

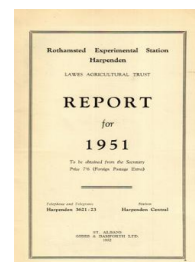
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## Chemistry Department

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## CHEMISTRY DEPARTMENT

By E. M. CROWTHER

### FERTILIZER INVESTIGATIONS

Supplies of sulphuric acid for the manufacture of superphosphate and other fertilizers are likely to be restricted for several years by the world shortage of elemental sulphur. In many countries renewed interest is therefore being taken in alternative methods for converting rock phosphate into a more active fertilizer and in finding conditions in which superphosphate might economically be replaced by other materials. In the United Kingdom fertilizer prices rose very steeply on July 1, 1951 through the combined effects of removal of subsidies, shortage of sulphur and higher prices for other imported raw materials. Towards the end of 1951 a new subsidy was announced for phosphate fertilizers only. These changes in supplies and price structure may have marked effects on fertilizer practice. It is well known that many farmers use fertilizers at heavy rates as part of a long-term investment programme, whilst others, especially on inherently poorer soil, use far too little. There is an urgent need for more field information on alternative forms, amounts and methods of application of the main fertilizers and on means of estimating the relative requirements of various crops and kinds of soils.

#### *Phosphate fertilizers*

The Ministry of Supply has published a series of reports by members of the Building Research Station and of this Department on the production and agricultural value of silico-phosphate, a fertilizer prepared by heating rock phosphate with sodium carbonate, sand and steam. A further report on other alternatives to superphosphate is in the course of preparation.

During 1951 a new series of field experiments was initiated by the Fertilizer Conference of the Agricultural Research Council and organized by G. W. Cooke of this department. The field work was carried out under the direction of the soil chemists of the National Agricultural Advisory Service and by the staffs of the Northern Ireland Ministry of Agriculture, the Macaulay Institute for Soil Research and Rothamsted Experimental Station. One series of experiments on swedes and potatoes compared dicalcium phosphate, silico-phosphate and ground Morocco mineral phosphate, each supplying 0.5 cwt.  $P_2O_5$  per acre, with superphosphate supplying 0.33 cwt. and 0.66 cwt.  $P_2O_5$  per acre. The two rates of superphosphate, which were included to indicate the sensitivities of the tests, showed, as many earlier experiments had done, that quite small dressings often suffice to give good crops. The obvious adjustment to current shortages and prices is to reduce the amount of phosphate in fertilizer dressings on land with appreciable residues from past treatments but to make sure of adequate supplies on the more deficient soils.

On the average of thirteen potato experiments in 1951 dicalcium phosphate behaved very well, giving yields equalling those from superphosphate at the higher rate. Silico-phosphate, as in the



earlier series of field experiments, was less effective than equivalent superphosphate, giving mean yields close to those from the lower rate of superphosphate. As was to be expected, ground mineral phosphate was much inferior to superphosphate. For swedes dicalcium phosphate gave yields close to those from equivalent superphosphate; silicophosphate and mineral phosphate gave slightly lower yields. This series of experiments will be extended to new centres in 1952. The first year's results are, however, of interest in showing that, under conditions still to be defined more precisely, good results may be expected from some fertilizers in which the phosphorus is not soluble in water.

A second series of experiments tested so-called "Nitrophosphates." These fertilizers are made by attacking rock phosphate with nitric acid and then adding ammonia to produce a mixture of dicalcium phosphate and ammonium nitrate, but there is a large variety of alternative products according to the steps taken to reduce the proportions of calcium nitrate in the final mixture. In one process some of the calcium nitrate is removed before adding ammonia. In another ammonium sulphate is added before the ammonia in order to form calcium sulphate. The physical and chemical properties of the final product may be materially influenced by what at first sight may appear to be details of chemical engineering. The rate at which phosphate diffuses in the soil may depend on the surface area of the dicalcium phosphate exposed and on the amount and form of the other calcium salts present. Two kinds of "Nitrophosphate" were compared in field trials against superphosphate and a nitrogen fertilizer, which were tested separately and together. In six experiments on grass cut for hay there were clear responses to the nitrogen fertilizer but not to superphosphate. In these experiments the two "Nitrophosphates" gave similar yields which were slightly higher than those from superphosphate and "Nitrochalk." In the four experiments which gave good responses to superphosphate, two "Nitrophosphates" behaved differently, the one prepared by removing excess calcium nitrate giving better yields than the one prepared by incorporating ammonium sulphate. The two materials had markedly different physical properties; the first consisted of angular flakes, which readily broke down in water, and the second of hard large granules, which retained their form when wetted. It is possible that the phosphate from the first form became more quickly accessible to plant roots. Recent field experiments by the Tennessee Valley Authority on somewhat similar materials have shown that small granules (between 20 and 50 mesh sieves) were more active than larger ones. The British results are preliminary ones from a small number of experiments but, like the American ones, they suggest the physical form of fertilizers containing dicalcium phosphate may be of great practical importance. Granulating less soluble materials introduces quite different problems from those involved in granulating mixtures containing superphosphate or ammonium phosphate.

On the average of eight experiments on potatoes both "Nitrophosphates" gave slightly lower yields than equivalent superphosphate and ammonium sulphate.



*Fertilizer placement*

The efficiency of fertilizers may sometimes be markedly increased by placing them in bands near, but not too close to, the seeds so as to secure the benefits of high initial concentration of nutrients for the young plant. A series of field experiments on row crops was continued by G. W. Cooke and F. V. Widdowson in 1951 for a final year. The results of experiments over several seasons are summarized below. A granular PK fertilizer was placed in a band about two inches to the side of the seed and three inches below the soil surface and compared with equivalent dressings broadcast either at an early or a late stage in preparing the seed-bed.

			Increase in yield in cwt. per acre from		
	No. of expts.	Unmanured yield cwt. per acre	Broad-casting fertilizer	Early over late broadcast	Placing over broadcast
<i>Threshed peas</i>					
1947 ..	3	13.2	0.3	—	2.8
1948 ..	5	12.6	1.3	0.8	2.2
1949 ..	6	13.7	0.3	0.0	1.2
1950 ..	3	16.1	1.0	-0.3	1.2
<i>Green peas</i>					
1949 ..	1	76.6	5.5	-2.9	19.5
1950 ..	3	83.8	1.2	1.5	13.0
1951 ..	3	58.5	3.8	9.9	2.2
<i>Winter beans</i>					
1950 ..	3	18.0	1.5	0.9	1.1
1951 ..	6	16.2	1.5	0.0	0.9
<i>Spring beans</i>					
1949 ..	3	13.5	0.1	1.3	1.3
1950 ..	4	19.0	0.8	1.8	2.2
1951 ..	3	15.4	1.0	0.0	0.1

In 1951 early and late dressings of broadcast PK fertilizer (14 per cent  $P_2O_5$ , 14 per cent  $K_2O$ ) gave similar yields of winter and spring beans. For peas picked green, early dressings ploughed in gave much higher yields than dressings broadcast on the seed-bed. Placing fertilizer in a band beside the seed gave higher yields of winter beans and green peas than broadcasting the same dressing, but in 1951 spring beans gave similar average yields from broadcast and placed fertilizer.

On the average of all experiments over four seasons, placing fertilizer beside the seed gave higher yields than broadcasting for each of the crops. The use of suitable drills should therefore prove profitable to farmers growing appreciable areas of these crops. In some seasons early dressings of broadcast fertilizer worked deeply into the soil gave higher yields of beans and peas than late dressings harrowed into the seed-bed. Where special placement drills are not available farmers are advised to broadcast fertilizer for peas and beans before cultivating to prepare the seed-bed; when possible, the broadcast dressings should be ploughed in.

G. W. Cooke and F. V. Widdowson carried out experiments in 1950 and 1951 on permanent pasture, leys and sainfoin to compare a granular PK fertilizer applied broadcast with the same dressing

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applied in bands three inches below the soil surface, and generally about 10 inches apart. The fertilizer placement drill built for row crops was used to apply the fertilizer in bands. Broadcast fertilizer gave more hay than banded fertilizer in six out of seven experiments, the difference being significant in four experiments. The advantage of supplying nutrients fairly uniformly to all plants in a sward outweighs any disadvantage there may be in having the fertilizer on the soil surface. At most centres cutting grooves with the fertilizer coulters slightly reduced yields on plots without added fertilizer, but even where the "cultivation effect" was negligible on unmanured plots broadcasting still gave better yields than banding. Two experiments were made on lucerne drilled in the spring of 1950 with the row-crop fertilizer placement drill, testing a granular PK fertilizer (10 per cent  $P_2O_5$ , 20 per cent  $K_2O$ ). At one centre with high yields and low fertilizer responses the first cut in 1950 gave significantly better yields from broadcasting than from banding, with no differences in subsequent cuts over two seasons. In the second experiment there were large and equal responses by the two methods. Dressings applied half in 1950 and half in 1951 were slightly inferior to those given wholly at sowing. Since lucerne develops an extensive root system it is able to use broadcast fertilizers effectively.

G. W. Cooke, M. V. Jackson and F. V. Widdowson carried out fourteen experiments on potatoes in 1951 using a simple potato planter with a fertilizer attachment made by the National Institute of Agricultural Engineering. National Compound No. 1 (7 per cent N, 7 per cent  $P_2O_5$ , 10.5 per cent  $K_2O$ ) was applied in the following ways:

- Broadcast on the seed-bed immediately before planting.
- Placed in front of the seed-shoe of the planter.
- Placed in contact with the seed.
- Placed in one band beside and below the level of the seed.
- Half the dressing broadcast and half placed in contact with the seed.

In all the experiments the machine worked on flat land, planting the potatoes and covering them over with a ridge of soil. When fertilizer was broadcast or placed in front of the seed-shoe its position within the ridge varied according to the condition of the seed-bed. With soil of "average" texture and moistness fertilizer applied by either method was thrown to the middle of the ridge and concentrated above the seed. With very wet soil much of the fertilizer remained on the outer surface of the ridge, but when the soil was very dry fertilizer was deposited beneath the seed.

On the average of all experiments broadcast fertilizer and fertilizer placed before the seed-shoe gave similar yields for both rates of application. Fertilizer placed in contact with the seed gave slightly higher mean yields than fertilizer drilled in bands beside the seed, and both methods gave much higher yields than broadcasting fertilizer or placing it in front of the seed-shoe. Placing half the fertilizer in contact with the seed and broadcasting the remainder gave somewhat lower yields than placing the whole dressing in contact, but the method was much superior to broadcasting all the



fertilizer. Placing fertilizer gave consistently higher yields than broadcasting; fertilizer in a side-band gave higher yields than broadcast fertilizer at twelve of the fourteen centres and higher yields than fertilizer before the seed-shoe at eleven centres. Emergence and early growth was generally checked by heavy dressings of fertilizer placed in contact with the seed. Later in the season the crops on these plots recovered at most centres. In assessing the value of contact placement it should be remembered that in 1951 the seed-beds were wet and there was ample rain in May with low temperatures in May and June. The experiments will be continued to determine whether the method is safe under other weather conditions. Until further results have been obtained, growers having planters fitted with fertilizer attachments are recommended either to modify their machines so that fertilizer is placed in a band beside the seed or to split heavy dressings, applying half in contact with the seed and broadcasting the remainder.

#### *Rates of action of nitrogen fertilizers*

Reserves of soil organic matter, crop residues and bulky organic manures owe some of their special merits in soil fertility and crop production to the slow liberation of ammonia and other plant nutrients. It is, however, singularly difficult to distinguish between these nutritional effects and others brought about more indirectly by changes in the physical properties or the micro-flora of the soil. The general problem might be simplified if it were possible in field experiments to employ suitable nitrogen fertilizers to produce ammonia slowly at rates comparable with those from bulky manures but without the associated indirect effects. Slowly-acting nitrogen fertilizers might also prove useful in practice for certain horticultural crops and for other purposes in which it is undesirable or inconvenient to give repeated small dressings of rapidly acting nitrogen fertilizers. Slowly-acting nitrogen fertilizers are, however, very difficult to prepare. Some of the materials favoured by horticulturists, such as dried blood or crushed hoof and horn, liberate their ammonia fairly rapidly in moist warm soil. In field and pot experiments in several years we have found that a plastic waste, formalized casein, acts much more slowly than crushed hoof and may give greater aggregate yields. In a pot experiment on repeatedly cut perennial ryegrass, set up early in 1950 and continued until the summer of 1951, formalized casein falling between 1 mm. and 2 mm. sieves gave about the same yields as crushed hoof (either 1-2 mm. and 5-6 mm.) in the first six cuttings but nearly twice as high yields in the next ten cuttings. Coarse formalized casein (5-6 mm.) naturally gave lower early yields, but the later yields were similar to those from finer fractions. The rate of action of crushed hoof was markedly slowed down by treating it with formalin, the fine fraction of formalized hoof being about as active as the coarse fraction of the formalized casein. Attempts have been made in the United States and in the United Kingdom to prepare slowly-acting forms of nitrogen fertilizer synthetically from urea and formaldehyde. Some of these products are relatively inactive, but the best of a series proved to be rather more rapidly-acting than fine hoof between 1 mm. and 2 mm. sieves. No sample proved more active



than fine hoof in the later stages of the pot experiments. Several other methods of retarding the breakdown of hoof and other proteins have been tested but so far no product has yet been found to equal formalized casein in steadiness of action and aggregate effect over long periods. Formalized hoof may have special merits where little immediate benefit is wanted.

In pot experiments conducted in 1951 the cuttings were arranged so as to give fairly steady yields per cutting from pots receiving constant amounts of urea after each cut. Other pots receiving all of their nitrogen initially in organic forms were cut at the same times. Under these conditions coarse and fine hoof and several urea-formaldehyde preparations had passed their peak yield by the fourth cutting. Fine formalized casein gave its peak about the sixth or seventh cutting. Coarse formalized casein and formalized hoof continued to give increasing yields up to about the tenth cutting but the yields from formalized hoof throughout were much below those from formalized casein. Fairly steady yields over all cuttings were obtained from mixtures of untreated hoof with formalized hoof.

In each of three seasons the pot experiments on repeatedly cut grass included a standard series in which varied quantities of urea were given periodically, the rates of application being changed at intervals to provide the factorial combinations of low and high rates early with low and high rates late in the season. In each season it was noted that the responses to heavy late nitrogen were less from pots with heavy early nitrogen. This suggests limitation by what is commonly termed "pot-binding," but in some of the experiments the maximum yield from the heaviest combination of urea dressings was less than those from some of the organic manures used at much heavier rates. It did not appear that the urea pots had reached any absolute limit, but that in some way the large early growth produced by abundant available nitrogen interfered with the efficient use of later nitrogen supplies. Such a state of affairs is well-known in manuring pastures or grass crops intended for silage or drying. The spring flush from early fertilizer dressings may lead to lower yields later in the year. This is commonly ascribed to the clovers being crowded out by the extra growth of grass, but there may be an additional factor. Where moisture and temperature allow, grass normally yields up to the limit set by the supply of available nitrogen. The top growth is accompanied by a more or less proportionate growth of root material of very low nitrogen content. When the tops are removed available nitrogen is used in rotting away cellulose from the roots and in consequence leaf growth may suffer through lack of sufficient nitrogen. Pastures and cut grass may show the field equivalent of "pot-binding." Additional nitrogen from fertilizers, urine or clovers may be needed to maintain mid-season growth and counter-balance the effects of the early flush. It may be partly for this reason that it is commonly recommended that old pasture and leys should be grazed heavily to give "a urine-soaked seed" before being ploughed up. In many parts of the world it is well-known that cereals and grass leys leave soils deficient in available nitrogen.



*Nutrition problems in forest nurseries*

Investigations in collaboration with the Research Branch of the Forestry Commission, reviewed over the period 1945 to 1949 in the Rothamsted Report for 1949, were continued. B. Benzian was in charge of the field experiments at six nurseries and several forests and R. G. Warren, H. A. Smith and J. E. A. Ogborn of the associated laboratory work. The Soil Microbiology Department co-operated in detailed soil examinations over three seasons at one of the nurseries. The wet seasons of 1950 and 1951 allowed good growth with striking responses to many kinds of treatment. Excellent first-year seedlings were obtained by appropriate treatments on very acid sandy soils taken over from heathland or conifer forest, and also on established nurseries of the agricultural type on which commercial production of conifer seedlings had to be abandoned as a failure. There are, however, a number of important theoretical and practical problems still to be solved before the new methods can be adopted generally. Conifer seedlings, especially of Sitka spruce, have proved very sensitive to a large variety of nutritional and other soil factors. They can be grown successfully in plots of one square yard, or even less, and it thus becomes possible to test on inherently poor soils many points beyond the present range of field experimentation on agricultural and horticultural crops. "Partial sterilization" by steam and formalin has given outstanding successes in the older nurseries, and a clear analysis of its mechanism may reveal factors of general interest in soil fertility studies.

The application of formalin at the rate of 250 ml. per square yard, suitably diluted, a month, or even several months, before sowing, consistently improved growth in all experiments on neutral or moderately acid soils which had been used as nurseries for many years. There have also been benefits in some experiments in newer nurseries with very acid soils. Good results have been obtained from the solid polymer, paraformaldehyde, but the best conditions for this material may not have been found, since it has occasionally proved less effective than formalin. Attempts are to be made in 1952 to inject neat formalin, as a step towards possible mechanical application. Apart from steam, acidification and repeated top-dressings of ammonium sulphate, no other treatment has given improvements at all approaching those from formalin. A variety of fungicides and the heavy urea treatment used successfully in the south-east United States for tobacco seed-beds have failed for conifer seed-beds in our experiments. The effects of formalin are difficult to analyse because profound changes are brought about in the soil flora and fauna. Formalin destroys most of the common soil fungi, checks nitrification and alters numbers of many kinds of micro-organisms for long periods. In some experiments formalin has reduced the numbers of plants destroyed by cockchafer and, in observations by B. Goodey of the Nematology Department, reduced the numbers of eelworms on or around the roots of Sitka spruce. Steam and formalin treatment still show some residual effect in a second Sitka spruce crop, sown in the following year. Drastic soil acidification may have more prolonged residual benefits, though there is a risk of damage in the year of treatment. In an experiment continued for three years at Ampthill Nursery, Bedfordshire, the



benefits from steam and formalin treatments given in February 1949 were outstanding in the first and second crops but had disappeared in the third crop; treatment with dilute sulphuric acid destroyed the crop in the 1949 drought but showed good effects in 1950 and still gave some improvement in the poor crop of 1951.

*One-year seedlings of Sitka Spruce*

		Mean height in inches		
		1949	1950	1951
Untreated .. ..	..	1.1	1.3	0.9
Steam .. ..	..	2.5	1.7	0.7
Formalin .. ..	..	2.1	1.8	0.8
Steam + formalin ..	..	2.6	2.0	0.8
Acid .. ..	..	failed	2.0	1.0
Steam + acid ..	..	failed	2.8	1.1
Standard error		$\pm 0.13$	$\pm 0.11$	$\pm 0.04$

Some of the chemical results of the microbiological changes induced by steam and formalin applied early in March 1950 in an adjoining experiment at Ampthill Nursery are shown by the following data for the averages of soil samples taken on six occasions from April 4th to July 31st 1950. The soils were analysed soon after sampling and again after incubation for fourteen days at 25°.

	Nitrogen in parts per million dry soil				CO <sub>2</sub> production	One year Sitka spruce seedlings
	Field soils		Incubated soils		in parts per million soil	Mean height in inches
	as NH <sub>3</sub>	as NO <sub>3</sub>	as NH <sub>3</sub>	as NO <sub>3</sub>		
No treatment	4	7	2	17	186	1.8
Formalin ..	8	6	11	11	250	2.9
Steam ..	15	10	20	11	260	2.8
Both ..	14	6	16	7	252	3.0
Standard error						+0.11

"Partial sterilization" increased the ammonia contents of the field soils and the carbon dioxide production on incubation. After incubation the treated soils had much more ammonia and less nitrate than the untreated ones. Many of the effects observed in several nurseries and seasons could be explained on the assumption that Sitka spruce seedlings grow better with ammonia than with nitrate. Repeated top-dressings of ammonia sulphate have given much better results on Sitka spruce seedlings than equivalent dressings of "Nitro-chalk" in several old forest nurseries. On the light soils commonly used for forest nurseries the pH values can be appreciably reduced in this way, at least for some months. It is possible that continued use of ammonium sulphate, together with the other fertilizers needed, may restore some "worn-out" soils to productivity. By contrast, it may be necessary on light soils used for agricultural and horticultural crops to pay careful attention to the acidifying effects of the large quantities of ammonium sulphate now being used, especially in compound fertilizers.

Some of the older forest nurseries have revealed an irregularity which might sometimes be overlooked in agricultural soils. There may be enough fragments of calcium carbonate to give abundant effervescence with acid in a field test, and yet the pH values, as measured by indicators or the glass electrode, may be as low as 5.5.



Agricultural and horticultural methods permitting a wide choice of cultivated crops normally maintain fairly high pH values and thus favour the rapid conversion of ammonia to nitrate. It has been suspected for several years that the failure of similar methods in forest nurseries was associated in part with the undue use of liming materials and calcareous manures or seed-covers. In experiments at several nurseries on very acid soils the growth of Sitka spruce seedlings has been seriously reduced by treatments with ground limestone or calcareous seed-covers, and at several other nurseries, which had been overlimed, growth was improved by acidifying the soil. At one nursery both kinds of change were effected experimentally within a single experiment.

Although on acid soils fertilizers have generally given as big or bigger seedlings than composts, the plants treated with fertilizer have sometimes shown discolourations suggesting some deficiency or other nutritional disturbance. Discoloration of the tips of the youngest needles following nitrogen top dressings in midsummer have recently been identified as a symptom of potassium-deficiency. A yellow discoloration and hardening of the upper needles late in the season, on plots with phosphate and potassium with late supplies of ammonia has been identified as a symptom of magnesium deficiency and controlled by supplying either magnesium sulphate or dolomite in preparing the seed-beds. To indicate the sensitivity of Sitka spruce on light soils it may be mentioned that in one experiment in an old nursery on moderately acid light sand the application of high-calcium or dolomitic limestone at the rate of 15 cwt. per acre reduced growth; the dolomitic limestone controlled the yellow symptoms but the high calcium limestone did not.

The Forestry Commission has attached great importance to the use of composts and rotational green crops for maintaining soil fertility, especially in the new heathland nurseries, but from the current investigations there appears to be little justification for heavy expenditure on composts for forest nurseries. Thus, in seventeen out of twenty-three comparisons in 1950 fertilizers gave slightly larger plants than composts. No consistent difference has been found in the subsequent behaviour in forests of seedlings or transplants raised with compost and fertilizers respectively. In rotation experiments at two centres with results over three seasons there has, so far, been no consistent improvement by interrupting a series of continuous seed-beds for a season under green crops or leys. The technique of small plot experimentation in forest nurseries has now been developed to the point at which it has been found feasible to start in 1951 two new series of rotation experiments (with suitable precautions to prevent the spread of soil between plots) to measure the long-term effects of altering the organic matter contents of light soils subjected to intensive cultivation. If the experiments succeed, they should in time provide interesting soil samples for studying the effects of cultural conditions on soil organic matter.

#### SOIL INVESTIGATIONS

##### *Soil organic matter*

J. M. Bremner has extended his previous work on the chemical



nature of soil nitrogen by studying the acid-insoluble (i.e. humic) fractions of alkali and pyrophosphate extracts of soils previously examined without preliminary fractionation. Determinations by the highly specific ninhydrin method of the amounts of  $\alpha$ -amino nitrogen liberated by acid hydrolysis of these humic preparations have shown that at least one-third of humic nitrogen is in the form of protein. The amino-acid composition of this protein material has been studied by the paper chromatography technique and the following amino-acids identified: aspartic and glutamic acids, serine, threonine, hydroxyproline, proline, arginine, histidine, lysine, phenylalanine, leucine, isoleucine, alanine, valine, glycine, tyrosine,  $\beta$ -alanine,  $\alpha$ -amino-n-butyric acid and  $\delta$ -amino butyric acid. Two unidentified ninhydrin-reacting substances and the oxidation products of methionine and cystine (or cysteine) have also been detected.

In the course of this work it was found that 10-15 per cent of the nitrogen present in the humic fraction of soil extracts could be accounted for as amino-nitrogen by the Van Slyke nitrous acid method. Since it appeared unlikely that such a large proportion of the humic nitrogen of soil is in the form of free amino groups, the effect of nitrous acid on substances likely to be present in soil extracts was investigated. It was found that nitrogen is evolved when lignin is treated with nitrous acid under the conditions employed in the Van Slyke method of analysis and that the reaction between lignin and nitrous acid leads to a large increase in the nitrogen content of the lignin. For example, a sample of wood lignin, containing 0.11 per cent N, was found to contain 2.5 per cent nitrogen after treatment with nitrous acid. Only 30-40 per cent of the nitrogen fixed by lignin in the reaction with nitrous acid is removed by strong acid hydrolysis. Most of this hydrolysable nitrogen is in the form of ammonia.

In continuation of the work described in the 1950 Report an attempt was made to follow the alkaline decomposition of threonine, serine, cystine and cysteine quantitatively. Results obtained in duplicate experiments were found to be inconsistent although recovery of the products of decomposition was practically quantitative. It is concluded that these alkaline decompositions are catalyzed by material dissolved by the alkali from the glass reaction vessels.

Earlier work in conjunction with R. H. Kenten of the Biochemistry Department on the paper chromatography of amines was completed and prepared for publication. This work involved the determination of the  $R_F$  values of a large number of amines in various solvents. Ninhydrin was found to be an effective spray for the detection of primary aliphatic amines on paper chromatograms. The results obtained suggested that amines likely to be present in biological materials could be separated and identified by paper chromatography.

#### *Soil phosphorus*

J. B. Rickson used the radiotracer technique to follow the exchange of phosphate ions between solution and solid in aqueous suspensions of calcium phosphates. It was possible to distinguish



between two kinds of exchange. A rapid one, generally complete in a few hours, probably represents an exchange on the surfaces of the particles; a much slower one may be due to pseudo-diffusion or recrystallization within the solid. Dicalcium phosphate showed only the rapid process, the total amount of exchange being equivalent to about 2 per cent of the total phosphorus present. Laboratory preparations of more basic calcium phosphates showed much higher rapid exchange and considerable slow exchange. The extent of both processes was reduced as the preparations were aged. Of the three rock phosphates, Curacao, Naura and Florida, the rapid exchange was least for the Curacao phosphate and the slow exchange greatest for the Florida phosphates. In similar experiments with North African phosphates it was necessary to add a little ammonium sulphate to obtain measureable amounts of water-soluble phosphate. Under these conditions the total exchange was appreciable and the first surface exchange continued for a much longer period with the Gafsa phosphate than with the other materials tested.

#### ANALYTICAL

##### *Exhaustion land, Hoosfield*

An account was given in the Rothamsted Report for 1949 of the history of plots which showed striking residual benefits in that season from farmyard manure or superphosphate applied in annual dressings for many years up to 1901, with none subsequently. The yields and total phosphoric acid contents of the 1949 barley crop were given in the Rothamsted Report for 1950 (p. 43). As 1949 was a drought year, it was possible that some of the striking long-term residual effects in that year might have been due to a stimulus to early root development from quite small additional supplies of available phosphate at a critical period. The 1950 season presented a marked contrast in weather, being much wetter. Comparable crop data for 1950 are given below.

Plots	Manuring to 1901	1950 Barley crop (cwt. per acre)		
		Dry matter Grain	Straw	P <sub>2</sub> O <sub>5</sub> in total crop
1, 2	None .. ..	11.0	15.2	0.104
5, 6	Nitrogen only .. ..	11.4	13.6	0.098
7, 8, 9, 10	Superphosphate .. ..	20.9	22.4	0.206
3, 4	Farmyard manure .. ..	22.2	24.0	0.243

In the wetter season the plots without residues from superphosphate or farmyard manure yielded better than in the dry season, but in both seasons the crops on plots with residues from superphosphate or farmyard manure contained about 0.1 cwt. P<sub>2</sub>O<sub>5</sub> per acre more than the crops on plots without these residues. The manurial residues trebled the total phosphorus content of the crop in the dry year and doubled it in the wet one. The results for the two seasons show that a small fraction of the phosphorus in fertilizers and farmyard manure may remain available to crops over very long periods and that the aggregate recovery of phosphorus over long terms may be much higher than is commonly assumed from experiments over one or two seasons.



Figures given in the Report for 1950 showed that one of the plots (7-1) in the Hoos Permanent Barley experiment still contained appreciable residues of organic nitrogen from annual applications of farmyard manure from 1852 to 1871, with none since. Data are given below for citric-soluble phosphoric acid and potash from a detailed examination by R. G. Warren of soil samples taken in 1946 from all plots in this experiment.

### Hoosfield Permanent Barley Plots

Annual Manuring  
since 1852

Series C	Rape cake
AAS	Sodium nitrate and sodium silicate
AA	Sodium nitrate
A	Ammonium sulphate
O	No nitrogen

Strip 1	None
2	P as superphosphate
3	KNaMg as sulphates
4	PKNaMg

Series	Strip	citric-soluble $P_2O_5$ mg. per 100g. soil				citric-soluble $K_2O$ mg. per 100g. soil			
		4	3	2	1	4	3	2	1
C .. .. .		PK	K	P	O	PK	K	P	O
AAS .. .. .		76	10	96	12	30	31	5	6
AA .. .. .		78	7	103	8	32	33	3	4
A .. .. .		65	6	91	6	31	31	3	6
O .. .. .		61	3	92	5	26	31	3	4
O .. .. .		86	5	98	5	32	34	4	5

Additional plots

		citric-soluble mg. per 100g. soil	
		$P_2O_5$	$K_2O$
6-1	Unmanured .. .. .	5	5
6-2	Coal ash .. .. .	7	6
7-1	Farmyard manure 1952-1871, then unmanured	10	8
7-2	Farmyard manure annually .. .. .	122	49

Plot 7-1 with farmyard manure for 20 years and then unmanured for 75 years showed appreciably higher citric-soluble phosphorus and potassium than the adjoining plot (6-1) unmanured throughout the whole period. The plot with 14 tons farmyard manure per acre annually had more citric-soluble P and K than the plots receiving inorganic fertilizers only. The addition of sodium silicate slightly increased yields and phosphorus uptake in the absence of added phosphate; it also increased the citric-soluble phosphorus in the soil on plots with added superphosphate as well as on plots without superphosphate. Some of the low values for citric-soluble phosphorus and potassium on Strip 4 may depend on the fact that from the commencement of the experiment this Strip had less calcium carbonate than Strips 1 to 3 and some of the plots in Strip 4 are now acid.

### GENERAL

During 1951 J. B. Rickson, E. H. Cooke and A. H. Green resigned their posts and G. E. G. Mattingly, O. Talib-udeen and K. Shaw were appointed. J. B. Rickson took up a post in the fertilizer industry and A. H. Green one on plantations in the Solomon Islands. G. E. G. Mattingly will work on radiotracer methods, O. Talib-udeen,



who transferred from the Pedology Department, on physico-chemical problems of soil and fertilizer phosphates and K. Shaw on the nitrogen availability of soil organic matter and organic manure. A. C. Venn, who worked in the department for a year as a Colonial Office Scholar, was appointed to the South African High Commission Territories to initiate soil fertility investigations, starting in Basutoland. J. K. R. Gasser, another Colonial Office Scholar, spent a year in the Department. M. V. Jackson of the National Agricultural Advisory Service was seconded to the Department for two years to gain experience in field experiments. C. P. Kirkland of the Forestry Commission was seconded to assist in the forest nursery experiments.

In the spring of 1951 E. M. Crowther made an eleven week tour of the eastern half of the United States with an E.C.A. grant to study soil fertility and fertilizer investigations. He held the posts of President of the Agriculture Section of the British Association for 1951, President of the British Society of Soil Science for 1951 and 1952 and President of the Fertilizer Society for the 1951-52 session. He was also appointed Chairman of the Scientific Sub-Committee of the Standing Advisory Committee under the Fertilizers and Feeding Stuffs Act 1926, and Chairman of the Soils Sub-Committee of the Committee for Colonial Agricultural, Animal Health and Forestry Research.