Report for 1961

[Full Table of Content](#)

Chemistry Department

G. W. Cooke

CHEMISTRY DEPARTMENT

G. W. Cooke

F. J. Seabrook completed fifty years of service to Rothamsted in May 1961. We were delighted that he was awarded the British Empire Medal in the Queen's Birthday Honours List.

M. St. J. Foale left at the end of the year. In June P. W. Arnold and G. W. Cooke visited research institutes, experimental farms and a potash-producing mine in Germany as guests of Ver-kaufsgemeinschaft Deutscher Kaliwerke G.m.b.H. Several members of the Department attended a very successful conference of the British Society of Soil Science in Dublin in September. Cooke visited research institutes and fertiliser-producing plants during a meeting of the Fertiliser Society in Holland in March. During a private visit to Israel, B. Benzian was a guest of Dead Sea Works Ltd. for a few days and visited research institutes and forest nurseries.

The following worked in the Department during the year: Dr. N. J. Barrow (Australia), Dr. A. Karim (Pakistan), Mr. Y. C. Lin (Hong Kong), Mr. S. Oliver (Spain), Mr. R. C. Salmon (Rhodesia), Mrs. Branka Savic (Yugoslavia), Dr. R. E. Shapiro (U.S.A.), Dr. L. V. Vaidyanathan (India), Mr. L. Verini (Italy), Dr. J. M. Walker (U.S.A.) and Dr. Y. Yamada (Japan). Vaidyanathan obtained the Ph.D. Degree of London University.

Organic Manures and Soil Organic Matter

Farmyard manure

In our programme of work intended to show how farmyard manure (FYM) affects crops, an experiment at Woburn compared 7·5 and 15 tons/acre of FYM (supplying 150 and 300 lb. K_2O/acre) for sugar beet with three NK fertilisers supplying the same amounts of K_2O. The $N : K_2O$ ratios of the fertilisers tested were $2 : 10$, $3 : 10$ and $4 : 10$, providing from 30 to 120 lb. N/acre. Sodium chloride supplying as much Na as 15 tons/acre of FYM was also tested; superphosphate (1·5 cwt. P_2O_5/acre) and magnesium sulphate (50 lb. Mg/acre) were given to all plots. Such high concentrations of fertiliser salts applied to the seedbed harmed germination in 1960, so all fertilisers were dug in in late March in 1961.

There were good increases in yield from FYM and from NK fertilisers, but no extra increase from applying sodium as well. Yields of roots and sugar from FYM treatments were close to those from the fertiliser with $N : K_2O$ ratio of $4 : 10$; 15 tons/acre of FYM gave 70 cwt./acre of sugar and the fertiliser gave 69 cwt. Although these yields were about 40% greater than the yields from plots receiving no N or K, the response curves with the $4 : 10$ ratio fertiliser, and with FYM, did not reach a maximum. In contrast, the other two fertilisers with $N : K_2O$ ratios of $2 : 10$ and $3 : 10$ gave only small increases for the extra nutrients supplied by the double

rate, although at the single rate they were as good as the single rates of both FYM and of fertiliser with $N : K_2O$ ratio $4 : 10$.

Yields of tops behaved differently and were directly proportional to the amounts of N supplied by the fertilisers; the $4 : 10$ ratio fertiliser was best; it supplied 120 lb. N/acre at the high rate and gave 7 tons/acre of extra tops. The tops response curve with FYM was also linear and was almost identical with the curve for the $2 : 10$ ratio fertiliser, but not with the $4 : 10$ ratio fertiliser.

Yields of roots and sugar with FYM were equalled by using $4 : 10$ ratio NK fertiliser, but this fertiliser gave 4 tons/acre more tops. Lowering the amount of fertiliser-N to decrease top growth, while maintaining the same level of K as was supplied by FYM, also lowered the yields of roots and sugar. We have no explanation for these differences between FYM and fertilisers; the sodium supplied by the FYM was not the cause, and it is unlikely that magnesium was a factor, because a basal dressing was given. (Warren and Johnston.)

Liquid manures

Some modern methods of keeping stock indoors continuously produce large volumes of liquid manure. As it may become illegal in some places to run these effluents into sewers or streams, their value as manures applied direct to land is being considered. Several samples of liquids resulting from intensive pig-keeping were analysed; two extreme results were:

				Sample 1	Sample 2
				(% (w/v))	
Total solids	...	...	...	4·1	7·5
N *	...	...	...	0·3	0·9
P_2O_5	...	...	...	0·2	0·7
K_2O	...	...	...	0·1	0·7

* Of the total N, more than two-thirds was ammonium.

Both liquids were valuable sources of N, P and K; 1,000 gallons of sample 2 supplied about 90 lb. of N, 70 lb. of P_2O_5 and 70 lb. of K_2O. Where large volumes of such effluents are produced, they are important sources of plant nutrients, and they should be used efficiently. More research may be needed on the best ways of conserving the N, P and K, and of applying the liquids. (Williams and Cooke.)

Decomposition of labelled plant material in soil

The experiments started in April 1959 (*Rep. Rothamst. exp. Sta.* for 1960, p. 43) continued with two soils from Broadbalk, viz. Plot 2B, which receives FYM each year and contains 2·4% carbon, and Plot 3, which receives no FYM or fertilisers and contains only 1·0% C. After one year in the field about a third of the added plant carbon remained in soil, and after two years about a quarter; losses were the same in both soils. Similar amounts of plant carbon were lost under " natural " conditions in the field as in laboratory incubations at 25°. Very long incubation periods will be needed to measure rates of turnover of the inert fractions of soil organic matter accurately.

The distribution of newly-added labelled plant material throughout the soil organic matter, after it has decomposed for a year in the field, is being examined by both chemical and biological methods. Several of the chemical methods partially differentiated between new and old organic matter. The most striking effect was with cold 0·1N-HCl, which dissolved less than 1% of the total organic carbon of the soil, but one-tenth of this was derived from the added labelled plant carbon. Some separation of the new organic matter was obtained by treatments involving 6N-HCl, cold anhydrous formic acid and 2·5% H_2O_2. The humic acid fraction isolated from an alkaline extract had a smaller percentage of labelled carbon than the fulvic acid fraction.

Biological fractionation was done by measuring the labelled and unlabelled CO_2 evolved from soils incubated for 10 days at 25° after they had been pretreated in various ways. The percentage of labelled CO_2 evolved from soil from Plot 2B was six times as much as in the soil organic matter as a whole; for soil from Plot 3 the CO_2 evolved was four times as rich in labelled C as the soil organic matter. Oven-drying the moist soil, or exposing it to chloroform vapour, increased both the total CO_2 evolved, and also the percentage of labelled C in the CO_2. When the soil was oven-dried at 80° before incubation, more CO_2 was evolved than with any of the other pretreatments, although the percentage of labelled carbon in the CO_2 evolved was slightly less than after pretreatment with chloroform. Five successive oven dryings and incubations removed about 5% of the total amount of organic carbon in soil from Plot 2B, and this contained one-quarter of all the labelled carbon; 7% of all the carbon in soil from Plot 3 was lost by the same treatment, and this also contained one-quarter of all the labelled carbon present. The amounts of labelled carbon evolved fell off much more rapidly with successive incubations than the amounts of unlabelled carbon. When these experiments were repeated after the soils had spent a further year in the field the labelled carbon evolved on incubating the undried soil at the end of the second year fell to roughly half the corresponding value for one year. The labelled carbon evolved after oven drying was two-thirds the value obtained after one year in the field.

When added plant material is " incubated " with soil in field conditions about two-thirds of the carbon is lost in the first three months; afterwards decomposition is much slower. A considerable proportion of the labelled carbon remains in forms that are more soluble in some reagents than the bulk of the soil organic matter, and is also decomposed preferentially in laboratory incubations. The microbial population is largely killed by partial " sterilisation " (heat, chloroform, radiation); when the soil is incubated after sterilising, a new microbial population builds up using the killed section of the first population as a substrate. But mineralisation of microbial carbon after the death of the organisms cannot be the only process liberating CO_2 after the soils are oven dried, otherwise the *percentage* of labelled carbon in the CO_2 evolved in successive incubations would be constant. Probably some of the unlabelled organic matter in the soil becomes less resistant on oven drying, is incorporated in microbial tissue during incubation and is released

later when the organisms decompose. On this basis about 2% of all the carbon of Plot 3 soil is in the " biomass " (organic matter in living organisms). About one-quarter of the labelled carbon remaining after one year in the field is in the biomass; this is equivalent to about one-tenth of the labelled plant carbon originally added. If all the parts of the biomass in the soil decompose at the same rate, its half-life is 2–3 years, to be compared with a half-life for soil organic matter as a whole perhaps ten times longer. (Jenkinson.)

Carbon monoxide evolved from soil

A mixture of CO_2 and CO was evolved from soil refluxed with 6N-HCl; Broadbalk Plot 2B soil evolved 8% of its organic carbon as CO_2 and 0·4% as CO during 3 hours refluxing. The carbon monoxide may be produced when α-hydroxy, or α-keto acids present in soil organic matter decompose. (Jenkinson.)

FIELD AND LABORATORY EXPERIMENTS WITH FERTILISERS

Alternative nitrogen fertilisers for spring barley

Four experiments on Chalk soils and one at Rothamsted compared urea and calcium nitrate with ammonium sulphate for barley. When the fertilisers were broadcast on the seedbed, urea and ammonium sulphate gave similar yields, but calcium nitrate gave more. When combine-drilled with the seed, ammonium sulphate was best, probably because it damaged early growth least. At centres where the barley was sown late in dry weather all fertilisers checked growth considerably and lowered yields; urea killed some of the plants and lowered yield most. The check to growth was less when the fertilisers were placed 1 inch to the side of the seed; gains from side-placement were greatest with urea and least with ammonium sulphate. With crops sown early in moist soil, combine-drilling gave better early growth and often better yields at harvest than side-placing. With crops sown later in dry weather, side-placement lessened early damage and gave better yields than did combine-drilling.

Side-placement requires a special drill or modifying an existing

TABLE 1

Average yields of barley given by three forms of nitrogen fertilisers in five experiments in 1961

(cwt. of grain/acre at 15% moisture content)

Yield without nitrogen, 20·8

	Ammonium sulphate	Calcium nitrate	Urea
0·35 cwt. N/acre			
Broadcast	26·9	27·9	26·6
Combine-drilled	28·3	27·9	26·8
Side-placed	28·8	27·5	28·4
0·70 cwt. N/acre			
Broadcast	30·1	33·0	30·9
Combine-drilled	30·3	31·1	29·6
Side-placed	30·3	32·0	33·1

combine-drill. The average gains from side-placement over combine-drilling, or seedbed broadcasting, were not enough to justify the extra cost of the special drill when either ammonium sulphate or calcium nitrate was used. But the experiments suggested that urea gives maximum yields of barley safely only when side-placed; the average gain from side-placement, about 2 cwt. grain/acre, would quickly pay for the extra equipment. However, most barley receives either ammonium or nitrate salts, so at present, side-placement is unlikely to have much general application. (Widdowson and Penny.)

Plant counts and samples were taken from the Rothamsted experiment 5 weeks after sowing. Urea was the only fertiliser that decreased plant numbers by more than 10% of the numbers growing on plots without N fertiliser; there was no damage with broadcast urea, serious damage with combine-drilled urea and some damage, though less serious, with side-placed urea. 0·7 cwt. N/acre as urea caused more damage than the half dressing. Samples taken 5 weeks after sowing were heavier with ammonium sulphate, however applied, than where no N had been given. At this stage calcium nitrate gave a smaller " yield " than ammonium sulphate for each method of application, and where the nitrate was combine-drilled, " yields " were 20% less than with no N. Urea also gave smaller plants than ammonium sulphate, was particularly damaging when combine-drilled and the dry matter produced was only half of that on plots without N fertiliser. (Gasser.)

Losses of ammonia from urea and from ammonium sulphate

In laboratory experiments urea and ammonium sulphate were either broadcast on the soil surface or mixed with a layer of soil 3 cm. deep, at rates equivalent to 100 lb. N/acre. One soil was a flinty loam containing 25% $CaCO_3$, the other had 75% $CaCO_3$. About 10% of the added nitrogen was lost to air drawn over the soil when the fertilisers were spread on the surface, about 5% was lost when they were mixed with the top-soil. With surface broadcasting losses were greater from ammonium sulphate, but after mixing the fertilisers with soil, more ammonia was lost from urea. On average nearly twice as much ammonia was lost from the very calcareous soil as was lost from the flinty loam. Increasing the temperature of the experiment from 5° to 25° slowed the rate of loss from the highly calcareous soil slightly, but doubled the loss from the flinty soil.

Other laboratory experiments measured losses of ammonia from urea supplied in different physical forms to different soils. Whether applied as pellets, crystals or solutions mattered little, but soil type was more important; the least loss (2% of the N added) was from a flinty loam, and the most (9%) was from a poor sandy soil. (Gasser.)

Effects of urea on germination

The damage to germination by urea, often shown in the field, was studied in pots under glass, and in the open using bottomless boxes filled with a range of soils. Germination of kale in pots was

slightly decreased by increasing rates of urea, but damage was not serious, even when urea equivalent to 300 lb. N/acre was applied. When harvested 18 days after sowing, 100 lb. N/acre gave maximum yields. Germination of wheat and barley in the boxes was irregular because of bad weather at sowing time in the first experiment sown in February. In the second, sown in April, germination was affected much more by the moisture contents imposed on the soils when the experiment was started than by the presence of urea. A third experiment was sown in June; high rates of urea decreased numbers, heights and weights of the plants, but the amount of damage again differed with different soils and with their moisture contents.

Damage by urea is thought to be caused by the ammonium carbonate and bicarbonate formed when the fertiliser decomposes in soil. These compounds may be dangerous because of high pH and/or free ammonia in the soil solution near to the fertiliser particles. Laboratory tests on the germination of kale, barley and wheat in presence of solutions of ammonium and potassium carbonates and bicarbonates showed that high concentrations (100–200 m.e./litre) of all these salts lowered germination; at the lower concentrations the ammonium salts caused most damage. Kale was damaged more than barley, and barley more than wheat. In the range of concentrations causing severe damage ammonium carbonate caused more than the bicarbonate. (Gasser.)

Tests of a concentrated fertiliser and of forms of nitrogen

An experiment at Rothamsted compared a concentrated fertiliser containing 20% N, 10% P_2O_5 and 10% K_2O with a mixture of ammonium sulphate, superphosphate and muriate of potash for kale, Italian ryegrass and barley, at rates supplying 1·0 and 2·0 cwt. N/acre for grass and kale, and 0·3 and 0·6 cwt. N/acre for barley. Differences between fertilisers were small; for barley and grass 20 : 10 : 10 was best, but for kale the mixture gave higher yields. The experiment also compared ammonium sulphate with ammonium nitrate, calcium nitrate and urea on the same crops and at the same rates of N. The high rate of ammonium sulphate and of urea checked establishment of Italian ryegrass, whereas 20 : 10 : 10 did not; ammonium nitrate and calcium nitrate checked growth only slightly. With kale the double doses of ammonium sulphate and calcium nitrate checked growth, whereas 20 : 10 : 10 did not; urea and ammonium nitrate checked growth slightly. With the single rate of N no crop was damaged. Calcium nitrate was best for kale at each level of manuring; for grass urea was worse than the other N fertilisers at each of two cuttings; all N fertilisers gave similar yields of barley. (Widdowson and Penny.)

Side-placement of concentrated fertiliser for barley

Three experiments compared broadcasting, combine-drilling and side-placing of a concentrated compound fertiliser containing 17% N, 11% P_2O_5 and 22% K_2O, at the rates needed to supply 0·3, 0·6 and 0·9 cwt. N/acre. The 1961 spring was dry, and combine-drilling checked growth considerably at two March-sown centres; placement checked growth less. At a February-sown centre combine-drilling

gave better growth. Placing the fertiliser 1 inch to the side of the seed gave more grain than did broadcasting; combine-drilling gave less grain than broadcasting with 0·6 cwt. N/acre at one centre and with 0·9 cwt. at two. (Widdowson and Penny.)

Methods of applying superphosphate for barley

The combine-drill modified for side-placement work with N fertilisers was used to test on barley different methods of applying 0·3, 0·6 and 0·9 cwt. P_2O_5/acre as superphosphate. Responses to P were small and 0·3 cwt. P_2O_5/acre was enough for full yields. Average yields at the three centres are stated below. Broadcasting the superphosphate either over the whole seedbed or in a restricted band immediately over the seed gave less grain than drilling the dressing. Side-placing gave slightly more barley than combine-drilling. (Widdowson and Penny.)

Yields of barley (cwt./acre)

Without phosphate	34·0
With broadcast super—	
over whole seedbed	36·7
in restricted band	37·2
With drilled super—	
combine-drilled	37·7
side-placed	38·2

Comparisons of solid fertilisers with solutions

A liquid N fertiliser (believed to be made mainly from urea) containing 20% N was compared with equivalent solid urea on Italian ryegrass. Both fertilisers were applied at several rates (the maximum 1·0 cwt. N/acre/cut) to grass 6–8 inches high. At 0·8 or 1·0 cwt. N/acre/cut, the liquid fertiliser scorched the grass, whereas solid urea did not. At each of three cuttings the solid fertiliser gave slightly more grass than the solution. The total gain from using the solid was not great; it was least (0·2 cwt. of dry matter/acre) with 0·2 cwt. N/acre/cut, and most (5·7 cwt. of dry matter) with 0·4 cwt. N/acre/cut.

A compound fertiliser in solution containing 14% N, 6% P_2O_5 and 8% K_2O was compared on kale with an equivalent mixture made from solid urea, superphosphate and muriate of potash. Both fertilisers were tested at 1·0 and 2·0 cwt. N/acre, and they were applied either to the seedbed before sowing or in mid-June over the crop, which then covered the ground completely. Solid fertiliser gave more kale than the solution in three of four comparisons; late dressings were better than seedbed dressings. There was no serious scorching. (Widdowson and Penny.)

Another experiment on Italian ryegrass compared ammonium sulphate, ammonium nitrate and sodium nitrate applied as solids and as solutions containing 5% N. All fertilisers gave significantly higher yields, and the grass took up significantly more N, when they were used as solids. This confirms earlier work (*Rep. Rothamst. exp. Sta.* for 1958, p. 47), and although the gains from using solid N fertilisers have been small, they have been consistent. (Nowakowski and Penny.)

Nitrogen and potassium fertilisers for Italian ryegrass

An experiment was started at Rothamsted in 1958 to measure the K fertiliser needed by grass manured with increasing levels of N. Yields from grass grown without NK fertiliser were compared with yields from 0·3, 0·6 and 0·9 cwt. N/acre/cut (as " Nitro-Chalk ''); tests were made of 0·0, 0·3 and 0·6 cwt. K_2O/acre/cut (as muriate of potash). Responses to superphosphate were measured only with heavy dressings of NK fertilisers. Table 2 summarises results over 4 years. Nitrogen gave large and consistent increases in yield when 0·3 or 0·6 cwt. N/acre/cut was used, but the extra N supplied by 0·9 cwt. N/acre/cut produced much less extra grass, and was probably not worth-while. Potassium had little effect on yield in 1958 and 1959. In spring 1960 the site was ploughed and resown, K dressings increased yields significantly at the first cutting, but later K had little effect. There were similar and very small increases in yield over the 4 years from both P and K fertilisers. Although K had little effect on yield, it greatly increased the percentage of K in the grass. Without K fertiliser the level of acid-soluble K in the surface soil fell seriously where N was applied; K levels in soil were maintained by using 0·3 cwt. K_2O/acre/cut and were increased by giving 0·6 cwt. K_2O/acre/cut, even though the grass took up much more K than was supplied by the fertiliser.

TABLE 2

Results of an experiment with N and K fertilisers on Italian ryegrass at Rothamsted, 1958–61

Treatments (all dressings are per acre for one cut)	Total yield of dry grass in 1958–1961 (cwt./acre)	Total uptake of K by grass in 1958–1961 (cwt./acre)	Acid-soluble K in surface soil in August 1961 (mg. K/100 g.)
Without N or K fertiliser ...	99	2·9	8·0
0·3 cwt. N plus:			
No K	227	6·2	5·2
0·3 cwt. K_2O ...	227	7·1	8·6
0·6 cwt. K_2O ...	229	7·3	18·0
0·6 cwt. N plus:			
No K	290	7·7	5·1
0·3 cwt. K_2O ...	297	9·0	7·9
0·6 cwt. K_2O ...	303	9·8	12·2
0·9 cwt. N plus:			
No K	312	8·1	4·6
0·3 cwt. K_2O ...	315	9·4	7·6
0·6 cwt. K_2O ...	324	10·8	13·5

The surprising feature of this experiment was that the soil could supply so much potassium over the four years, for the average withdrawal was about 2 cwt. K/acre/year with the heavier rates of N manuring. There was no indication that the rate of release of K fell off in the later years, although acid-soluble K in the soil became very low (Table 2). The small response to K dressings where heavy nitrogen was used (about 12 cwt./acre of dry matter in the four years) was not enough to pay for the fertiliser. On this soil no K manuring was needed to obtain full benefit from heavy N dressings, but this involved depleting soil K reserves. If the aim is to maintain soil K

D

status, the analyses in Table 2 show that 0·3 cwt. K_2O/acre/cut is enough even when the grass receives 0·6 or 0·9 cwt. N/acre for each cut.   (Widdowson, Penny and Williams.)

The effect of previous cropping with grass on yield of following wheat

Three levels of N fertiliser were tested on pure swards of cocksfoot, meadow fescue, perennial ryegrass and timothy grown from 1958 to 1960; the produce was cut and removed and the results were summarised in last year's Report.   After ploughing the grasses, spring wheat was sown in 1961 to measure the residues of the N fertilisers given and also the effects of fresh N and K fertilisers. Potassium had little effect on yield of wheat, even on plots where the grass had received 0·6 cwt. N/acre/cut and where the surface soil contained little K soluble in dilute acid.   Wheat grown after grass dressed with N yielded more than wheat after grass without N. After ryegrass and meadow fescue, the wheat yielded better than after cocksfoot or timothy.   (Widdowson and Penny.)

Grazed reference plots

A long-term experiment to test the effects of fertilisers on grazed grassland was started at Rothamsted in 1959 on an old parkland sward with little clover; the area had been limed, but the soil contained little soluble P or K.   Grazing by sheep and beef cattle was unrestricted.   Ammonium sulphate and calcium nitrate are compared, both applied in four equal dressings every second month through spring and summer; superphosphate and muriate of potash are applied as single winter dressings.   Fertilisers have changed the sward but only slowly.   Clover was suppressed by nitrogen (1·0 or 2·0 cwt. N/acre in the year), but grew freely when it was omitted.   In 1961 the annual total N dressings were increased to 1·5 and 3·0 cwt. N/acre, and dry matter production was estimated in each two-monthly period by using cages to protect the grass from grazing.   PK fertilisers increased yields, but when N was also used yields were nearly doubled; the higher rate of N gave no more grass than the lower rate.   Ammonium sulphate scorched the grass and checked growth; calcium nitrate did not.   Patches of grass died where 3·0 cwt. N/acre was applied as ammonium sulphate during the year.   Sampling in October 1961 showed that ammonium sulphate soon made the surface soil acid; with the high rate of N as ammonium sulphate the pH was 5·4, with calcium nitrate 7·3; plots that had received no N had unchanged pH values (6.7).   Lime will be applied in future where ammonium sulphate is given.   (Widdowson and Penny.)

Effects of nitrogen fertilisers on the forms of soluble nitrogen and soluble carbohydrates in grass

Italian ryegrass was grown in a field experiment testing ammonium sulphate and sodium nitrate each applied at 0·5 and 1·0 cwt. N/acre.   The fertilisers were applied to the established grass on 4 July, sampling began 10 days later and was repeated three times at 10-day intervals.   Table 3 gives results from the first and

last samplings. The amounts of water-soluble nitrogen fractions in the grass were similar to those measured previously (*Rep. Rothamst.*

TABLE 3

Soluble carbohydrates and soluble nitrogen in Italian ryegrass treated with N fertilisers

		Sampling		Sampling	
		First	Last	First	Last
		Fructosan		Total soluble carbohydrate	
	lb. N/acre	% in dry matter			
Without N	0	4·1	16·0	11·8	27·4
Sodium nitrate ...{	56	0·6	8·6	5·4	18·9
	112	1·2	5·9	8·9	15·4
Ammonium sulphate ...{	56	0·8	9·6	7·0	20·8
	112	0·6	5·5	7·2	16·4

		Ratio of			
		$\dfrac{\text{Fructosan}}{\text{Soluble-N}}$		$\dfrac{\text{Total soluble carbohydrate}}{\text{Soluble-N}}$	
Without N	0	14·5	93·3	42	159
Sodium nitrate ...{	56	0·5	20·7	4	46
	112	0·9	6·5	7	17
Ammonium sulphate ...{	56	0·9	44·2	8	96
	112	0·5	5·8	6	17

exp. Sta. for 1960, p. 54). The N fertilisers decreased the total amounts of water-soluble carbohydrates in the grass considerably, causing small changes in glucose, fructose and sucrose, but a very large decrease in fructosan. The ratios of fructosan : soluble N and of total soluble carbohydrates : soluble N were both decreased by increasing amounts of nitrogen fertiliser; the ratios were particularly narrow in the earlier stages of growth. These ratios may have some bearing on the nutritional value of grass and on the digestive disorders sometimes reported when ruminants eat grass dressed heavily with nitrogen; they may also be important in silage-making. (Nowakowski.)

SITKA SPRUCE ON ARABLE LAND AT WOBURN

Twenty-five square-yard plots sown with Sitka spruce were added to a series of " reference plots " on farm crops and soft fruit started on old arable land in Stackyard Field at Woburn in 1960 (*Rep. Rothamst. exp. Sta.* for 1960, p. 55). Seedlings on unmanured plots were only 0·3 inch high at the end of the season, but those with full inorganic manuring (NPK + Mg) averaged 1·3 inches. Phosphorus and, to a less degree, nitrogen were responsible for this large increase—P increased the size nearly four times and N increased it by a third. This spectacular response to P on conifer seedlings is of special interest on a site where the other agricultural and horticultural crops responded only little to P. Neither K nor Mg had any effect on the size of seedlings, though slight yellowing typical of Mg-deficiency developed on the " no Mg " plots late in the season. Formalin (a " partial sterilant ") added to plots with full inorganic manuring increased height by 60%; whatever its mode of action,

formalin cannot, on this land, have controlled a population of soil pathogens specific to conifers, which have not grown on this site for at least 100 years. (Benzian.)

NITROGEN IN SOILS

Fixed ammonium

Ammonium in soil that cannot be exchanged by KCl solution is said to be " fixed ". Fixation depends on the kinds of clay minerals present; vermiculite fixes NH_4 very strongly, most montmorillonites less strongly and illite is intermediate. Methods that are said to measure fixed NH_4 have been developed, but little is known of its physico-chemical properties. It is not known whether fixed NH_4 is truly non-exchangeable; should it be very slowly exchangeable, increasing fixed NH_4 could add to the reserves of slowly available N in soils. The exchange properties of fixed NH_4 are therefore being examined by using $^{15}NH_4$, which makes the measurements very sensitive.

Hydrobiotite (intermediate in composition and properties between biotite and vermiculite) fixed much NH_4 and was used in early experiments. The fixation and exchange capacities of the mineral were saturated by repeated treatment with N-NH_4Cl at 70°. The product was then shaken with $0.01M$-NH_4Cl, containing up to 30% of ^{15}N, for varying times; the NH_4 and ^{15}N in the solution, in the fraction exchangeable with KCl, and remaining in the mineral were then measured. Unexpectedly, only one-half to three-quarters of the NH_4 exchanged by KCl was exchangeable with labelled NH_4, and the reason is being investigated. The fraction of fixed NH_4 which exchanged was approximately proportional to the square root of the time of contact. This suggests that the process governing the rate of exchange is diffusion of NH_4^+ in the layers of the mineral and that the exchange of fixed NH_4 differs in degree, rather than in kind, from exchange of Ca^{++} or Mg^{++}, which are not much fixed. The work is now being continued with hydrobiotite from which potassium in the mineral structure has been removed by sodium tetraphenyl boron. (Oliver and Newman.)

Up to 80% of the potassium in micaceous minerals can be extracted by sodium tetraphenyl boron ($NaBPh_4$), which forms an insoluble compound with K. The hydrobiotite used here contained nearly 4% K; it was treated for a week with N-NaCl containing $NaBPh_4$ to see if NH_4-fixation capacity would increase when K was removed. The solid remaining, a mixture of mineral and $KBPh_4$, was saturated with N-NH_4Cl and the $KBPh_4$ dissolved away by washing with 70% aqueous acetone containing NH_4Cl, to prevent the dissolved K from the $KBPh_4$ re-entering the mineral lattice. In this way 98% of the K in the mineral was removed. The original hydrobiotite had 1·03 m.e. K/g., after extraction it had only 0·02 m.e. K/g.; but its capacity for fixing ammonium had increased from 0·59 to 1·29 m.e./g. The difference between the K extracted (1·01 m.e./g.) and the increase in fixed NH_4 (0·70 m.e./g.) was accounted for by Na^+ (0·35 m.e./g.), which was trapped as the lattice contracted on the NH_4^+. These results show that ammonium and potassium fixation are similar in character and mutually dependent. (Newman.)

Fixation of nitrogen by soils incubated with straw

Fixation of N was not detected when moist soil was incubated with straw, whether or not oxygen was present. However, when the soil was waterlogged fixation occurred (for example, 5 g. soil with 0·7 g. straw and 15 ml. of water fixed nearly 2 mg. of N in 56 days) provided air was present above the incubated mixture, but not when the air was replaced by nitrogen. Hence fixation depended on the incubation proceeding with a zone where oxygen was deficient but not absent. (Barrow and Jenkinson.)

PHOSPHATE IN SOILS

The effects of ammonium sulphate and sodium nitrate on solubility of soil phosphate

Twelve calcareous soils (with $\frac{1}{2}$–$3\frac{1}{2}\%$ $CaCO_3$) from the Rothamsted and Saxmundham Classical Experiments were used, five of which had received superphosphate every year for over 60 years and seven had never received phosphate fertilisers. In an experiment with ryegrass growing in pots differences between yields from equal amounts of N as ammonium sulphate and from sodium nitrate increased as the experiment continued, and $(NH_4)_2SO_4$ gave more grass. The poor soils that had never received P fertiliser gave better yields with $(NH_4)_2SO_4$ than with $NaNO_3$ from the beginning of the experiment, and at the end yields were twice those with $NaNO_3$. Grass grown on the five soils that had received superphosphate regularly did not respond to extra phosphate, and yields from the two forms of N were similar until the fourth cut, when $(NH_4)_2SO_4$ gave larger yields. These differences were because $(NH_4)_2SO_4$ released more phosphate than did $NaNO_3$ from calcareous soils, and they were much greater with Saxmundham Chalky-Boulder-Clays than with calcareous Clay-with-Flints from Rothamsted. After 20 weeks in the pot experiment, soils treated with $NaNO_3$ had unchanged $CaCO_3$ contents, but those treated with $(NH_4)_2SO_4$ had lost $0·8\%$ of their initial $CaCO_3$. To get such a loss of $CaCO_3$ in the field would require giving 2 cwt./acre of $(NH_4)_2SO_4$ every year for 80 years; similarly, this treatment would be needed to release from $CaCO_3$ particles the amount of P released in the greenhouse experiment, and in any one year the amount released by $(NH_4)_2SO_4$ to field crops would be trivial.

A further pot experiment used soils from a field experiment on Carboniferous Limestone done by Mr. R. D. Russell (National Agricultural Advisory Service). Where $(NH_4)_2SO_4$ had been given in the field experiment yields of grass, P uptakes and A values in the pot experiment were all significantly greater with soils that received 2 cwt./acre of $(NH_4)_2SO_4$ for 5 years in the field experiment than from soils receiving no N fertiliser. (Mattingly and Barbara Close.)

Laboratory measurements of isotopically exchangeable phosphorus (P_e) in the Rothamsted and Saxmundham soils used in these pot experiments, before and after cropping, showed that more P was removed by the grass receiving either form of nitrogen than was accounted for by the fall in P_e. The release of non-exchangeable P

from $CaCO_3$ particles dissolved by heavy doses of $(NH_4)_2SO_4$ (350 mg. of N/100 g. of soil in the course of the experiment) is to be expected, as most native calcium carbonates contain phosphorus, but the release of non-exchangeable P when $NaNO_3$ was given has no ready explanation. The dressing of sodium in the pot experiment (25 m.e. Na^+/100 g. soil) is much larger than would be supplied by normal fertiliser dressings for arable crops, and it is not certain that using $NaNO_3$ would affect P release in the field. (Mattingly and Talibudeen.)

Ion-exchange resins in soil phosphate studies

A mixture of anion- and cation-exchange resins saturated with chloride and sodium extracted only the rapidly exchanging component of the total isotopically exchangeable phosphorus from very acid soils (pH values of 3·6–4·6). The extraction was complete in 2 weeks. In less-acid soils (pH values 5·6–6·6) the resins removed some of the " slow " isotopically exchangeable P and the rapidly exchanging fraction was completely extracted in ½–1 day. In less-acid soils containing residues of P fertilisers, isotopically exchangeable phosphate was more labile and therefore easily removed by ion exchangers; only half of the total exchangeable P was removed by resins from the very acid soils, but 80% or more was extracted from less-acid soils. Total isotopically exchangeable P was well correlated with the P extracted by the resin mixture.

The resin extracted more calcium from less acid soils, though more slowly, than from the more acid soils. The aluminium extracted from all the soils increased exponentially with time. The total amount of Ca + Al extracted (in milli-equivalents) was only slightly greater in the near-neutral soils than in the very acid soils, suggesting that the two metals together occupied the greater part of the total base-exchange capacity of the soils. Higher exchangeable Al in the more acid soils was associated with lower mobility of isotopically exchangeable P. There was no stoicheometric relationship between either the total P extracted or its rapidly and slowly extracted components, and the Fe and Al removed by cation-exchange resin; this suggests that the resin mixture cannot distinguish between phosphates of stoicheometric compositions and the other sources of Fe and Al that may be present.

The processes that control the speed at which resins extract phosphate may involve the movement of ions from the inside of a soil particle to its surface, and then across the thin layer of liquid that is the diffuse electrical double layer surrounding the particle. Graphical analyses show that several first-order reactions probably occur simultaneously. With soils above pH 5 a single " bulk " diffusion process accounted adequately for *all* the data, and in more acid soils this process accounted for most of the extracted phosphate. (Vaidyanathan and Talibudeen.)

The processes of isotopic exchange in acid soils

Soils supplied by Mr. J. W. Blood from an experiment at N.A.A.S. Headquarters, at Shardlow, Derbyshire, where fertilisers and levels of acidity are tested, show that residues of phosphate fertilisers re-

maining in soil are more mobile at higher pH's. On soils of pH 3·6–5·6 only about one-half or two-thirds of the total isotopically exchangeable P is rapidly exchangeable. While the rapidly exchanging fraction is being removed, a single first-order reaction equation fits the data, suggesting that " film " diffusion through the electrical double layer controls the rate. Afterwards diffusion of phosphate from *inside* the soil particles governs the speed at which exchangeable P is liberated. (Talibudeen and Vaidyanathan.)

Phosphorus soluble in 0·01M-$CaCl_2$ solution in equilibrium with soils

There are good theoretical reasons for using the concentrations of P in 0·1M-$CaCl_2$ solutions in equilibrium with soils as measures of P that is immediately useful to crops. Some factors that may affect the concentrations were studied. Common agricultural factors, such as recent dressings of fertilisers or the presence of decomposing straw, had little effect. Values were reproducible and not affected by details of laboratory technique, such as methods of shaking. The standard time of contact of soil and solution adopted was 15 minutes, longer times had only small effects. Usually 20 g. of soil and 100 ml. of solution were used; P-concentrations with twice as much or half as much soil were a little greater or smaller. P-values were increased by grinding soils finely and were affected by the way the soils were dried.

Possible seasonal variations were investigated by sampling several sites with contrasted histories at both Rothamsted and Woburn at monthly intervals through the year. P-concentrations in $CaCl_2$ solutions were always less with fresh than with air-dried samples. Values in heavy soils at Rothamsted were remarkably constant and showed no seasonal variation on each site, except they were increased where FYM or phosphate fertilisers were added during the year. The P-concentrations were also constant in the poorer of the light soils at Woburn, but in very rich Woburn soils P-values fell slightly during the year. None of the changes that occurred during the season altered the classification of P-status for practical purposes.

In the Rothamsted soils that have received FYM each year P-concentrations in $CaCl_2$ solutions were greater than the values in soil of plots treated annually with superphosphate that has supplied about as much P as was supplied by FYM. Where both FYM and superphosphate have been applied, P-values were greater than the sums of values on plots receiving FYM and superphosphate separately; a given amount of P applied to soil retains a higher solubility when FYM is regularly applied. (Blakemore and Cooke.)

PHOSPHORUS DEFICIENCY IN BARLEY

The plots of the old Rotation Experiment in Agdell Field which received superphosphate every fourth year from 1848 to 1948 grew good barley in 1959 and 1960. Fresh dressings of superphosphate did not increase yields on plots containing the most P-residues, but there were small increases on plots containing less. The crops appeared normal throughout both seasons. In 1961, however, the older leaves of young barley plants growing on Plot 1 with only a

moderate amount of P-residues, and with no new dressings of super-phosphate, became yellow when the plants were about 3 inches high. Where fresh superphosphate was broadcast on parts of this plot the plants were normal and were 6 inches high by the beginning of May, when the yellow plants had stopped growing. Table 4 shows analyses of plants with different intensity of yellowing taken from plots with different P fertiliser treatments.

TABLE 4

Analyses and appearance of barley grown on Agdell Field in 1961

P-residues from Rotation Experiment 1848–1948	Recent superphosphate treatment 1959–60	1961	Colour of plants	N	P	K
				\% in dry matter		
Plot 1 medium residues	P	P	Green	4·4	0·30	4·6
	O	P		4·0	0·25	4·2
	P	O	Yellow	3·2	0·12	3·0
	O	O	Very yellow	3·1	0·11	3·2
Plot 3 largest residues	P	P	Green	4·2	0·27	4·6
	O	P		4·2	0·30	4·4
	P	O		3·9	0·30	4·7
	O	O		4·2	0·22	4·5
Plot 5 no residues	P	P	Green	4·1	0·24	4·0
	O	P		4·7	0·30	4·8
	P	O	Purple tinge	3·9	0·16	4·1
	O	O		3·9	0·11	4·0

From experience of young barley on the Rothamsted and Woburn Farms, the yellowing on Agdell would be diagnosed as a deficiency of N or K (% N and % K both being about 3), or both. As NK basal fertiliser was applied to the seedbed, however, the low values were not because N and K were lacking in the soil, but because P was inadequate in the soil of Plot 1. The dressings of P given in 1961 not only increased the P-contents of the plants but also increased the N and K contents to levels at which there was no yellowing. The level of the old P-residues, adequate to prevent yellowing in 1959 and 1960, was inadequate in 1961, as were residues from super-phosphate applied in 1959 and 1960. Plot 3, which has much larger old P-residues, was free from yellowing. Plants on Plot 5, the un-manured plot of the old Rotation Experiment, with a very low level of soil P showed the purpling usual for deficiency, and they contained only 0·1% P.

A. Sorteberg (1960, *Landbrukshögskolens Institutt for jordkultur, Saertrykk* nr. 46) investigated similar spring-time yellowing of barley in Norway. Yellow plants had small and poorly developed roots, and an average K content of 2·6%. Pore space in the soil was less, and the ratio of air to water much less, where the barley was yellow. The yellow symptoms were attributed to poor root development limiting uptake of K. No physical measurements were made on Agdell soils, but seedbeds in 1961 were poor after a wet and mild winter, and were worse on Plot 1 than on Plot 5. This difference may account for the differences in colour symptoms and in uptakes of N and K where phosphate in the soil was low in these two plots. The yellow colours on Agdell disappeared as the

weather became drier and warmer, but yields were affected, and about 10 cwt. grain/acre were lost where the crop had been yellow.

This experience shows how the effects on barley of a poor seedbed may be lessened by a fresh dressing of superphosphate where the soil has only moderate levels of soluble P. (Warren and Johnston.)

SOIL POTASSIUM

Measuring " available " potassium

Exchangeable potassium measurements are useful in classifying the K-status of soils that are either " very low " or " very high ", but are much less useful in assessing " medium " soils. The K removed by grass in short-term experiments from about fifty soils was poorly correlated with exchangeable-K for soils containing 10–20 mg. K/100 g. soil. But K uptakes by the grass were closely related to values for $pK-\frac{1}{2}pCa$ (measured at equilibrium with $0.01M$-$CaCl_2$ solutions) and to the free-energy changes calculated for the replacement of K by Ca. (Arnold and Barbara Close.)

Values for $pK-\frac{1}{2}pCa$ measured in equilibrium $CaCl_2$ solutions before and after adding K (as KCl) are being used to develop a way of estimating the amount of K-fertiliser needed by crops. $pK-\frac{1}{2}pCa$ is almost linearly related to the amounts of K added, and the values do not generally depend on whether the soils are fresh or air-dried. (Arnold.)

The amounts of K were measured in the equilibrium $CaCl_2$ solutions used to study seasonal changes in P values (p. 55). Many samples were taken from the site of the Barnfield Experiment fallowed in 1961; the values were quite constant through the year on plots receiving no K fertiliser or FYM and where the soil was very low in K. On other plots the values were increased by the usual annual dressings of FYM and of K fertilisers, but there was no other seasonal change. In sampled fields growing crops in 1961 K values fell in spring and summer; they rose again after mid-summer in fields under grass or cereals, but under sugar beet they remained low until autumn. These differences may be connected with lengths of growing seasons and with cycles of root growth. (Blakemore and Cooke.)

Release of non-exchangeable potassium

Much information about the release of non-exchangeable-K has been obtained by continued cropping in the greenhouse. In many illite-rich English clays K releases are five to ten times more than the fall in exchangeable K. A few soils released much K because they contained glauconite (identified by I. Stephen, Pedology Department). The K-releasing power of the soils used was related to soil series identified by the Soil Survey. (Arnold and Barbara Close.)

Potassium–magnesium relationships

Field experiments are being done at both Rothamsted and Woburn to test potassium (as K_2SO_4) and magnesium (as $MgSO_4$) on ryegrass. (Magnesium in crops and soils has been determined

by A. Weir, Pedology Department.)   These fertilisers affected crop composition more on Woburn sandy loam than on clay-loam at Rothamsted.   Table 5 gives analyses for the first harvest in the second year of the sward at Rothamsted and for the first cut of

TABLE 5

Effects of K and Mg dressings on the ratios of K : Mg in Italian ryegrass

(all quantities of K and Mg were in equivalents)

	Mg applied (lb./acre)			
	0	58	0	58
	Rothamsted		Woburn	
K applied (lb./acre)	Ratios of K/Mg			
0	5·8	4·4	6·4	4·2
95	8·7	6·6	9·0	6·6
190	9·6	7·9	11·4	8·4

newly sown grass at Woburn.   At Rothamsted % Mg in the dry grass ranged from 0·09 to 0·15, and at Woburn from 0·12 to 0·22.   Potassium dressings increased yield of grass slightly at Rothamsted and more at Woburn.   Magnesium had no effect on yields at Rothamsted and gave a small but significant increase at Woburn.   (Arnold and Penny.)

THE VALUE OF RESIDUES OF PK FERTILISERS IN SOILS

Continuous Barley site at Woburn

Further estimates of the values of old residues of P and K fertilisers were obtained from a micro-plot experiment on the site of the Permanent Barley Experiment on Stackyard Field at Woburn, where the "classical" treatments started in 1876 and stopped in 1927.   Table 6 shows the increase in yields of three crops caused by the P and K residues in the soil.   (Warren, Johnston and Penny.)

TABLE 6

Increases in yields of barley, potatoes and sugar beet caused by residues of P and K fertilisers in soils of the Classical sites at Woburn

			Barley (grain) (cwt./acre)	Potatoes (tons/acre)	Sugar beet (sugar) (cwt./acre)
			Increases from P residues		
1960	...	...	6	1	—
1961	...	...	4	2	9
			Increases from K residues		
1960	...	...	0	3	—
1961	...	...	0	3·5	13

Effects of methods of applying P and K fertilisers on comparisons of new dressings with old residues in soil

Micro-plot experiments on Agdell Field at Rothamsted and on Stackyard Field at Woburn in 1959–60 showed that the way fertilisers are applied to poor land may control their effectiveness. Estimates of the values of P and K residues obtained by comparing

yields of crops grown on land with residues, with yields from land without residues, were lower than estimates of residual values derived from the response curves given by fresh dressings of fertilisers. Although the new fertiliser dressings were considered enough for maximum yields, the highest rate of fertiliser on plots without PK residues often gave yields below those on the plots with residues. The new fertiliser dressings were broadcast just before preparing barley and sugar-beet seedbeds; for potatoes the fertilisers were broadcast between ridges immediately before hand-planting at Rothamsted and on the flat before machine-planting at Woburn. As the two estimates of the values of the PK residues may differ because of differences in the positions in the soil of the residues and the new dressings, comparisons of broadcast applications with ploughed-in dressings were started in 1961. With the high rate of fresh superphosphate ($1\cdot5$ cwt. P_2O_5 per acre on Agdell, $1\cdot0$ cwt. P_2O_5 per acre on Stackyard Field), ploughing-in gave better yields than broadcasting for barley and sugar beet; method of application did not affect yields of potatoes. With the half rate of P the results were variable, ploughing-in P was sometimes less effective than broadcasting. Potassium dressings were tested only at Woburn, where differences between methods of application were all small. (Warren, Johnston and Penny.)

SOIL MAGNESIUM

All our staff who have worked with magnesium in crops and soils have benefited by using the new equipment for direct-reading spectrographic-determination of magnesium, built and operated by A. Weir of the Pedology Department (*Rep. Rothamst. exp. Sta.* for 1960, p. 81).

A group of English and Welsh soils is being cropped exhaustively in glasshouse pot experiments; the soils contain $0\cdot2$–$1\cdot0\%$ total Mg, mostly in the clay. Mg exchanged by ammonium acetate varies from 40 to 240 lb. Mg/acre (2–12 mg. Mg/100 g. of soil). Although in glasshouse cropping ryegrass may contain up to $0\cdot7\%$ Mg in dry matter, yield is unaffected by lack of Mg until it has less than $0\cdot1\%$ Mg, and crops have been grown with only $0\cdot04\%$ Mg. Different plants remove different amounts of Mg, radishes three or four times as much as grass.

After 6 months continuous cropping, ryegrass has not removed more Mg than was originally present in exchangeable form. The amounts of Mg taken up are not related to the original exchangeable Mg values. Uptakes decline steadily after 2–3 months of cropping, suggesting that release of non-exchangeable Mg is less important than the corresponding release of non-exchangeable K. Probably measurements of exchangeable Mg fail to predict uptake because the other bases present interfere. At constant base saturation, Mg : Ca ratios in grass are proportional to the ratios of exchangeable Mg : Ca in soil. High K levels depress Mg uptakes by grass seriously, especially in soils rich in Mg.

Ion activity ratios such as $\dfrac{\sqrt{\mathrm{Mg}}}{\mathrm{K}}$ and $\sqrt{\dfrac{\mathrm{Mg}}{\mathrm{Ca}}}$, calculated from

measurements in dilute electrolyte solutions in equilibrium with soils, may help to explain cation uptake by plants, but their use is complicated by changes in the base status of soils during cropping. (Salmon and Arnold.)

CATION–ANION RELATIONSHIPS IN CROP NUTRITION

The uptake of ions by plants is influenced by the presence of other ions, uptake usually being decreased by ions of similar charge and increased by those of opposite charge. Samples of Italian rye-grass (*Lolium multiflorum*) from many places in Britain were ana-lysed to see if the ratio of total cations : total anions was constant. The cations measured were: Na^+, K^+, Ca^{++} and Mg^{++}; the anions were NO_3^- (assumed responsible for the uptake of N), $H_2PO_4^-$, SO_4^{--} and Cl^-. Silicon was also measured. Forty-five individual samples grown on different soils in five seasons with varied fertiliser treat-ments, and cut at different stages of growth, were examined. Total anions and total cations each ranged widely (100 g. of dry grass contained from 80 to 170 m.e. of total cations and from 130 to 500 m.e.) (including silicon) and 100–400 m.e. (omitting silicon) of total anions. In the whole group of samples total cations were closely correlated ($r = 0.59^{***}$ with silicon and $r = 0.69^{***}$ without silicon) with total anions.

Twenty ryegrass samples from an experiment at Rothamsted in 1960 were analysed. They had been cut at the same stage, but had received different fertiliser treatments. Total cation contents (from 130 to 180 m.e./100 g. dry grass) were well-correlated ($r = 0.77^{***}$) with total anions (240 to 350 m.e./100 g. of dry grass) when silicon was included. The correlation ($r = 0.94^{***}$) between total cations and total anions (180–280 m.e./100 g. of dry grass) was even better when silicon was excluded.

These relationships are being examined in more detail by micro-plot field experiments at Rothamsted and Woburn. On each farm one experiment on ryegrass and one on kale tested the effect on ion uptake of varying those ions, excluding micro-nutrients, which may be important in crop nutrition. Preliminary data on the grass show the expected relationships between cations: increased uptake of Na, K and Mg depresses uptake of Ca; where K uptake increases Na decreases, and increasing Mg uptake decreases K. Increasing NO_3^- uptake has the greatest effect; it depresses Cl^- uptake, but increases uptake of all other ions.

As much of the NH_4^+ was converted to NO_3^- before it was ab-sorbed, its effect resembled that of NO_3^- but was less pronounced. Cl^- depressed NO_3^- and SO_4^{--} uptakes, and increasing SO_4^{--} de-creased Cl^- uptake. (Cunningham.)

W. Dijkshoorn (*Netherlands J. agric. Sci.* 1957, **5**, 233) stated that anion contents of ryegrass (omitting silicon) do not exceed 400 m.e./100 g. of dry matter and that the corresponding maximum total cation content is 200 m.e. In the work described above the total cation and anion contents do not exceed these values when silicon is excluded. Pot experiments are now being done to see if there are values for total ions in grass that are not normally exceeded. (Karim and Cunningham.)

SURFACE AREAS OF ROOTS

Imperfect agreement between laboratory measurements of " available " nutrients and crop performance is often caused by assuming that the whole of the ploughed layer of soil is " swept " by roots. This is rarely true with annual crops; the proportion of the soil from which nutrients are taken depends on soil structure and permeability as well as on the root characteristics of particular crops. Attempts are now being made to estimate *in situ* the surface areas of roots of growing plants by electrical measurements. The amounts of maize roots growing in soils, sand cultures and nutrient culture solutions were estimated by measuring capacities and resistances. (Walker.)

MICRONUTRIENTS

Interactions of phosphates and manganese salts

When superphosphate is applied for crops two interactions with soil manganese are possible. Some workers have reported that superphosphate increases the availability of soil Mn and that, when superphosphate is drilled in contact with seed on Mn-deficient soils, mixing a small quantity of Mn salt with the super is more effective in controlling Mn-deficiency than applying the dressings separately. At the other extreme some acid soils contain much soluble Mn which is toxic to plants, and toxicity is decreased by soluble phosphates which precipitate Mn. The effects of Mn/P ratios, and of pH, on the precipitation of manganous phosphate were investigated by measuring the pH values at which precipitates started to form when KOH was added to mixtures of $MnSO_4$ and H_3PO_4. With Mn : P ratios of 0·1 and 1·0, Mn began to precipitate at pH 5–6 and precipitated completely above pH 6·5. With a Mn : P ratio of 10 some Mn remained in solution until pH 8·2; both Mn and P were redissolved at pH values above 10. With manganese concentrations of 10^{-2} and $10^{-3}M$ and an initial Mn : P ratio of 1 the composition of precipitates was $Mn(OH)(PO_4)_{0·65}$. At a Mn : P ratio of 0·1 the precipitates corresponded to $Mn(OH)_{10}PO_4$ and $Mn(OH)(PO_4)$ for the above Mn concentrations. With Mn : P ratios of 10 ill-defined compounds were precipitated at the Mn concentrations used; more basic phosphates were generally precipitated at the higher pH's used. (Heintze.)

The effects of various treatments on exchangeable manganese

Prolonged air-drying, or steam sterilising, of soils generally increases readily soluble Mn. In laboratory experiments soluble Mn was not increased after treating soils with chloroform or mixed γ radiation. Drying soils at 80° for 24 hours increased exchangeable Mn, and steaming did so even more. As exchangeable manganese was unaffected by treatments that eliminated microbiological action without heating, its increase by heat probably depends on a chemical process. (Heintze.)

Total micronutrients in soils

The total amounts of manganese, copper, molybdenum and zinc were determined in seventeen soils ranging from heavy clays to

light sandy loams.   The sites used had known histories; six were pastures in Yugoslavia.   The work is being done to give information on total reserves of these micronutrients in different soils, and to show whether different treatments, continued over long periods on similar soils, have affected reserves.   Two methods of extracting micronutrients from soils were compared—fusion with sodium carbonate and digestion with hot fuming nitric acid.   H. H. Le Riche (Soil Survey of England and Wales) measured the micronutrients by separate spectrochemical methods and also determined the amounts remaining in the silica residues left after extracting chemically.

Manganese.   On average more than 90% of the Mn extracted by fusing with Na_2CO_3 was also removed by digesting with fuming HNO_3; acid was less effective on soils with much sand.   The spectrochemical results for total Mn were often higher than those from both chemical methods.

Copper.   Usually fuming HNO_3 extracted about 75% as much Cu as was extracted by the fusion method.   The acid method also gave more variable results with Cu than with Mn, and the lowest values for Cu extracted by HNO_3 were with soils rich in sand. The spectrochemical results followed those obtained by HNO_3 and were lower than those by the fusion method.

Molybdenum.   Variable proportions of the total Mo in the soils used were extracted by fuming HNO_3, and fusing with Na_2CO_3 was much more reliable.   The proportion of the total Mo extracted by HNO_3 was highest with soils that had been under grass for a long time and with soils that had received organic manures for many years.

Zinc.   The amounts of Zn extracted by fuming HNO_3 agreed well with those extracted by fusing with Na_2CO_3.   Nitric acid seems quite satisfactory for determining Zn, and is preferred, as it is much quicker than the fusion process.

Total potassium and iron were also determined in the extracts. From 5 to 40% of the total K in the soils (determined by the fusion method) was extracted by fuming HNO_3.   The amount of K extracted by acid was related to the previous treatment of the soil, and was most from land given organic manures regularly or land under permanent grass.   Most of the iron extracted by fusion was also extracted by digesting with HNO_3; the acid method was accurate enough for most work on the soils used.   (Savic and Williams.)

NATURAL RADIOACTIVITY IN SOILS

The β-radioactivity of 35 British soils was measured (accurate to $\pm 1\cdot3\%$) using total counting time of 30 minutes for each soil. The γ-radioactivity spectra of these soils is now being explored. Natural radioactivity will then be related to the total potassium, uranium and thorium in the soils.   (Talibudeen and Yamada.)

EXPERIMENTAL METHODS

Determining nitrate-nitrogen in soil and plant extracts

For the last 6 years titanous sulphate was used here as the reducing agent when determining nitrate-nitrogen in soil and plant extracts (J. M. Bremner & K. Shaw, *J. agric. Sci.* 1955, **46**, 320–328). This reagent is now difficult to obtain in the United Kingdom, and supplies may stop completely. As an alternative, the old well-known Zn–Cu couple method was tested. Williams (*J. chem. Soc.* 1881, **39**, 100–111) was the first to apply the reducing action of a Zn–Cu couple in determining nitrates in water; in the 1880s Warington used Williams' method to determine nitrates in soils from the Classical Experiments at Rothamsted. The method (E. J. Russell, *J. agric. Sci.* 1914, **6**, 18–57) continued to be used here until about 1920, when it was replaced by the Devardas' alloy method. Reduction by the Zn–Cu couple was slow, and 2 days at 25–30° were allowed to convert nitrate to ammonium.

The Institute of Water Engineers has adopted an improved Zn–Cu couple method, in which nitrate is reduced much more quickly (*Approved Methods for Physical and Chemical Examination of Water*—Joint Committee Report, Institute of Water Engineers, London, 3rd ed., 1960). Granulated Zn is used to prepare the couple and up to 1,000 μg. NO_3-N can be reduced either at room temperature for 2 hours or at 37° for 1 hour. In our tests of the Zn–Cu couple method this year Zn powder was used to make the couple; CuO was also added because this increased the vigour of reaction. Because nitrate is reduced at the point where hydrogen is evolved, the rate of reduction will depend on the speed at which the solution of nitrate passes over the solid Zn–Cu couple, or the speed at which the couple moves through the solution. The increased vigour of the reaction, obtained by using Zn powder for preparing the Zn–Cu couple and by adding CuO, reduced 100 μg. NO_3-N in $\frac{1}{2}$ hour at room temperature. Our results agree well with those using the titanous sulphate method. Further tests are being made of the most suitable amounts of Zn–Cu couple, of CuO and of the minimum time for complete reduction. (d'Arifat and Warren.)

Total sulphur in plant materials

Existing rapid methods for measuring sulphur in plant material are unreliable, and a new method using indirect flame photometry was developed. Sulphur in plants is first oxidised to sulphate by digesting with fuming nitric acid and then ashing with magnesium nitrate at 450°. Sulphate is precipitated as the barium salt, washed, dried and then dissolved in ammonium EDTA solution. The barium in this solution is measured by a flame photometer. The method is quick, reliable and accurate. (Cunningham.)

Mass spectrometer

The sensitivity of the mass spectrometer was increased twenty-fold by fitting a vibrating condenser amplifier for measuring very small D.C. currents. With this modification much smaller samples can be analysed (the optimum with the old arrangement was 0·4 mg.

N), and quantitative corrections can be made for air contamination. In 1961 300 samples were analysed. (Newman.)

Using ryegrass in pot experiments

Perennial ryegrass has been used as a test crop in greenhouse pot experiments for more than 10 years. It is adequate for most problems that can be dealt with by pot experiments and grows well on a wide range of soils. Recently the range of very acid soils used was extended, and the growth of ryegrass was independent of pH between 3·6 and 8·0 (measured in $0·01M$-$CaCl_2$ solution) provided adequate phosphate was given. A single soil maintained in the field at pH 3·2 gave much lower yields; other soils of pH values below 4·5 gave constant yields for the first four cuts, afterwards yields fell by about one-tenth. (Mattingly and Barbara Close.)