Report for 1959

Chemistry Department

G. W. Cooke

CHEMISTRY DEPARTMENT

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J. M. Bremner left in August to take a post at Iowa State University. I. K. Otter joined the staff temporarily in September. A. C. D. Newman returned from Russia, where he spent a year working at the University of Moscow under an exchange scheme organised by the Russian Ministry of Agriculture, the British Council and the Agricultural Research Council. B. P. Pleshkov returned to the Timiryazev Agricultural Academy, Moscow, in July. T. Z. Nowakowski was invited to attend a Conference on " Organic Manures and the use of Peat in Agriculture " at Szczecin in Poland, where he gave a paper on British work on organic manures. G. W. Cooke visited experimental stations and farms in France where research is being done on fertilisers, and on new kinds of cropping, at the invitation of Société Commerciale des Potasses d'Alsace. In October Cooke was invited by the Swedish Federation of Fertiliser and Lime Industries to visit Stockholm and read a paper on British work on fertilisers, soil fertility and crop production. He also took part in a Round Table Conference arranged by the Royal Swedish Academy of Agriculture and Forestry.

D. P. H. Tucker of the Colonial Research Service left in September to continue his training at Cambridge. R. G. Heathcote joined the Department for training in field experimentation and soil-fertility work. P. Arambarri (Spain), M. Birecki (Poland), S. N. Chakravarti (India), M. Kushizaki (Japan), M. Salomon (U.S.A.) and L. V. Vaidyanathan (India) all worked in the Department during the year.

J. M. Bremner was awarded the D.Sc. Degree of London University. S. N. Chakravarti was awarded the London Ph.D. Degree.

ORGANIC MATTER IN WOBURN SOILS

E. M. Crowther (Russell, E. J. and Voelcker, J. A. (1936), *Fifty years of field experiments at the Woburn Experimental Station.* London: Longmans, pp. 315–345) discussed changes in organic carbon contents of the soils of the Continuous Wheat and Barley Experiments at Woburn. The results were difficult to interpret because of the systematic arrangement of the treatments and the presence of elementary carbon in some of the wheat plots. With continuous cereals grown with fertilisers, but no farmyard manure, the percentage of organic carbon in the soil fell from about 1·5% in 1876 (when the experiments started) to about 1·0% in 1927. Recent deeper ploughing may have increased the organic matter in layers of soil originally unploughed. The 1959 samples were therefore taken to several depths, so that analyses could be adjusted for comparison with earlier results when the land was ploughed less deeply. Organic matter has been lost at about the same rate, or a little faster, from 1927 to 1959 as between 1888 and 1927 on the plots

that had inorganic fertilisers in which sodium nitrate supplied the nitrogen. With ammonium sulphate instead of sodium nitrate, organic matter was lost more quickly in the recent period. Organic matter may have oxidised more rapidly on the ammonium sulphate plots because they have been fallowed more. On the nitrate plots the *annual* loss of organic carbon between 1888 and 1959 was about 0·009 per cent (of C), twice the rate with old organic residues on one of the plots (7–1) of heavier soil on the Hoosfield Permanent Barley Experiment at Rothamsted.

The soils of both sites at Woburn now contain very little organic carbon; the barley site is lower than the wheat, and the lowest values (0·56% C) are on the plots that received ammonium sulphate. Soil is now lost from these sites by water erosion, perhaps because the soil contains too little organic matter. Otherwise the agricultural significance of these low levels of organic matter is not known; nor is it known whether crop yields would be higher if the levels were higher. (d'Arifat and Warren.)

THE DIFFUSION OF IONS IN SOIL

Crops can only take up nutrients when root and nutrient ion are in contact. Mobile ions, such as nitrate, may meet roots by being washed downwards in water percolating through soil, otherwise contact can only occur as ions migrate by diffusion in films or pockets of water in or on soil particles. Although the processes by which ions move must affect the value of plant nutrients supplied by soils and by fertilisers, the factors that influence diffusion have rarely been studied systematically. Newman began work on ion-diffusion processes in soil and related materials while at Moscow University and continued it when he returned to Rothamsted.

An apparatus was developed from that used to determine diffusion coefficients of aqueous solutions, in which the porous medium is a diaphragm confined between two sintered glass disks. Ions from an aqueous solution on one side of the diaphragm diffuse through to a less concentrated solution on the other. At a steady state the amount of diffusing substance which passes through the diaphragm in a given time is determined chemically.

Sand was washed, ground and fractionated by sedimentation into the size ranges $10–20\,\mu$ and $20–50\,\mu$ and used as the porous medium. Two conductivity measurements were made, one with sand and electrolyte between the plates, and the second with electrolyte alone. The number of ions migrating by either conductivity or diffusion is proportional to the area available for migration and inversely proportional to the distance they travel. Hence the function (effective area/path length) describes the resistance of the media to migration; the ratio of the value of this function (determined from diffusion or from conductance measurements) to the value calculated from the physical dimensions of the compartment in which the diaphragm is confined is defined as the migration permeability (P). Some values of P already obtained show approximate agreement between the two independent methods for obtaining the migration permeability, and confirm that inert materials in particles of size $10\,\mu$ or greater interfere with migration only by

blocking the path of the ions. With smaller particles the diffuse double layer may interfere with this simple pattern, and techniques are being improved to test this. (Newman.)

CATION-EXCHANGE CAPACITIES OF PLANT ROOTS

In continuing work on the cation-exchange capacities (CEC) of plant roots (*Rep. Rothamst. exp. Sta.* for 1958, p. 58), reasons were examined for the drift to acid pH values after suspensions of roots in salt solutions are neutralised in determining CEC. In collaboration with Holden (Biochemistry Department) the drift was shown to resemble that with minced leaf suspensions and caused by pectin-esterase breaking pectin into pectic acid and methanol. Neutralised root suspensions contained methanol and showed pectin-esterase activity. Pretreating the roots with boiling water, and with solvents of pectin, greatly decreased the CEC values of legume roots. The buffer curves of roots also indicated that pectin is important in exchange reactions.

No close relationships were found between CEC values and apparent dissociation constants calculated from pH values in N-KCl of roots previously saturated with H^+ by HCl treatment, or with the nitrogen contents of roots. In pot experiments with several crops, CEC values changed only slightly during the first two or three months of growth, but as the crops matured the CEC values for coarse and fine roots differed; for example, with kale the values for coarse and fine roots were respectively 26 and 67 m.eq./100 g. of dry matter, and smaller differences occurred with other crops. Variations of this kind partly invalidate the conception that each crop has a specific value for CEC of its roots, and show that a better basis than dry-matter weight is needed for expressing results. Work reported last year showed CEC values of 13–16 m.eq./100 g. dry matter for clover roots; other workers have reported 40 m.eq. The higher values have now been found for clover roots from cultures in flint and nutrient solutions, but the lower values, which are characteristic for cover grown out of doors in soil, were found when plants were grown in sand–vermiculite mixtures. It might be argued that values with clover from the field are low because the finer and more active roots are lost in sampling, but this cannot be so with plants grown in sand and vermiculite when all roots are extracted.

The present circumstantial evidence does not prove that CEC values are very important for understanding ion-adsorption processes. Some published results for uptake of mono- and divalent cations agree qualitatively with what might be expected if the Donnan theory of membrane equilibria governed ion adsorption. In the present investigation, when clover and perennial ryegrass grew under similar conditions, corresponding K/Ca ratios of plant tops were 0·31 and 2·1 for CEC values 48 and 22 m.eq./100 g. D.M. respectively. The correlation coefficient for $\frac{CEC_1}{CEC_2} \times \frac{K_2}{K_1}$ for 24 pairs of comparisons of various crops was $+0\cdot4654$, which was just significant. (Heintze.)

NITROGEN IN SOILS

Mass spectrometer

A small mass spectrometer made by Vacuum Industrial Applications Ltd., Wishaw, Scotland, was installed in 1959, which will help our work on soil nitrogen and provide facilities for other departments that wish to use stable isotopes of light elements. A series of difficulties prevented it from becoming fully operational. Several minor and major technical faults in the apparatus as delivered have now been rectified, but delivery of components for the handling equipment for the gas admission part of the spectrometer was also delayed. The gas-line necessary for converting samples of ammonium salts to nitrogen gas is now almost complete. (Newman.)

Some experiments with ^{15}N were started on the fixation of atmospheric nitrogen in a poor soil by microbes that are not symbionts, to see how fixation is affected by oxygen, carbon dioxide, and by additions of plant material and nitrate. (Birecki, Jenkinson and Newman.)

Fixation of ammonia by soil organic matter

Recent work suggests that, when soils are fertilised with gaseous or liquid ammonia, more ammonia is fixed by the organic fraction than by the clay fraction, and an attempt was made to determine the ammonia fixed by the organic matter in mineral and organic soils. Various techniques, including saturating the soils with potassium and removing clay minerals with hydrofluoric acid before treating with ammonia, showed that much ammonia was fixed by soil organic matter in moist or air-dry soils, but there was no satisfactory way of measuring this fixation in soils containing ammonia-fixing clay minerals. The theory that fixation by soil organic matter and by lignin involves oxidation of phenolic hydroxyl groups at which ammonia is then fixed could not be substantiated. Fixation of ammonia by lignin and by organic soils occurs without oxygen, and the reaction of lignin with ammonia does not destroy phenolic hydroxyl or methoxyl groups, or the units responsible for forming aromatic aldehydes when lignin is oxidised with alkaline nitrobenzene. Very little, if any, of the ammonia-N fixed by lignin is in the form of free amino groups as determined by the Van Slyke nitrous acid method. (Bremner.)

Mineralisable-nitrogen in soils

The relationship between mineralisable nitrogen in soils, determined by laboratory incubations, with crop performance was examined in pot and field experiments. In the pot experiments (with Close) yields of dry ryegrass, and nitrogen uptakes, were significantly correlated with the mineral-N in freshly sampled soils, and with the mineral-N released by incubating soils that had been air-dried and re-wetted; there was no significant correlation with the mineral-N released on incubating the fresh soils. With 22 soils used for field experiments on barley, yields of barley grown without nitrogen fertiliser were correlated with the amounts of mineral-N in fresh soils, and also with the amounts released by incubating soils that had been air-dried. Soils from 14 potato experiments

showed no significant correlations between unfertilised yields and laboratory measurements of " available " nitrogen.

Both the mineral-N contents, and also the amounts of mineral-isable-N released on subsequently incubating air-dried soils, increased during storage, were less when the soils were stored in sealed polythene bags than when in paper bags; the increases were much smaller when air-dry soils were stored at $-10°$. (Gasser.)

Movement of fertiliser nitrogen dressings in soil and uptake by wheat

100 lb. of fertiliser N per acre were applied as calcium nitrate or as ammonium sulphate, either in the autumn or in the spring for winter and for spring wheat crops on light soil at Woburn; adjacent plots of uncropped soil were also dressed. Nitrogen applied in autumn was leached from the surface soil; by December just over half of the total quantity remained in the top 36 inches, but by March only 10% of the nitrate dressing and 20% of an ammonium sulphate dressing remained in the top 36 inches of soil, and most of this was in the 18–36-inch layer. In contrast, the whole of the dressing of either form of nitrogen applied in spring to bare land was in the sampled depth, and most was in the upper 18 inches, until the final sampling in August. Both winter and spring wheat removed almost all of the fertiliser nitrogen by the end of May, and at harvest even the soils given fertiliser contained very little mineral-N. Little of the fertiliser-N applied in autumn was recovered by winter wheat and none by spring wheat. Similar amounts of fertiliser-N applied in the spring as ammonium sulphate or calcium nitrate were recovered by winter and spring wheat, but whereas more of the total nitrogen recovered was in the grain of winter wheat at harvest with ammonium than with nitrate, the reverse was true with spring wheat. The uptake of fertiliser-N by the wheat was maximal at the end of May; at harvest winter wheat contained 8% and spring wheat 32% less nitrogen than this maximum. (Gasser.)

SOIL PHOSPHATE

Phosphate equilibria in calcareous soils

In previous work the total isotopically exchangeable phosphate (P_e) was divided into fractions exchanging at different rates which were affected by external factors in different ways (*Rep. Rothamst. exp. Sta.* for 1957, p. 62; for 1958, p. 49). The total surface phosphate (P_s) (given by P_e–P_{ss}, P_{ss} being phosphate in the soil solution) in 40 calcareous soils from England and Spain was divided into " rapid " and " slow " exchanging fractions (the half-times of exchange were 3·70 hours and 32·9 hours respectively). The " rapid " and " slow " exchanging phosphate values, expressed as ratios of the total surface phosphate, were positively related to both the clay and the $CaCO_3$ contents of the soils. (Arambarri.)

" Lime potential " and " phosphate potential " values (*Rep. Rothamsted. exp. Sta.* for 1949, p. 29) were calculated from concentrations of calcium, phosphate and hydrogen ions in the soil solutions for 53 calcareous soils from England and Spain whose total phosphate (P_t) and P_e values were between 21–533 mg. and 1·9–

24·8 mg. P/100 g. soil respectively. The lime potential values were in the range 6·43–6·85, and variation from the theoretical value of 6·60 at the partial pressure of CO_2 in air (0·0003 atmos.) was presumably related to the nature of the calcium carbonate surfaces. The monocalcium phosphate potential ranged from 7·23 to 8·59, suggesting the presence of calcium phosphates similar to, and slightly more basic than, octocalcium phosphate.

The influence of $CaCO_3$ content on phosphate equilibria was examined in groups of soils obtained from pairs of adjacent sites where $CaCO_3$ and the other mineral constituents were thought to be of similar origins. There was a linear relationship between $\frac{P_{slow}}{P_{surface}}$ and $CaCO_3$ content for two groups of soils with more than 8% of $CaCO_3$. Isotopic exchange experiments using ^{45}Ca on a few of the soils from different sites showed that the specific surface of their $CaCO_3$ varied between 6·4 and 23·8 M^2/g. (of $CaCO_3$). The ultimate crystallites of the soil $CaCO_3$ must be very small, because the specific surface of calcite is about 0·151 M^2/g. for crystals of average diameter 25 μ (*Rep. Rothamst. exp. Sta.* for 1958, p. 50). With soils of similar $CaCO_3$ and total P contents, high specific surfaces of $CaCO_3$ are related to high values for the ratio: $\frac{P_{slow}}{P_{surface}}$.

10 mg. of P were added (as monocalcium phosphate) to these soils and recoveries were measured after incubating for 1, 2 and 6 months at constant temperature and field moisture capacity. The values of the ratios $\frac{P_{rapid}}{P_{surface}}$ and $\frac{P_e}{P_t}$ were nearly at equilibrium after incubating for between 2 and 6 months, and were significantly greater than the values obtained for the untreated soils. Lower recoveries were obtained with soils containing much $CaCO_3$ of high specific surface. The total isotopically exchangeable phosphate (P_e) was linearly related to the equilibrium phosphate concentration in 0·02M-KCl; both values decreased with time, and the fall was proportionately more for the phosphate concentrations than for the total labile phosphate. (Arambarri and Talibudeen.)

Phospate equilibria in acid soils and phosphated clay minerals

In extending work reported earlier (*Rep. Rothamst. exp. Sta.* for 1958, p. 49) clay minerals were treated with $5.10^{-5}M$ phosphate for times up to 9 months. Kaolinites retained twice as much phosphate as did montmorillonite and glauconite, reflecting their lower negative surface charge density and higher edge : sheet area ratio. The net proton uptake by the clays was approximately proportional to the equilibrium pH and was much larger than the phosphate uptake, presumably because of the relatively high chloride concentration used. In a subsidiary experiment " Merck " kaolinite in equilibrium with 0·02M-KCl at pH 3 was treated with potassium phosphate at pH 3 in concentrations varying from 5.10^{-1} to $5.10^{-5}M$ for times buffers up to $4\frac{1}{2}$ months. The calculated net proton uptake per g. of clay was several times greater in $5.10^{-1}M$ and $5.10^{-2}M$ treatments than in the other treatments, indicating that more of the clay mineral was broken down. Phosphate uptake was greater at the higher

concentrations and was linearly related to the net proton uptake per g. of clay after $4\frac{1}{2}$ months.

A comparison of soil suspensions and the clays that had been treated with $10^{-5}M$ phosphate showed that phosphated montmorillonite had ion-activity products for (Fe^{3+} or Al^{3+}) $(OH)_2.H_2PO_4$ similar to those obtained with 28 British soils; 26 Indian soils gave values less than those with montmorillonite and approaching the ion-activity products of phosphated kaolinite and glauconite. Kaolinite treated with stronger phosphate solutions formed insoluble phosphates that were more acidic than variscite or strengite and resembled the precipitated synthetic phosphates containing Fe or Al in amounts equivalent to the phosphate. (Chakravarti and Talibudeen.)

Rates of growth and phosphorus uptake by ryegrass on calcareous soils

Calcareous soils from Rothamsted with a lime potential (pH -0.5 pCa) of 6·4 and with less than 15 mg. (P) of isotopically exchangeable phosphate per 100 g. of soil show an approximately linear relationship between the phosphate concentration in equilibrium with $0.01M$-$CaCl_2$ and total isotopically exchangeable phosphate. In glasshouse experiments with ryegrass in Rothamsted soils, yield increases and phosphorus uptakes were closely correlated with either of these measurements, although one is a measure of intensity and the other is a quantity.

A pot experiment with three groups of soils (pH -0.5 pCa $= 5.9$–6.4) derived from different calcareous parent materials was done to see whether phosphate concentration, or total isotopically exchangeable phosphate, governed the growth of ryegrass when N, K and micronutrients were optimal. The soils in each group had approximately the same total exchangeable phosphate, and between groups the phosphate concentration differed by a factor of two or three. Table 1, which gives the yields of grass on five of the soils at the first four harvests, shows that the first yields, after 41 days, were closely correlated with phosphate concentrations and were almost independent of the total isotopically exchangeable phosphate. First yields from soils 1, 2 and 3 were almost identical, although soil 3 had twice as much exchangeable phosphate as soil 1. At later harvests, the fourth 113 days after sowing is a good

TABLE 1

Yields of ryegrass, phosphate concentration and total isotopically exchangeable phosphate for 5 calcareous soils in a pot experiment

Parent material of soil	pH-0·5pCa	Isotopically exchangeable phosphate (mg. P/100 g.)	P concen-tration (micromoles P/litre)	Yield (g. dry matter/pot)			
				41 days	64 days	90 days	113 days
1. Silurian limestone ...	6·46	6·5	0·7	0·53	0·42	0·48	0·26
2. Oolitic limestone ...	6·39	9·3	0·8	0·52	0·72	0·84	0·59
3. Oolitic limestone ...	6·21	13·7	0·7	0·58	0·81	1·02	0·92
4. Clay-with-flints ...	6·35	13·9	1·4	0·89	0·91	1·13	1·01
5. Keuper marl ...	5·93	13·7	1·7	1·48	0·96	1·25	0·99

example, yields of grass were not related to phosphate concentration, but were proportional to isotopically exchangeable phosphate. This work confirms that described earlier (*Rep. Rothamst. exp. Sta.*

for 1957, p. 59). On both calcareous and acid soils the initial rate of growth of ryegrass depends mainly on phosphate concentration in the soil, but total yield is approximately proportional to total isotopically exchangeable phosphate. (Mattingly, Kuskizaki and Close.)

Measuring " available " phosphorus

Earlier work (R. G. Warren. *Proc. Fertil. Soc.* no. **37**) on the Exhaustion Land and Four-course Rotation Experiments suggested that sodium bicarbonate is a more reliable extractant than acids for estimating the P status of slightly calcareous soils. The soils of the old Rotation Experiment on Agdell were used to extend the work and to estimate more precisely the level of soil P below which superphosphate increases the yield of barley. The critical level in extracting with bicarbonate is 1 mg. P/100 g. soil, agreeing closely with Mattingly's value of 0·9 mg. P obtained in pot experiments with ryegrass. Potatoes respond to superphosphate when soil P is greater than this. The critical level was not determined because potatoes responded to superphosphate on all the soils used. Field experiments on soils with higher levels of P are needed, and some plots of the Barnfield Continuous Mangold Experiment will be used. These differences between the behaviour of potatoes and barley are important when interpreting soil analyses for farmers; they may depend on differences in physiological processes within the crops or in the nature and extent of their root systems.

A tentative conclusion is that extractants with pH values above 4 are more satisfactory than those below. Different methods of soil analysis are compared most simply on old arable soils, where biological changes affect nutrient supplies much less than on soils where green crops, old grassland or bulky organic manures have been ploughed in. In these last conditions mineralisable organic phosphorus may be important. (Johnston and Warren.)

POTASSIUM IN SOILS

In pot experiments seventy-six soils from a wide range of soil types are being continuously cropped. The potassium reserves of many were soon exhausted, but some have continued to supply ryegrass satisfactorily for 18 months. The amounts of non-exchangeable potassium released in this period have varied from nothing to more than 2,000 lb. K/acre. (Arnold and Close.)

Relation of potassium supply to size of clay

A group of eighteen arable soils which had not received heavy dressings of potassium fertilisers were used in laboratory work to investigate the value of potassium held by soils. Measurements of " fine " clay ($< 0·1\,\mu$), and its potassium content, separated the soils into three groups which fitted the following rates at which non-exchangeable K was released in the pot experiment:

Rate of release				Equivalent amount (lb. K/acre)
Low	...	...	...	...	<200
Medium ...	...	...	...	200–1000
High	...	...	...	...	>1000

One exceptional soil released K from particles of silt size; with all other soils releases of K were correlated with amounts of fine clay and with K levels in the fine clay. Measurements of $0 \cdot 1$–$0 \cdot 3 \ \mu$ clay fractions were nearly as useful as those of fine clay for grouping the soils according to their power of releasing non-exchangeable K to grass, but measurements of $0 \cdot 3$–$2 \ \mu$ fractions were poorly correlated with this power. Chemical extraction of mechanically separated fractions from a range of soils containing more than 1% of total K, showed that from half to three-quarters of the K occurs in particles too large to contribute significantly to the K provided by the soil. (Arnold.)

Relation of potassium supply to clay minerals

Little success has yet been achieved in relating the potassium supply from soils to crops with the clay minerals present, but the behaviour of the minerals most important in soil–potassium rela-tionships (principally micas and hydrous micas) has been too little studied. X-ray-diffraction data for $< 2 \ \mu$ clay separates are of only limited use for assessing what amounts of K soils of different origins will supply to crops, probably because the micas and hydrous micas in the " coarse " clay of this fraction, although they dominate the X-ray spectrograms, contribute little potassium to crops.

The potassium distribution in mechanical separates of soils from the long-continued Rotation I Experiment at Saxmundham was determined before and after continuous cropping with ryegrass for 18 months in the glasshouse. The non-exchangeable K released from the soil which had received K fertiliser annually for 60 years and the unfertilised soil were respectively 60 and 16 mg. K/100 g. Cropping in the greenhouse lowered the K content of the mechanical separates of the K-fertilised soil to the level in the unfertilised soil. More than two-thirds of the potassium released came from the $< 0 \cdot 3 \ \mu$ fraction in both soils. The internal surface areas of the clay fractions ($< 2 \ \mu$) of the K-treated and untreated soils at Saxmund-ham (measured by R. Greene Kelly) were respectively 260 and 290 m.^{2}/g. These values may differ because the micas and hydrous micas of the untreated soil were depleted of potassium.

The amounts of potassium removed by crops from the Sax-mundham soils over 60 years were estimated by Cooke *et al.* (*J. Soil Sci.* (1958), **9**, 298); they suggest that from one-half to two-thirds of the " native " K removed must have come from the subsoil. Sub-soils are usually less weathered than top-soils, and they may often be important in supplying non-exchangeable potassium to deeply rooting crops. (Arnold.)

Potassium fixation

In measuring added potassium that has been fixed in soils of some long-term experiments at Rothamsted, sulphuric and hydro-fluoric acids were used instead of nitric acid to " strip " the soils progressively. A simplified method is being developed to determine what part of the " fixed " fertiliser K acts as a reserve to maintain the exchangeable K level in Rothamsted soil. This K value may supplement, or even substitute for the exchangeable K value, es-

pecially with soils that have been sampled immediately after an exhausting crop has been grown, and before equilibrium between exchangeable K and fixed K has been re-established. (Johnston and Warren.)

FIELD EXPERIMENTS ON N, P AND K FERTILISERS

Nitrogen for winter wheat

In four field experiments with winter wheat, nitrogen top-dressings in late February caused more lodging than the same amount of nitrogen given either when sowing in October or at the end of April. Nitrogen in April increased yields more than February dressings, which, in turn, were a little more effective than October dressings. The experiments were on heavy soils; only on such land is nitrogen applied in autumn effective, for similar experiments on light land at Woburn showed no response to autumn dressings. (Widdowson and Penny.)

Nitrogen for barley

Six field experiments testing ammonium sulphate on barley showed that combine-drilling was superior to broadcasting on the seedbed at four of the six centres when 0·3 or 0·6 cwt. N/acre was given, but with 0·9 cwt. N broadcasting was better. From fifteen experiments of this kind with barley done in the last 3 years, the average gains from combine-drilling over seedbed broadcasting were:

Rate of N fertiliser				Extra yield of grain from combine-drilling (cwt./acre)
Low...	...	...	...	...	0·9
Medium	...	...	...	...	0·8
High	...	...	...	...	−0·4

The experiments also tested divided dressings. When the medium rate was applied half by combine-drill and half as a late-spring top-dressing, splitting the dressing gave higher yields than drilling at fourteen of the fifteen centres, and the average gain was 1·2 cwt./acre of grain. In 1957 and 1959, but not in 1958, dividing the heavy dressing gave higher average yields than applying all by combine-drill. Combine-drilling the highest rate of nitrogen may have led to the fertiliser injuring germination, and attempts are being made to develop a coulter that separates seed and fertiliser.

In other experiments with barley, 0·5 cwt. K_2O/acre increased yields significantly at two of five centres; twice as much potassium was not worthwhile at any centre. Large increases in yield resulted from 0·3 cwt. N/acre at four centres; 0·6 cwt. further increased yields at only two. The nitrogen response was affected by potassium fertiliser at only one centre. The two years' work shows that 0·5 cwt. K_2O/acre generally suffices for cereals, even on soils with little " available " potassium, and that nitrogen fertilisers give a full return with this level of potassium manuring. (Widdowson and Penny.)

Urea for barley

Urea and ammonium sulphate were compared in four experiments on barley by combine-drilling the fertilisers at rates supplying

0·25, 0·5 and 0·75 cwt. N/acre. The highest rate greatly checked germination and decreased plant establishment, and the medium rate checked growth, though less. Although the heaviest rate of ammonium sulphate slightly checked growth, it gave consistently more grain than urea. Differences between ammonium sulphate and urea were less at two centres drilled in February and greater at the other two drilled in March, in which urea gave significantly less grain than ammonium sulphate at each level of manuring. (Widdowson and Penny.)

Nitrogen for grass

A stand of Italian ryegrass on heavy clay-loam at Rothamsted was used to compare top-dressings of nitrogen applied on 4 November, 4 February or 11 March. When cut on 11 April autumn dressings gave the highest yields; calcium nitrate and ammonium sulphate behaved similarly. This work on grass, like that on winter wheat (described above), shows that nitrogen applied in autumn is not easily leached out from the upper layers of heavy soils, and autumn applications may sometimes be better than spring dressings.

Tests of nitrogen and potassium fertilisers on pure stands of grass in the experiments begun in 1958 (*Rep. Rothamst. exp. Sta.* for 1958, pp. 46–47) were continued in 1959. Fresh dressings of urea–formaldehyde fertiliser were less effective at each cutting than half the equivalent amount of nitrogen applied as " Nitro-Chalk ". The residual effects in 1959 of urea–formaldehyde dressings given in 1958 were no greater than the residual effects of equivalent " Nitro-Chalk " applied in 1958. The experiment begun in 1958 to test different levels of nitrogen and potassium fertilisers on Italian ryegrass showed large gains from nitrogen over the season. Potassium had little effect on yields of the first cut, but increased the second and third cutting slightly. (Widdowson and Penny.)

Effects of fertilisers on forms of nitrogen in grass

Work started in 1958 to examine how fertilisers affect the forms in which nitrogen accumulates in grass was extended in 1959. Italian ryegrass grown on clay-loam soil at Rothamsted contained much more nitrate with sodium nitrate applied before sowing than with ammonium sulphate. Early in the season plots given 1·0 cwt. N/acre produced dry grass containing 0·64% NO_3-N with nitrate and 0·28% NO_3-N with ammonium sulphate. It is worth noting that some people consider that 0·2% of NO_3-N may be dangerous to stock. Grass given ammonium sulphate contained more NH_4-N, amide-N and α-amino-N than when given nitrate. These experiments are being repeated on Italian ryegrass grown on light soil at Woburn. At the first cutting ammonium sulphate, ammonium nitrate, sodium nitrate, calcium nitrate, magnesium nitrate and urea all supplying the same amount of nitrogen gave similar yields. The dressings were repeated for a second cut, but drought stopped growth; the check from drought was accentuated by nitrogen fertiliser, and where heavy dressings had been given, some of the plants died; nitrate caused most damage. (Nowakowski.)

RESIDUAL EFFECTS OF PHOSPHATE FERTILISERS

Acid soils

An experiment started in 1954 to measure the residual values of superphosphate and Gafsa rock phosphate on an acid soil was completed in 1958; results have been reported for the first three years (*Rep. Rothamst. exp. Sta.* for 1955, p. 46; for 1956, p. 48). Table 2 shows grain yields in 1957 and 1958 when barley was grown with adequate nitrogen and potassium fertiliser but with no further phosphate.

TABLE 2

Residual effects of phosphate fertilisers on barley in 1957 and 1958

		Yields of grain (cwt. dry matter/acre)	
		1957	1958
Without P fertiliser		29·4	21·8
Increases due to residues from 3·0 cwt. P_2O_5/acre applied as:			
Superphosphate ... ... { 1954		+5·9 **	+6·5 **
{ 1955		+6·0 **	+4·9 **
Gafsa rock phosphate ... ... { 1954		+2·6	+5·1 **
{ 1955		+3·2	+5·2 **
Standard error of increases ...		±2·01	±0·88

In both years superphosphate applied 2, 3 or 4 years earlier increased yields significantly; in 1958 (but not in 1957) Gafsa rock phosphate applied 2 or 3 years previously gave yields of barley similar to those from residues of superphosphate. Soil samples taken in 1958 were used in a glasshouse experiment (with Close) to measure the residual values of the phosphate fertilisers applied in 1954 and 1955. About 60–80% of the phosphate remaining in the soil from both superphosphate and rock phosphate was isotopically exchangeable and increased yield and phosphorus uptake by ryegrass to the same amount as did an equivalent amount of fresh monocalcium phosphate. The values of superphosphate and Gafsa rock phosphate 4 years after they were applied did not differ in either the glasshouse or the field experiment. A further field experiment, designed to last 6 or more years, was started to compare the residual effects of superphosphate, basic slag, Gafsa rock phosphate, potassium metaphosphate and several nitrophosphates with different water-solubilities. (Mattingly and Widdowson.)

A greenhouse experiment using ryegrass (done with Close) measured the residual value of superphosphate in acid (pH 5·0–6·0) and very acid soils (pH 4·0–5·0) taken from nine field experiments in Great Britain and Japan. The soils differed greatly in mechanical composition and in parent materials, and they had received from 50 to 450 lb. of P/acre. On average about 70% of the residual phosphate was isotopically exchangeable, values for individual soils varied from 36% for a soil from basalt, to 100% for soils from Silurian shales. The mean value is similar to that on acid soil at Rothamsted and is much higher than values for calcareous Rothamsted soils. The residues of superphosphate increased both yield and phosphorus uptake by ryegrass significantly with all soils except that from basalt. The residual value of superphosphate

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was as great on acid volcanic ash soils from the Hokkaido Agricultural Experiment Station in Japan as on an acid soil from Rothamsted. The pH of the soils, and their mechanical compositions, were not correlated with the amounts of isotopically exchangeable phosphate they contained. (Mattingly and Kushizaki.)

Calcareous soils

In calcareous soils at Rothamsted about one-third of the residual phosphate from the continuous application of superphosphate remains isotopically exchangeable (*Rep. Rothamst. exp. Sta.* for 1957, p. 61), a considerably smaller fraction than in acid soils. Some of the factors were studied that influence the amount of exchangeable phosphate in soils from long-term experiments at Rothamsted and Saxmundham. The proportion of the residual phosphate that remains isotopically exchangeable increases with decreasing soil pH. Table 3 shows this effect, and that of continuous manuring with ammonium sulphate on some Rothamsted soils. Ammonium sulphate increased the proportion of residual phosphate in soils that remains isotopically exchangeable, even when soil pH is near 7·0. Applying magnesium and potassium sulphates annually for nearly 100 years to Barnfield has not changed the amounts of isotopically exchangeable P in the soil, either on plots without phosphate or on those that have superphosphate each year. Where nitrogen was given as sodium nitrate, both on Barnfield and at Saxmundham, it increased the size of the crops and decreased both the total amount of exchangeable phosphate and the proportion that remains isotopically exchangeable.

TABLE 3

Effects of ammonium sulphate and soil acidity on the percentage of residual phosphate in some Rothamsted soils receiving superphosphate that is isotopically exchangeable (" A ") in glasshouse experiments

Field			Soil pH	Increase in " A " (mg. P/100 g. soil) from applying superphosphate in the field	Increase in " A " as % of increase in total P
No nitrogen:					
Barnfield	...	...	7·3	13·1	26
Hoosfield	...	...	7·2	27·4	35
Ammonium sulphate:					
Barnfield	...	...	7·3	25·7	42
Broadbalk	...	...	7·0	24·3	44
Agdell	...	...	6·1	8·1	48
Acid soils:					
Sawyers	...	...	5·0	5·0	78

On both the calcareous and the slightly acid Rothamsted soils, and on the calcareous Boulder Clay from Saxmundham, the uptake of P by ryegrass was closely correlated with the total amount of exchangeable soil phosphate. Phosphorus uptake was, however, about 20% greater per unit of exchangeable phosphate from the Saxmundham soils than from the Rothamsted soil. (Mattingly and Close.)

Comparisons of potassium fertilisers

Muriate of potash (containing 60% K_2O) supplies most of the potassium fertiliser used in the United Kingdom. There is no evidence that the chloride benefits crops, although chlorine is an essential micronutrient. With heavy dressings of potash, the chloride raises salt concentrations and may damage growth when fertilisers are applied too close to seed. To avoid this, and to improve quality, some potato growers, and many horticulturists, prefer to use potassium sulphate. Small amounts of potassium bicarbonate (containing 46% K_2O) intended as a fertiliser can now be obtained for experiments. Using bicarbonate removes the risk of injuring crops by the co-ion in potassium fertilisers, and it was compared with muriate of potash and potassium sulphate for potatoes. The yields at Rothamsted were:

				Tons of potatoes/acre
Without potash... ...	...	...	...	7·2
With muriate of potash	...	...	...	10·3
With potassium sulphate	...	...	...	10·6
With potassium bicarbonate ...	...	...	10·8

Bicarbonate gave the highest yield. The tops and tubers contained most chloride with muriate of potash and most sulphur with potassium sulphate. (Cooke, Widdowson and Williams.)

Potassium fertilisers increased yields in three out of six experiments on potatoes done on commercial farms. Yields from muriate and sulphate of potash did not differ consistently. (Widdowson and Penny.)

Concentrated fertilisers

Fertilisers may affect crops through the substances other than the N, P and K they supply. Other ions present increase salt concentrations and may damage crops or affect the intake of other nutrients. Some fertilisers may also be important sources of sulphur, calcium and magnesium. Compound fertilisers have become more concentrated recently. Greater concentration lowers cost to farmers by cheapening packaging, freight and spreading charges; concentrated fertilisers may be better than dilute ones provided they contain less of the useless ions that only increase salt concentrations in the soil, but they might be less satisfactory if the " diluents " in the less-concentrated materials supply plant nutrients. Concentrated fertilisers are therefore being compared with the older standard materials used in most of the field experiments done in this country.

Two concentrated fertilisers, prepared from ammonium nitrate, diammonium phosphate and muriate of potash were compared in 1959 with mixtures of ammonium sulphate, ordinary superphosphate (18% P_2O_5) and muriate of potash that supplied the same amounts of plant nutrients as the newer materials. In potato experiments the concentrated fertiliser contained 15% N, 10% P_2O_5 and 20% K_2O; all fertilisers were applied in the furrows before planting. For barley concentrated fertiliser (containing 20% N, 10% P_2O_5, 10% K_2O) was compared with a granulated mixture of ordinary ingredients (containing 12% N, 6% P_2O_5, 6%

K_2O); both fertilisers were combine-drilled. Table 4 summarises results at Rothamsted and Woburn.

TABLE 4

Comparisons of concentrated and " ordinary " fertilisers

		Without fertiliser	With ordinary fertiliser		With concentrated fertiliser	
			Single rate	Double rate	Single rate	Double rate
Potatoes, yields in tons/acre						
Rothamsted	...	8·5	11·5	13·4	11·5	13·7
Woburn ...	...	4·0	6·7	7·1	6·6	8·0
Barley, yields of grain in cwt./acre						
Rothamsted	...	14·4	27·6	37·7	27·6	37·5
Woburn ...	...	13·8	24·9	30·8	24·4	33·0

Yields of potatoes at Rothamsted and Woburn were identical from the ordinary fertiliser and its concentrated equivalent at the lower rate of dressing, but at the higher rate (1·5 cwt. N, 1·0 cwt. P_2O_5, 2·0 cwt. K_2O/acre) the concentrated material gave slightly higher yields at both centres. The two forms of fertilisers gave identical yields of barley at Rothamsted, but at Woburn concentrated material at the higher rate (0·66 cwt. N, 0·33 cwt. P_2O_5, 0·33 cwt. K_2O/acre) gave significantly better yields. (Cooke and Widdowson.)

THE VALUE OF PHOSPHORUS AND POTASSIUM RESERVES IN SOILS OF THE LONG-TERM EXPERIMENTS

Exhaustion Land experiment

The history of the Exhaustion Land and recent experiments on this site are described elsewhere in this Report (pp. 230–239).

Agdell Rotation experiment

The results of the Agdell Experiment and a description of its soils have been published (*Rep. Rothamst. exp. Sta.* for 1957, p. 252). The site has a wider range of fertiliser residues than the Exhaustion Land, and recent work was planned to value them and to compare methods of soil analysis.

In 1958 and 1959 Italian ryegrass was grown on half of each of the old Rotation Plots. All plots had nitrogen fertiliser for each cutting. Two silage cuts were taken in 1958 and three in 1959 (by Widdowson and Penny), total yields of grass and the amounts of P and K in the crops (determined by Williams) are shown in Table 5 for the two years together. The residues from manuring in the old Rotation Experiment increased yield of grass greatly in both years. In the two years, the PK-treated plots provided 13·7 lb./acre of P, and the NPK-treated plots 19·5 lb/acre of P, more than the old unmanured plots; the average total extra uptake from the four treated plots was 16·6 lb./acre.

The grass removed much K, and average uptake from the four treated plots in 1958 and 1959 together totalled about 160 lb. K/acre more than was taken from the old untreated plots. At these annual

rates of recovery (8 lb./acre for P and 80 lb./acre for K) grass would exhaust the fertiliser residues accumulated during the first century of the experiment completely in about half a century for P and about 20 years for K. (The size of these reserves is interesting, for they were built up by the residues from 4 cwt./acre of superphosphate and 3 cwt./acre of potassium sulphate given once in 4 years.)

TABLE 5

Total yields of grass and contents of P and K for all cuttings taken from the Agdell Experiment in 1958 and 1959

Manuring treatment in Experiment (1848–1951)	Rotation (clover or fallow)	Yield of dry grass (cwt./acre)	P in crop (lb./acre)	K in crop (lb./acre)
None	Clover	53	9·4	156
	Fallow	77	13·9	206
PK	Clover	103	23·6	320
	Fallow	110	27·2	322
NPK	Clover	111	28·8	346
	Fallow	121	33·5	376

The other halves of the Agdell Rotation plots each grew strips of barley, potatoes and sugar beet in 1959. Fresh dressings of superphosphate were tested on each crop to measure the value of the residues from the old phosphate dressings. Although the soil was in poor condition in spring 1959, and the summer was dry, the best soils gave satisfactory yields per acre with full manuring (30 cwt. of barley, 11 tons of potatoes and 15 tons of sugar beet). The responses to fresh superphosphate (summarised in Table 6) confirm that phosphate residue in the soil enough for barley is too little for

TABLE 6

Responses in 1959 to fresh dressings of superphosphate on site of Agdell Rotation Experiment

Manuring and rotation treatment in old experiment		Barley grain (cwt./acre)	Potatoes (tons/acre)	Sugar beet roots (tons/acre)
Responses to 1·0 cwt. P_2O_5/acre applied in 1959				
None	Clover	16·3	3·3	0·3
	Fallow	9·7	4·9	2·2
PK	Clover	5·8	2·6	0·5
	Fallow	0·3	1·9	0·0
NPK	Clover	−1·9	3·2	1·6
	Fallow	0·1	3·6	0·3

potatoes, even though the two crops usually take up very similar amounts of P. The full dressing of superphosphate tested in 1959 (1·0 cwt. P_2O_5/acre) gave higher maximum yields of barley and potatoes on the old Rotation Plots that had received phosphate from 1848 to 1951 than on the old untreated plots, an unexpected result, perhaps attributable to bad soil conditions and dry weather in 1959. Sugar beet gave little response to superphosphate, even on the very P-deficient soils of the unmanured Rotation Plots. (Johnston and Warren.)

Woburn Continuous Wheat and Barley experiments

The classical manuring treatments in these experiments stopped in 1927, but cropping was continued. The previous PK fertiliser treatments affected crop growth, but all yields were poor, and they were irregular because of weeds and soil acidity. The sites were surveyed in 1953 and 1954, chalk was applied to restore all the soil to pH 6, at which the experiments started in 1877, and the land was fallowed to destroy weeds. In 1959 winter wheat was grown on half of each plot and spring barley on the other half, all with nitrogen fertiliser. Most of the plots carried a uniform plant, and samples of the young crops had P contents that were related satisfactorily to soil analyses. Plans are now made to have micro-plot experiments with potatoes and barley on this site in 1960 to measure separately the residual effects of P and K fertilisers applied between 1876 and 1926. (Johnston and Warren.)

MANURING EXPERIMENTS IN FOREST NURSERIES

An account of twelve seasons' work (1945 to 1957) done in collaboration with the Forestry Commission is being prepared for publication, and it is hoped that it will be ready in 1961 (Benzian).

Phosphorus toxicity to yellow lupins

Conifers and green crops are grown in a rotation experiment at a nursery on very acid heathland soil near Wareham (Dorset). The older leaves of yellow lupins (*Lupinus luteus*) grown with fertiliser often die, as sometimes do whole plants. The most severely affected plants contain 2·2% P, and pot experiments at Rothamsted using Wareham soil confirmed that the damage increased with the amounts of monocalcium phosphate applied and with the P contents of the plants. At another nursery near Oxford, on less acid sandy loam, yellow lupins grew normally with the same fertiliser treatment as caused damage at Wareham. (Warren and Benzian.)

MAGNESIUM IN CROPS AND SOILS

Measurements of the magnesium removed by crops and grass were obtained from experiments at Rothamsted and Woburn. Most of the crops examined remove from 4·5 to 6·5 lb. Mg/acre; potatoes at Rothamsted removed only 2·5 lb. Mg/acre, whereas lucerne and sugar beet removed more than 10 lb. Mg/acre. Permanent grass and temporary grass remove rather less than 10 lb. Mg/acre.

The hay crops from Park Grass in 1957 and 1958 were analysed to show the effects of chalk and K fertiliser on the percentage of Mg in the herbage. Where potassium was not supplied, chalk increased the percentage of Mg in the herbage in seven of eight comparisons, on average by about one-third. When potassium was given either as fertiliser or as farmyard manure, the % Mg in herbage was slightly decreased. Chalk and potassium may affect the percentage of Mg in herbage, wholly or in part, because they have changed the botanical compositions on the plots. Potassium has encouraged leguminous plants, which normally contain much Mg, whereas nitrogen has eliminated most of the legumes. Manuring and chalking

have also greatly changed the proportions of different grass species present. Magnesium fertiliser has not altered the effects of the chalk and potassium. One ton of local chalk contains about 10 lb. of Mg, so that the standard dressing, given once in four years, supplies about 18 lb. Mg/acre to the herbage (or 4·5 lb. each year), which is equivalent to about half the amount applied (10 lb. Mg/acre each year) as magnesium sulphate on the treated plots.

Rothamsted and Woburn soils contain about one-fifth as much Mg as K. Average values for Park Grass soils are 0·2% Mg and 1·1% K. The crops from some of the plots of Park Grass that receive only NP or N fertilisers show that the ratio of Mg : K in the crops is about 1 : 5·5. This is similar to the ratio of the total amounts of the elements in the soil, a result that might be expected from the "weathering" of the soil minerals if the Mg and K are closely associated in them. In the crops of the other Park Grass plots, however, the Mg : K ratio is less, varying from 1 : 7 to 1 : 8. (Warren and Smith.)

ARSENIC IN SOILS

Arsenite has been used as a haulm killer for potatoes at Rothamsted and, as there was no information on its after-effects, arsenic levels in soils were measured. Arsenate, formed by oxidation of arsenite, interferes in the method of analysis generally used for small amounts of P in soil extracts, and special attention was given to this aspect of the accumulation of arsenic. Some of the plots of Broadbalk contain 12–15 p.p.m. of As; the Highfield Ley–Arable Experiment soils contain from 5 to 17 p.p.m. Stackyard field at Woburn has 25 p.p.m. and other Woburn soils contain from 10 to 19 p.p.m. of As. The amounts of soil arsenic dissolved by some of the solvents used for readily soluble soil phosphorus were determined. There were no measurable amounts of arsenic in extracts of Highfield and Woburn soils with $0·01M$-$CaCl_2$, citric acid, acetic acid, hydrochloric acid and sodium bicarbonate solutions. The limit of detecting As under the conditions of these tests was 0·1 p.p.m.; this is sensitive enough for all but the $CaCl_2$ extracts, and with these it would be possible to add amounts of arsenic that would affect phosphorus values significantly. Citric acid solution extracted 2 p.p.m. As from Broadbalk soils, and acetic acid, hydrochloric acid and sodium bicarbonate dissolved 0·5 p.p.m. As. None of these amounts would affect the interpretation of phosphorus results for *normal* soils, but on very P-deficient soils, 0·5 p.p.m. As soluble in $NaHCO_3$ might be important.

The amount of arsenite used to destroy haulm is equivalent to about 3 p.p.m. of As in the surface soil. Both arsenite and arsenate react fairly rapidly with soil; in one test 5 p.p.m. of As was added and 60 hours later only 1 p.p.m. was extracted by citric acid, and calcium chloride solution did not extract a detectable amount. Using arsenite as a haulm killer in the normal way will not affect the citric acid, hydrochloric acid and acetic acid methods for determining readily soluble phosphorus in soils, partly because arsenic is rapidly fixed by the soil, and partly because large amounts of phosphorus are extracted relative to the amount of arsenic added.

With calcium chloride and sodium bicarbonate extracts the inter-
ference is likely to be small, because 2 μg. As are needed to give the
same amount of colour as 1 μg. P in the method generally used to
analyse small concentrations of P. Simple modifications to the
method for phosphorus analysis to eliminate interference by arsenic
are being considered.   (Foale and Warren.)

MICRONUTRIENTS IN CROPS AND SOILS

Molybdenum

The amounts of molybdenum in crops from Rothamsted and
Woburn extend over the range 0·50–5 p.p.m. of dry matter.   Be-
cause some lucerne at Rothamsted contained little Mo (0·1 p.p.m.),
special attention was given to this crop.   In reviewing the role of
Mo in plant metabolism Reisenauer (*Soil Sci.* 1956, **81**, 237) recom-
mended that leaves be analysed to diagnose deficiency instead of
whole plants, because he found that the percentage of Mo in leaves
was four times greater than in stems.   He concluded that a re-
sponse to Mo would not be expected when the leaves had more than
0·4 or 0·5 p.p.m. of Mo.

Leaves and stems of lucerne grown in the Ley–Arable Experi-
ments at Rothamsted and Woburn had the following Mo contents:

| | | | | P.p.m. of Mo in dry matter | |
				Leaves	Stems
Rothamsted					
Highfield	...	...	...	...	0·15	0·12
Fosters	...	...	...	...	0·78	0·76
Woburn					
Stackyard	...	...	...	...	0·34	0·20

The concentrations of Mo in the leaves and stems do not show the
large differences reported by Reisenauer, but the levels in lucerne
from the Ley–Arable Experiments in Highfield are well below the
limit he sets for a sufficiency of Mo.   Levels in the comparable
experiment on Fosters Field are well above this limit; at Woburn
the level is border-line.   Samples of lucerne from two other experi-
ments showed that P and K fertilisers did not modify the percentages
of Mo in lucerne; the samples were taken at different times of the
year and in different years, and they had between 0·3 and 0·6 p.p.m.
of Mo.   Other samples showed that the level of Mo in lucerne may
change with the time of the year and with the amount of growth,
but none of the variations from these two factors gave a high value
for Mo in the lucerne of the Highfield Ley–Arable Experiment.
Highfield soil may be deficient in Mo, and amounts in one or two
other soils may be marginal.   Field experiments testing rates of
Mo are planned.   (Warren and Foale.)

*The effects of fertilisers and farmyard manure on micro-nutrients in
    arable crops at Rothamsted*

A series of " reference plots " on Great Field IV at Rothamsted
started in 1956 measure the effects of combinations of N, P and K
fertilisers, and also of farmyard manure, on yields of wheat, barley,

clover, potatoes and kale grown in arable rotation in each year. Crop samples taken in 1956 were analysed for Cu, Mn, Mo and Zn to provide information on the uptake of these elements and to see whether manuring treatments affect the amounts of these micro-nutrients in the crops. N, P, K fertilisers and farmyard manure all depressed the percentages of Cu, Mo and Zn more often than they increased them, presumably because the treatments increased yields and " diluted " the micronutrients in the harvested crop, but the effects were not consistent. Mn contents were usually raised by all the manurial combinations tested. In most of the comparisons all crops (except kale) grown with farmyard manure removed more micronutrients than did crops with full dressings of NPK fertilisers, because farmyard manure gave higher yields than fertilisers. Kale grown with NPK fertilisers yielded better and removed more Cu, Mn, Mo and Zn than kale treated with farmyard manure. Table 7 shows the amounts of the elements removed by the five crops.

TABLE 7

Total amounts of micronutrients removed by five crops grown on the Rothamsted Reference Plots in 1956

	Without manure	With NPK fertiliser	With farmyard manure	With farm-yard manure + fertiliser
	Amounts of elements in g./acre			
Copper ...	58	118	148	147
Manganese ...	334	704	846	1015
Molybdenum ...	3·0	5·4	4·7	4·5
Zinc	295	541	601	743

The total amounts of these micronutrients in the surface soil are compared below with the amounts removed by the five crops together from plots treated with farmyard manure and fertilisers.

				Total amounts in soil	Amounts removed by five crops
				lb./acre	
Cu ...	...	...	...	52	0·3
Mn...	...	...	...	2800	2·2
Mo	...	...	...	2	0·01
Zn ...	...	...	...	220	1·6

If the total amounts present become available to crops these reserves of micronutrients in the top-soil will last for many years of cropping.

The dressings of fertilisers used supplied less micronutrients than any one crop removed; in contrast, farmyard manure replaced as much Cu, Mn and Mo as was removed by the five crops, and nearly as much Zn.

Individual crops removed varying quantities of micronutrients. Clover removed more of each of the elements than did wheat, barley or potatoes. Both clover and kale removed much more moly-bdenum than the other crops. (Williams, Stojkowska, Cooke and Widdowson.)

URANIUM IN CROPS AND SOILS DRESSED FREQUENTLY WITH SUPERPHOSPHATE

Rock phosphates contain about 0·015% of uranium, and superphosphate made from them is slightly radioactive. Soils and crops from several long-term experiments at Rothamsted having superphosphate for many years were analysed for uranium by Mr. G. H. Smith at the National Chemical Laboratory, Teddington, Middlesex. The uranium content of unmanured soils from Broadbalk (Permanent Wheat) and Hoosfield Exhaustion Land (now in barley) was 2·5 p.p.m. U, and there was no evidence that annual applications of superphosphate to Broadbalk (3·5 cwt./acre since 1843) or to the Exhaustion Land (about 3 cwt./acre from 1856 to 1901) have increased the amount of uranium. Cereal straws from both experiments contain $<0·02$ p.p.m. U; superphosphate did not increase the uranium content of the crop. (Mattingly.)

ANALYTICAL WORK

Organic carbon in soil

Determining organic carbon in soils by oxidising with dichromate and titrating the unused dichromate is fast and simple, and inorganic carbonates do not interfere. Many modifications of this basic procedure have been proposed, and several of these were tested. Oxidation of soil organic matter was not complete in any of the methods investigated, nor was 1 equivalent of dichromate oxygen found to be equivalent to 3 g. carbon in all soils. "Carbonised" carbon in materials like coal, soot, graphite and charcoal was partially oxidised so that the titration methods tested could not discriminate between "carbonised" material and soil organic matter. Oxidation of soil organic matter by potassium persulphate was tested with the hope of developing a more selective procedure. The method devised gave quantitative results with sucrose, glycine, oxalic acid, resorcinol, cellulose, chitin, lignin, wheat straw, dried grass, a compost and a range of non-calcareous soils. 2–5% of the carbon in bituminous coal was recovered, 0·2–2% from anthracite and 0–0·5% from graphite. But 40–45% of the carbon in wood charcoal was recovered, and even more from soot; persulphate oxidation therefore is not a promising way of distinguishing soil organic matter from other carbonised materials. (Bremner and Jenkinson.)

Scintillation counting of ^{14}C.

A method was needed to measure precisely the activity of carbon dioxide evolved when incubating soil with labelled plant material. A black dye was dissolved in the active solution, which was then placed in a cylindrical cell having a base covered with a thin film of plastic phosphor. The light pulses from the cell were counted in a scintillation counter. The results were independent of the volume and colour of the liquid in the cell, and of the chemical form of the carbon. Dissolved substances such as 10% solutions of glycine, sodium acetate, sucrose, sodium pyrophosphate and sodium sulphite had little effect and altered the count rate by less than 5%. Acid

solutions had to be neutralised before being put in the cell. Although the method is rapid and reproducible, it is inefficient, and for lower activities a liquid scintillation method based on the absorption of CO_2 in caesium hydroxide, which is being developed, is more promising. (Jenkinson.)

Forms of nitrogen in soils and plants

Work on nitrogenous constituents of soils and plants is hindered by lack of rapid and specific methods of determining different forms of nitrogen. When using labelled nitrogen the methods of analysis must give a product that can subsequently be analysed by the mass spectrometer; the favoured product is ammonia, which is converted to gaseous nitrogen by treating with alkaline hypobromite. To meet these requirements, progress was made with methods for determining ammonium-, nitrite-, nitrate-, hexosamine- and α-amino-N. The different forms of nitrogen are converted to ammonia, which is determined by steam distilling for 3–4 minutes using a specially designed micro-distillation apparatus. Ammonium-N is determined by steam distilling with magnesium oxide, and nitrate-N by continuing the distillation after adding titanous sulphate. When nitrite-N is present one sample of the test solution is treated with sulphamic acid to destroy nitrite, and a duplicate sample treated with acidified permanganate to oxidise nitrite to nitrate, the excess permanganate being destroyed with acidified ferrous sulphate. Both samples are distilled with MgO, and nitrite-N is estimated by difference. Hexosamine-N is determined from the ammonia liberated by steam distilling with a phosphate–borate–thiosulphate mixture (pH 11·2). α-amino-N (amino-acid-N) is determined by treating with ninhydrin at pH 2·5 for 10 minutes at 100° and estimating the ammonia liberated by steam distilling the ninhydrin reaction product with the mixture used in the method for hexosamine-N. These methods are simple and rapid, and the same apparatus and standard solution are used in each. They are not affected by inorganic salts likely to occur in plant or soil extracts and appear to be highly specific. With over fifty nitrogenous compounds, including amino-acids, purine and pyrimidine bases, and labile compounds such as glutamine, asparagine, glucosamine and urea, none yielded ammonia or volatile base under the conditions of the method used to determine ammonium-N. With plant extracts, results by this steam distillation technique agreed closely with those by a low-temperature vacuum distillation method of determining ammonium-N in the presence of labile nitrogen compounds. Ammonium-, nitrite- and nitrate-N added to soil and plant extracts was recovered quantitatively. The method of determining α-amino-N gave quantitative results with 19 of 26 amino-acids tested; low results were obtained with cystine, cysteine, tryptophan, proline and hydroxyproline, and high results with arginine and ornithine. Attempts (with Dr. M. Salomon) to determine α-amino-acids by estimating the ammonia formed in their reaction with peri-naphthindan-2 : 3 : 4-trione hydrate failed. (Bremner.)

Nitrogen in grass

Three methods of determining NH_4-N in water extracts from grass were compared. The microdiffusion method used by Bremner and Shaw (*J. agric. Sci.* **46**, 320) gave high values because ammonia was released from labile nitrogen compounds by enzyme action during the 40-hour incubation used. The new method developed by Bremner, and described above, agreed well with the established method of G. W. Pucher, H. B. Vickery and C. S. Leavenworth (*Ind. Engng Chem. Anal. Ed.* 1935, **7**, 152). (Nowakowski.)