hydrofluoric and hydrochloric acid at room temperature did not increase the amount of organic matter extractable by reagents such as 0·5*M*-sodium hydroxide or neutral 0·1*M*-sodium pyrophosphate. It was found, however, that a considerable amount of soil nitrogen was dissolved by such pretreatment and that a significant fraction of the nitrogen extracted from some mineral soils by *N*-hydrofluoric acid is in the form of ammonia. Attempts are being made to discover if this ammonia is derived from fixed ammonium nitrogen in clay minerals or is formed by hydrolysis of organic nitrogen compounds during the acid treatment. Experiments with vermiculite containing fixed ammonium nitrogen showed that whereas less than half of this nitrogen was released by treatment with *N*-hydrochloric acid, practically all of it was released by *N*-hydrofluoric acid.

Inorganic nitrogen in soils (G. W. Cooke and R. K. Cunningham)

Concentrations of nitrate and ammonium were measured at intervals during the summer both in uncropped soil and under ryegrass in an experiment on Rothamsted clay-loam soil. Levels of nitrate in the top 9 inches of soil remained high on uncropped plots through June and July, which were wet months; heavy and persistent rainfall in August had transported much of the nitrate into the subsoil by the beginning of September. These results were obtained both on unmanured plots and on plots which had received calcium nitrate. On uncropped plots additions of ammonium sulphate gave high concentrations of soil ammonium, which fell slowly during the summer; there was a corresponding rise in nitrate concentrations, but ammonium was converted to nitrate much more slowly than had been anticipated. Plots which were dressed with urea soon gave a high concentration of soil ammonium, which behaved in the same way as ammonium on plots receiving ammonium sulphate. On plots where grass had been sown there was a rapid fall in nitrate concentrations. In early July uncropped soil which

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had received either calcium nitrate or ammonium sulphate in April contained about 40 p.p.m. NO_3, whereas corresponding plots on which ryegrass was grown contained less than 10 p.p.m. NO_3. Where ryegrass was grown on plots which had received ammonium sulphate or urea ammonium concentrations fell rapidly and nitrate levels remained very low. On plots which received no ammonium salts or urea, ammonium concentrations remained surprisingly constant at 8–10 p.p.m., both in uncropped soil and under ryegrass. On uncropped plots there had been no loss of inorganic nitrogen from the surface 9 inches at the beginning of August; during the heavy rains of August and early September, nitrate was transported into the subsoil, and there was also a loss of total inorganic nitrogen from the surface 18 inches of soil which may have been due to leaching or to denitrification.

It seems that nitrate is not easily leached out of heavy soils with good structure by average summer rainfall which is sufficient to cause well-marked through drainage. It is possible that nitrate ions are retained inside structural aggregates and that rainfall percolates around the crumbs. Heavier and prolonged rainfall may remove nitrate by causing a deterioration in soil structure. The rapid fall in nitrate concentration under crops or grass which occurs when rapid growth is started must be due to uptake by crops and not to leaching. Quickly-growing grass appears able to remove a large amount of nitrate from the soil in a very short time.

An investigation has been started to develop simple methods of forecasting responses of crops to nitrogen fertilizers by chemical tests on the soils. Under suitable conditions measurements of nitrate concentrations in soil samples taken when field experiments were being laid down indicated whether a response was likely. Attempts are also being made to relate the amounts of inorganic nitrogen released on incubation of soils in the laboratory with the responses of cereals and potatoes to nitrogen fertilizers.

Decomposition of Plant Residues in Grassland Soils

(K. Shaw)

The effects of different conditions and treatments on the rate of decomposition of samples of "mat" (*Rep. Rothamst. exp. Sta. for* **1955**, 52) have been studied by measuring the carbon dioxide and mineral nitrogen produced on incubation at 25° C. for 80 days. Raising the pH of the materials to about 7 by the addition of calcium carbonate or calcium hydroxide increased both carbon dioxide and mineral nitrogen production, the addition of phosphorus as potassium dihydrogen phosphate with calcium carbonate or calcium hydroxide further increased the decomposition of the materials. Little information is available on the field moisture contents of "mats", but as they appear to be water-saturated for a greater part of the year under field conditions, the effect of different moisture levels on their rate of decomposition was investigated. Maximum carbon dioxide production occurred in the region of the water-holding capacity of the materials, i.e., between 200 and 300 per cent of water. Mineral nitrogen production was not, however, seriously affected by high moisture levels, which indicates that ammonification of the organic nitrogen is not inhibited under waterlogged conditions. Manganese, boron, molybdenum and copper added to "mat" materials in the presence and absence of calcium hydroxide did not increase the carbon dioxide or mineral nitrogen production under either condition. Since the incubation tests were carried out at 25° C., which is considerably higher than temperatures encountered in the field, the effects of lower temperatures on the rate of decomposition of the "mats" were studied. Experiments are now in progress in which the decomposition is being followed at temperatures between 0° and 25° C. So far, the results obtained show that below 10° C. the rate of decomposition is much less rapid than at 25° C.

This work confirms field experience that liming accelerates decomposition of "mats" formed in grassland. The results also indicate that it would probably be an advantage to apply phosphate in addition to lime to assist breakdown and suggest that the slow rate of decomposition of "mats" is not due to their apparent high water content.

Isotopic Exchange of Phosphorus in Soils and Fertilizers

(O. Talibudeen)

Rothamsted soils

Preliminary calculations suggest that phosphorus on readily accessible soil surfaces can be estimated after isotopic exchange carried out for periods varying from 10 to 20 hours, and that the amounts constitute between 50 and 80 per cent of the total surface phosphorus.

Mono-calcium phosphate was added to the Hoosfield Exhaustion Land and Highfield soils used in previous work (*Rep. Rothamst. exp. Sta. for* **1955**, 48) at the rate of 10 mg. P/100 g. soil, and the soils were sampled at intervals of one, two and three months. The increment in the total surface phosphorus due to added phosphate remained unchanged, 66, 71, 75 and 100 per cent of the added P being recovered respectively on the soils of Hoosfield Plots 1, 3 and 9 and Highfield. In the Hoosfield soils the increment in "readily accessible" phosphorus decreased by an amount equal to 20 per cent of the added P between the first and third sampling. There was no similar change in the Highfield soil, three-quarters of the added phosphorus remaining readily accessible. In the Hoosfield soils, between one-quarter and one-third of the applied phosphorus appears to be inaccessible to the soil solution a month after it has been added. These soils contain about 2 per cent of calcium carbonate; 1 mg. of P added as orthophosphate is converted to a less-accessible form by each gram of $CaCO_3$ during a reaction period of three months.

The possibility of using different media for isotopic exchange work is being explored, and $0{\cdot}01M$-$CaCl_2$ and $0{\cdot}001M$-KCl have been tried. In soils having a low phosphorus status and containing much $CaCO_3$ it was difficult to determine the low phosphate concentrations in the solutions obtained in this way; much longer times

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were needed to attain isotopic equilibrium, and there was little control of pH when low soil : solution ratios were used.

The Highfield soil was progressively leached for increasing times with 0·001*M*-KCl and with 0·001*M*-neutral ammonium citrate in 0·02*M*-KCl. At very slow rates of leaching, when the extracting solution was nearly in equilibrium with the soil phosphate, the rate at which phosphate was extracted was very similar to the rate at which isotopic exchange took place in the equilibrium suspension. The total amount of phosphorus extracted was, however, only 40 per cent of the phosphorus estimated by isotopic exchange.

Rock phosphates

Work previously reported (*Rep. Rothamst. exp. Sta. for* **1953**, 47) was continued, and measurements similar to those made on soils were carried out on rock phosphates in a buffer solution of 0·001*M*-phenyl-barbituric acid at pH 7·5. The phosphorus concentration of the solution at equilibrium was approximately inversely proportional to the amounts of carbonate and fluoride in the samples. Surface areas calculated from the isotopically-exchangeable phosphorus, although following the same trend, were much lower than those obtained by other workers using gas-absorption methods. The data obtained suggest that in samples ground to pass a 100-mesh B.S. sieve (particle diameter 150 μ) the average diameter of the crystallites is of the order 0·5–1 μ.

Soil Potassium

Potassium in crops and soils at Rothamsted and Woburn (R. G. Warren)

Good progress has been made on the analysis for potassium of samples of the leys and arable crops from three ley–arable experiments, two at Rothamsted and one at Woburn. The levels of potassium manuring for some of the treatments in the two Rothamsted experiments, Highfield and Fosters Field, have been inadequate and an acute shortage of soil potassium has developed. The scheme of cropping in these experiments produces a wide range in the amounts of potassium taken up by the different crops and also in the amounts removed from the soil. For cereals the quantities taken up and removed are moderate, but the grass crops grown in one year may contain 200 lb./acre of K. The whole of this amount is removed from the cut grass plots, but on the grazed plots the bulk of it is returned to the land by the sheep. Lucerne also removes large quantities of potassium but less than the cut grass.

Crops grown at Rothamsted frequently give sizeable responses to potassium manuring; at Woburn increases in yield given by potassium are generally much smaller. It appears that the Woburn soil is able to maintain a supply of potassium which, together with normal potassium dressings supplied by fertilizers, is sufficient for arable crops. Analyses now being made of the soils and crops of the Ley–Arable Experiment at Woburn will show whether supplies of soil potassium plus current manuring are quite adequate for the leys and the arable crops which follow.

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Potassium in soil extracts (A. W. Taylor)

Studies on the composition of solutions in equilibrium with soils have been applied to the measurement of potassium status. For soils where $a_K/\sqrt{a_{Ca}}$ was low this ratio was found to be constant for electrolyte concentrations ranging from below 0·001*M* to above 0·1*M*. On soils richer in potassium the ratio decreased steadily as the electrolyte concentration was increased.

The work was extended by taking samples of soil from several plots on Sections I, II, III and IV of Broadbalk in autumn 1955. The concentration of potassium ions which must be added to a solution containing a constant concentration of calcium ions (0·01*M*) to prevent any exchange when the solution is shaken with a soil sample was determined by trial and error. The values for potassium concentrations in solutions in equilibrium with 0·01*M*-calcium chloride are set out in Table 4. In Plot 2 (which receives farmyard manure) the equilibrium potassium concentrations fell steadily in years following the fallow period; on other plots the value did not vary regularly according to the time since the section had been fallowed.

TABLE 4

Potassium concentrations in equilibrium with 0·01M-calcium chloride and soil

	Treatment	Equilibrium potassium concentration in the presence of 0·01*M*-$CaCl_2$ ([K] × 10^{-4}*M*)
Plot 2	Farmyard manure	25·0
Plot 3	No manure	2·4
Plot 11	Ammonium sulphate, superphosphate	0·8
Plot 12	Ammonium sulphate, superphosphate, sodium sulphate	0·7
Plot 13	Ammonium sulphate, superphosphate, potassium sulphate	11·0

The range of values obtained for equilibrium potassium concentrations is wider than the range obtained by measurements of exchangeable ions, and this method of assessing the potassium status of soils may have practical uses. On theoretical grounds the method is desirable, since it gives a direct measure of the partial molar free energy of exchange of the ions which may prove important in studying potassium " fixation " processes.

MICRONUTRIENTS

Copper deficiency in poplar cuttings (B. Benzian and R. G. Warren)

In 1955 " needle tip-burn " on Sitka spruce seedlings grown at Wareham was shown to be due to copper deficiency. The black discoloration of the leaves of poplar cuttings (*P. robusta H*) grown on the same soil has now been diagnosed as a deficiency of the same micro-nutrient. The symptoms were greatly reduced by a soil application of a fritted trace element material containing Fe, Mn, Cu, Zn, Mo and B and by foliar sprays of copper applied as a lime-copper sulphate mixture. Table 5 gives scores for blackening, height in inches and copper content of the poplar leaves.

TABLE 5

Effects of copper treatment on poplar cuttings

	Scores for blackening	Height, inches	Cu, p.p.m.
No fritted trace elements	9	20·6	1·3
With fritted trace elements ...	2	29·8	3·1
No Cu foliar spray	8	18·6	1·8
With Cu foliar spray	2	33·1	4·2

Soil manganese (S. G. Heintze)

The effects of long-continued fertilizer treatments on some fractions of soil managanese were studied by estimating the exchangeable, readily-reducible and pyrophosphate-soluble manganese in selected plots of the Rothamsted Experiments. The small exchangeable manganese fraction varied with soil pH, and there were no effects from fertilizer treatments. From 5 to 75 per cent of the total manganese was in a readily-reducible form, and there were only small seasonal variations. Where farmyard manure had been applied both on arable and grassland the readily-reducible manganese was decreased. Ammonium sulphate or rape-cake, which both reduced soil pH, had no effect on this fraction on those plots which did not receive minerals or which received farmyard manure. Where full mineral fertilizer dressings were given, long-continued application of ammonium sulphate increased readily-reducible manganese on the arable land of Barnfield and Long Hoos, but the same treatment applied to both limed and unlimed plots of the Park Grass Experiment caused a large reduction. This fraction of soil manganese also decreased where legumes had been grown.

The quantity of manganese dissolved by brief extraction with pyrophosphate was much less than the readily-reducible fraction. Ammonium sulphate or mineral fertilizers had only small effects on pyrophosphate-soluble manganese; there was some increase in this fraction where farmyard manure had been applied except in the Park Grass Experiment. Previous cropping with legumes increased pyrophosphate-soluble manganese. Some preliminary work was done on redox levels of soils. Soils containing sufficient available manganese had higher redox levels than comparable soils where manganese deficiency occurred in crops.

ANALYTICAL

Fluorine (A. C. D. Newman)

In extending previous work on the solubility of rock phosphate it became necessary to develop a reliable method for determining small quantities of fluorine. The effects of fluoride on the colours produced by the reactions of a variety of organic compounds with aluminium salts were examined. Quinalizarin sodium sulphonate was finally chosen. A solution of the reagent in water, buffered to pH 3·9 and treated with an equal volume of 0·0005*M*-aluminium potassium sulphate, produced a stable coloured solution. The reduction in the colour of this reagent caused by addition of fluoride solutions was measured photo-electrically, and good agreement was obtained with solutions standardized by the macro-method involving precipitation as lead chlorofluoride. The effects of elements which interfere with the reaction were examined. Metals which interfere (aluminium, ferric iron, thorium, beryllium, titanium and zirconium) may be removed from solution by a cation ionic-exchange resin. High concentrations of phosphate (relative to fluoride) also interfere. When appreciable quantities of phosphate were present, they were separated from fluoride using an anion-exchange resin. Quantitative recovery of fluoride from solutions containing several times as much phosphate was achieved. The comparative insensitivity of the method to small quantities of phosphate, together with the ease with which large amounts of phosphate may be removed by ion exchange, makes the method promising for determining fluorine in solutions derived from rock phosphate.