Report for 1958

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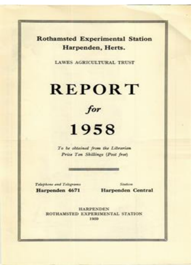

Chemistry Department

G. W. Cooke

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CHEMISTRY DEPARTMENT

G. W. Cooke

G. H. Owen left in January to take a post at the University College of North Wales. T. Z. Nowakowski joined the staff in April, M. St. J. Foale in May and Miss Marie Blakemore in August.

J. M. Bremner returned after a year in the U.S.A. on a Rockefeller Foundation Fellowship. A. C. D. Newman went to Russia in July, where he will spend a year working mainly at the University of Moscow under an exchange scheme organized by the Russian Ministry of Agriculture, the British Council and the Agricultural Research Council. His place has been taken by Dr. B. P. Pleshkov of the Timiryazev Agricultural Academy, Moscow. B. Benzian and J. K. R. Gasser attended a meeting of Commissions II and IV of the International Society of Soil Science in Hamburg in August. F. V. Widdowson studied field-experiment techniques and results at experimental stations in Denmark, Sweden and Norway. G. W. Cooke attended the Third Congress of the Association Internationale d'Études Phosphatières at Biarritz in October and gave two papers.

P. W. W. Daborn of the Forestry Commission returned to the Commission's Research Station in August. J. W. O. Jeffery of the Colonial Research Service left in November for Sierra Leone after receiving training during the year in field experimentation and soil fertility work. D. P. H. Tucker joined the department in October for similar training. B. O. E. Amon (Nigeria), P. Arambarri (Spain), H. H. Bluejack (Nigeria), S. N. Chakravarti (India), M. Kushizaki (Japan), J. Rodriguez (Spain), M. Salomon (U.S.A.) and Miss A. Stojkovska (Yugoslavia) all worked in the department during the year.

K. Shaw, now of the National Agricultural Advisory Service, obtained the Ph.D. Degree of London University for work carried out in the department.

Soil Organic Matter

Organic matter binds soil particles together and increases aeration, drainage, root range and water-holding capacity. Some of these important effects are not easily achieved in other ways. The practical value of increasing the supply of organic matter in a soil is difficult to define because the physical effects of improved soil condition on plant growth depend on the type of soil, the season and the kind of crop; in addition, the changes in nutrient supply, which are linked to changes in organic matter, themselves affect crop growth, and it is rarely possible to separate and measure physical effects alone. Organic matter may be increased by applying organic manures or waste materials; as these also supply plant nutrients, organic manuring increases both the physical and chemical sides of soil fertility. Soil organic matter is also increased by growing grass continuously, but when the grass is cut and carried away so many plant nutrients are removed that chemical fertility is depleted although organic matter reserves, and soil condition, may be improved by the grass. Some of the factors that affect the balance between additions and losses of organic matter are being investigated together with the changes in plant nutrient supplies that are involved.

Changes caused by leys and by arable cropping

Organic matter accumulates in soils under temporary or permanent grass and decreases when land is ploughed from grass for arable cropping. Changes of this kind are being measured in the soils of the ley–arable experiments on Highfield and Fosters Field at Rothamsted. The two fields provide an interesting contrast, as Highfield was ploughed from very old pasture when the experiment was started whereas Fosters had long been in arable cropping. Both experiments test 3-year rotations, a 3-year ley as treatment phase being followed by 3 years of arable test crops (wheat, potatoes and barley). Table 1 gives the organic carbon determined after one 6-year cycle, the losses from cropping (relative to the organic matter status under permanent grass on Highfield) and the gains from leys (relative to the organic matter level under permanent arable cropping on Fosters).

TABLE 1

Amounts of organic carbon in the soils of the Rothamsted ley–arable experiments

(Measurements refer to the surface 12 inches of soil)

	Highfield		Fosters Field	
	Carbon, %	Loss (relative to permanent grass), %	Carbon, %	Gain (relative to arable), %
Continuous treatment with				
Permanent grass ...	3·22	—	—	—
Reseeded grass	3·02	0·20	1·68	0·26
All-arable rotation ...	2·74	0·48	1·42	—
Ley–arable rotation, 3 years arable crops and				
3 years of lucerne ...	2·75	0·47	1·56	0·14
3 years of grazed ley ...	2·83	0·39	1·60	0·18
3 years of cut grass ...	2·78	0·44	1·64	0·22

On Highfield about one-seventh of the organic carbon present when the land was ploughed from grass was lost during 6 years of arable cropping; on this highly organic soil the rate of loss was much the same when 3 of the 6 years of arable crops were replaced by lucerne or by a grass–clover ley. At the lower level of organic matter on Fosters Field the introduction of three years of ley increased the carbon content by 10–15 per cent. Reseeded grass, grown for the whole of the 6-year period on Fosters, increased the original carbon content of the soil by nearly one-fifth. The results illustrate both the rapid loss in organic matter when grassland is ploughed for arable cropping and the slow increase when old arable land is sown to grass or is cropped with a rotation including a ley. (d'Arifat and Warren.)

On light soils continuous arable farming may decrease organic-matter levels so much that some crops do not succeed for reasons not clearly understood. On parts of the headland of Stackyard Field (Series C) at Woburn cereals grow very poorly. The land contains little organic matter and in 1958 the mineral nitrogen level in the soil determined the amount of growth made by barley; soil acidity also directly or indirectly affected growth, though much less. Some other factor or factors may be involved, and investigations will be continued in 1959. (Warren and Johnston.)

Changes caused by ploughing in straw

The changes in soil organic matter levels caused by ploughing in straw were measured in the Three-Course Rotation Experiment at Rothamsted. Dressings of straw ploughed-in at the rate of 53 cwt./acre every second year (and also compost made from the same amount of straw) increased the soil organic carbon level by 0·1 per cent and soil nitrogen by 0·005 per cent over 18 years. There was also a small increase in the value for " mineralizable " nitrogen on the plots that had had straw or compost. These changes in organic matter are inseparable from the changes in the potassium status of the soils caused by the straw. Values for K soluble in dilute acetic or hydrochloric acids were increased by 1 to 1·5 mg. K/100 g. of soil on plots that received compost or straw. (d'Arifat, Johnston and Warren.)

Forms of organic matter in soils

On land where arable crops have been grown continuously for long periods without adding organic manures, soil organic matter generally decomposes to release inorganic nitrogen at a slow but relatively constant rate. In contrast, recent additions of organic matter decompose rapidly and release nitrogen much more quickly. This behaviour complicates attempts to forecast the value of soil nitrogen reserves for crops. There is at present no chemical way of distinguishing between the " old " and " new " forms of soil organic matter, and an attempt is now being made to follow the changes when plant remains decay in soil. Ryegrass uniformly labelled with ^{14}C was grown from seed in a specially-constructed growth chamber and methods of following its decomposition in soil are being developed. (Jenkinson.)

NITROGEN IN SOILS

Fixed ammonium

Work on ammonium fixation in soil showed that much ammonia-N is taken up by soil organic matter when soils are treated with NH_3 gas. Treating such ammoniated soils with N–HF : N–HCl releases more ammonium-N than does treatment with N–KCl. The N–HF : N–HCl method of determining clay-fixed ammonium in soil previously described (*Rep. Rothamst. exp. Sta. for 1957*) should be modified for use with soils that have received nitrogen as ammonia gas or ammonium hydroxide by including a pre-treatment with hot *N*–KOH to eliminate interference by ammonia-N fixed by soil organic matter. Other investigations made in collaboration with workers at Iowa State College and at the University of Illinois show that methods of determining clay-fixed ammonium in soil based on the use of cation exchange resins or of fine grinding are unlikely to be useful. (Bremner.)

The effect of low-temperature storage on inorganic nitrogen in soil

When freshly taken samples of moist soil are stored at ordinary temperatures, their contents of inorganic nitrogen change, and any laboratory measurements of ammonium and nitrate must be done immediately. The effects of storage at temperatures near to, and below, freezing point, were therefore studied. Inorganic-N contents of a series of soils were doubled during 28 days storage at 2°. Alternate freezing (—10°) and thawing (2°) during 32 days, such as is necessary during repeated sampling of frozen soil samples, also greatly increased inorganic nitrogen. Both these pre-treatments also affected the amounts of inorganic-N released when the soils were incubated at 25° for 21 days. Continuous storage at —10° for 32 days had no effect on the inorganic-N contents of the soils or on their behaviour when incubated. Freezing the moist soils was also a good way of conditioning them for sieving and sub-sampling. (Gasser.)

Changes in inorganic nitrogen levels in soil

In an experiment on wheat a part of each plot was uncropped and inorganic-N levels were followed both under the crop and in adjoining bare soil. Nitrate fertilizer applied in October was lost from the upper 6 inches of uncropped soil by mid-January, but where ammonium fertilizer was applied some was still retained in the top-soil. The amounts of inorganic-N in the surface soil of all the plots which had received their nitrogen in autumn (either as ammonium or as nitrate) were the same as the amounts in unfertilized plots from March onwards. Nitrogen fertilizers supplying 100 lb. N/acre and applied in mid-March were taken up rapidly by the wheat. By June, three-quarters of the N supplied by ammonium sulphate had been removed, and five-sixths of a dressing of calcium nitrate. On uncropped plots the nitrogen fertilizers applied in March persisted through most of the season, but by September all of the calcium nitrate had been lost from the surface soil and only one-sixth of the inorganic-N from ammonium sulphate dressings remained.

In a field experiment on uncropped land, increasing the amount of cultivation did not increase the amounts of inorganic-N in the surface soil.

A few plots of the Broadbalk Wheat Experiment were sampled at intervals through one season, and the amounts of nitrate in the surface soil were determined to provide information relevant to the work at other centres. On the section of Broadbalk fallowed all summer, the soil on the plot that receives farmyard manure each year contained 44 p.p.m. NO_3–N in September; on plots receiving no manuring or inorganic fertilizers only, the levels were 10–15 p.p.m. NO_3–N. Where wheat had been grown the levels were only 5 p.p.m. on the farmyard manure plot, and 1–2 p.p.m. NO_3–N on the other plots. The nitrate content of the fallowed section fell steadily during autumn; nitrate levels in the sections which had carried wheat rose for a time during October through cultivating and ploughing the stubble. By November the nitrate levels of plots in sections that had carried wheat were the same as those of corresponding fallowed plots. On plot 15, which received 83 lb./acre of N as ammonium sulphate in autumn, the whole of this dressing had been lost from the surface 6 inches by March. Nitrogen fertilizers applied to other plots in March temporarily increased inorganic-N levels, but all the added N (83 lb./acre) had gone from the surface soil by mid-June. (Gasser.)

Mineralizable-N in soils

Investigations designed to correlate the "mineralizable-N" (measured by incubating soils) with the responses of crops to N fertilizers in field and pot experiments have been continued. (Gasser and Close.) The mineralizable-N values of air-dried soils stored for 6 months exceed those obtained when the soils are incubated immediately after air-drying. This appears to be a general effect; as it may interfere with the application of mineralizable-N values in assessing soil nitrogen status, the effects of various methods and times of storage are being studied. (Gasser.)

Field Experiments on Nitrogen Fertilizers

Cereals

Although farmers are generally advised that they should apply all the nitrogen fertilizer needed by autumn-sown cereals as a top-dressing in spring, many apply part or all of it at sowing time; in addition, there is little experimental evidence on the best time of applying spring dressings of nitrogen for modern stiff-strawed varieties. Capelle wheat was sown in October 1957 in six experiments which tested seedbed dressings of ammonium sulphate (supplying 0·6 and 1·2 cwt. N/acre) against equivalent top-dressings applied either in mid-March or in mid-May. Also, divided dressings, applied either at two, or at all three of the dates of manuring, were compared with single dressings. At harvest three of the experiments were standing and the other three were severely lodged. At the first three centres March dressings produced the highest average increases in yield, and May dressings the lowest; autumn applications were intermediate. Divided dressings gave lower yields than single dressings applied in March. There were large increases in yield from the first dose of nitrogen at all three centres, and the extra yields given by the second increment were profitable at two of the three centres. At the other three centres lodging decreased average yields; March dressings gave the lowest, and May dressings the highest, mean increases. March dressings caused severe lodging, May dressings slight lodging and autumn dressings had an intermediate effect.

Work on combine-drilling fertilizers with barley seed was continued in 1957 and 1958 to examine the possible risks of applying the whole of the nitrogen needed for a full crop through a combine-drill, and to see whether benefits from drilling as compared with broadcasting were maintained when heavier rates of manuring were used. In 1957 the barley was sown on badly prepared seedbeds, and a spell of dry weather followed. Under these conditions drilling a heavy dressing of ammonium sulphate (0·9 cwt. N/acre) delayed emergence by 7–10 days, 0·6 cwt. N/acre gave a slight check and 0·3 cwt. N/acre was not harmful. In 1957 drilling gave higher yields than broadcasting at the low and medium levels of manuring, but was inferior to broadcasting at the highest rate. There was no check to growth in the moister and better-prepared seedbeds used in 1958, and drilling ammonium sulphate gave more barley grain than broadcasting at each level of manuring. Drilling adequate quantities of nitrogen with the seed of spring cereals does not seem to be dangerous, and higher yields will usually be obtained from dressings applied in this way.

The amounts of potassium fertilizers usually recommended for barley are based on pre-war experiments with older varieties and much smaller dressings of nitrogen than are justified now that new stiff-strawed varieties are grown. Four barley experiments were laid down in 1958 on potassium-deficient soils to measure the effects of potassium dressings used with medium and high rates of nitrogen. Yields were decreased in two experiments by the high rate of nitrogen (0·8 cwt. N/acre), as the crops were severely lodged, and at these centres potassium fertilizer had little effect. In the other two experiments there were responses both to nitrogen and to potassium and 0·9 cwt. K_2O/acre gave higher yields than 0·45 cwt. K_2O/acre. (Widdowson and Penny.)

Forms of nitrogen for kale

One experiment on kale compared seedbed dressings of ammonium sulphate, calcium nitrate and urea supplying 1·0 and 2·0 cwt. N/acre. Seedbed dressings of calcium nitrate and urea both decreased plant establishment considerably, and urea more than calcium nitrate, but at harvest both these fertilizers gave higher yields than ammonium sulphate. The crop responded well to nitrogen fertilizers, and yields were increased five times by the heavy dressings; nitrogen applied partly to the seedbed and partly in mid-season gave slightly higher yields than dressings applied wholly to the seedbed. (Widdowson and Penny.)

Grass

Pure stands of four kinds of grass (perennial ryegrass (S.24), timothy (Scotia), cocksfoot (S.37) and meadow fescue (S.215)) were established in spring 1958 to measure the responses of the individual species to three levels of nitrogen. The grasses were cut at silage stage. Unmanured yields of the four species were similar; at the two cuttings taken in 1958 cocksfoot gave the largest responses.

Another experiment was laid down with newly sown S.22 Italian ryegrass to measure the response to several levels of nitrogen fertilizer in the presence and absence of potassium dressings. Three cuts produced a total yield of about 4 tons/acre of dry matter on heavily manured plots; 0·3, 0·6 and 0·9 cwt. N/acre were applied before each cut, and there were good responses for each additional dose. There were no responses in 1958 to potassium fertilizer at any of the levels of nitrogen given.

Attempts to obtain a slowly acting nitrogen fertilizer for grass have been continued. A commercially produced batch of urea–formaldehyde (" Urea-form ") was applied as a single dressing and compared with single and with repeated dressings of " Nitro-Chalk " supplying the same amount of total nitrogen in an experiment on S.22 Italian ryegrass. At the first cutting " Urea-form " gave a yield similar to that given by only one-third as much nitrogen applied as " Nitro-Chalk ", and afterwards " Urea-form " had little effect on the yield. When " Urea-form " and " Nitro-Chalk " were both applied as a single dressing before sowing, " Nitro-Chalk " gave consistently higher yields at the first and also at later cuttings. It is clear that a material of the type tested in this experiment is not as useful for grass as inorganic fertilizers and it is very much more expensive per unit of N. (Widdowson, Penny, Williams and Cooke.)

Ammonium sulphate, calcium nitrate, ammonium nitrate and urea were compared in small-scale field experiments on permanent pasture and on newly sown Italian ryegrass; both swards were cut several times at silage stage, and all the fertilizers greatly increased the yield. The materials listed were applied at 0·5 and 1·0 cwt. N/acre and were compared both as solids in the ordinary way and as solutions containing 5 per cent N. Tests were also made of dilute ammonia solution containing 5 per cent N. This damaged permanent grass severely and did not increase the yields; ammonia solution applied to the seedbed before sowing ryegrass did not affect germination but gave lower yields than the other nitrogen fertilizers. All the fertilizers tested (except ammonia solution) gave very similar yields from permanent grass, whether applied as solids or as solutions. Later in the season tests were made of dressings delayed by 14 days as compared with those usually applied immediately after taking a cut. " Late " dressings gave smaller responses than " normal " dressings, but the grass contained more nitrogen. In the experiment with Italian ryegrass, calcium nitrate was significantly better at both levels of dressing than the other fertilizers. Except for ammonium nitrate, all the fertilizers gave significantly higher yields when applied as solids than when applied in solution. However, the difference is small, so fertilizers in solution can be used on grassland when it is convenient to do so without much loss. (Nowakowski and Cooke.)

Effects of nitrogen fertilizers on the inorganic nitrogen in grass

Produce from the experiments testing solid and liquid fertilizers was used to investigate the effects of nitrogen dressings on the amounts of water-soluble ammonium and nitrate in the grass. A sample was macerated with water, and the ammonium and nitrate contents of the aqueous extracts were determined by the method of Bremner and Shaw (*J. agric. Sci.* **46** (1955), 320–328). Measurements of nitrate on both fresh and dried samples of grass were satisfactory, but labile nitrogen compounds appeared to be decomposed by the magnesium oxide used in the ammonium determination;

this cause of interference is being investigated. Ammonium levels in the grass were increased by increasing rates of nitrogen manuring, but the form of nitrogen fertilizer and the method of application had little effect. The type of fertilizer and the time and method of application had very large effects on the amounts of NO_3–N in the grass (Table 2). Nitrate contents of the grass rose to very high levels when calcium nitrate was applied; ammonium sulphate gave much lower levels and the values in grass grown with ammonium nitrate were intermediate. When dressings were applied late (i.e. 14 days after the normal dressings) nitrate levels were generally greater. In the experiments on both permanent grass and newly sown ryegrass the nitrate levels were higher when the fertilizers were applied as solids than when they were given in solution. (Nowakowski and Cooke.)

TABLE 2

The effects of nitrogen fertilizers on the nitrate-nitrogen in grass

(All fertilizers supplied 1·0 cwt. N/acre)

	Form	Time * of application	NO_3–N in parts per million in dry matter of grass	
			Permanent grassland	Newly sown ryegrass
Without N	—	—	61	29
Ammonium sulphate	Solid	Normal	481	474
	Solution		234	257
	Solid	Late	800	—
	Solution		336	—
Ammonium nitrate	Solid	Normal	1,492	1,409
	Solution		316	301
	Solid	Late	1,309	—
	Solution		848	—
Calcium nitrate	Solid	Normal	946	1,479
	Solution		221	564
	Solid	Late	2,134	—
	Solution		1,124	—

* "Normal" applications were given just before the grass had begun to grow, "late" dressings were 14 days after this date.

PHOSPHORUS IN SOILS

Phosphate in acid soils

Soils from the plots of the Park Grass and Broadbalk Experiments, which had received the same manuring on each field but differed in pH, were used to investigate the effect of changes in pH on labile phosphate values. In Broadbalk soils both the total labile pool, and the phosphate concentrations in 0·02*M*–KCl extracts, were lower on the more acid soils. In contrast, on Park Grass the more acid plots had larger pools of total labile soil phosphate and gave higher concentrations of phosphate when extracted with KCl solution. These differences may be related to the different contents of organic matter in the two soils. (Talibudeen.)

The equilibrium concentrations of iron, aluminium and orthophosphate ions were measured in suspensions of acid soils in 0·02*M*–KCl solution. The ionic products of the solubility of compounds of the type (Fe^{3+} or Al^{3+})$(OH)_2 \cdot H_2PO_4$ were calculated for groups of English and Indian soils. For soils with pH values (in 0·02*M*–KCl solution) of 3·6–4·2 the ionic products were very similar to the published solubility product values of synthetic preparations of iron and aluminium phosphates having the compositions stated. The ionic products calculated in this way for the phosphates in English soils were about 200 times greater than the average values for the Indian soils. The relationships between the potentials of dihydrogen phosphate and the hydroxide of the trivalent cation suggest that, in soils having pH values above 5·2, adsorption complexes of orthophosphate ions and the metal hydroxides are formed. In more acid soils compounds of the composition postulated above may exist in admixture with the hydroxides of iron and aluminium. (Chakravarti and Talibudeen.)

The reactions between 5 per cent suspensions (in 0·02*M*–KCl solution) of several clay minerals with a dilute phosphate solution ($4 \times 10^{-5}M$) were studied to find how phosphate influences the rate at which the minerals break down and the compositions of the products formed. For all the pH values used (3, 4 and 5), phosphate treatments raised the aluminium concentrations in the mineral suspensions. This effect was obtained with St. Austell and Merck kaolinites, with Wyoming bentonite and glauconite. Phosphate lowered the iron concentrations of the suspensions in contact with the kaolinites, but increased the concentration when the three-layer minerals were used. It appears that treatment with phosphate solution may degrade all clay mineral surfaces. The process is slow with kaolinites, and at pH 3 it probably reaches a peak 3 months after treatment begins; at higher pH values there is less total breakdown, but it is at a maximum only a month after applying the phosphate. With the three-layer minerals, breakdown was maximal after a month, at all pH values tested. A mild treatment with phosphate for 1 month dissolves aluminium and iron from three-layer minerals but with the two-layer minerals only aluminium is removed and the reaction is slower. With such degradation by phosphate, free silica must accumulate in the system. (Chakravarti and Talibudeen.)

Phosphate in calcareous soils

An investigation of the effects of organic anions and of temperature on the total labile phosphate (measured by isotopic exchange) has now been completed. In neutral and calcareous soils the labile soil phosphate is decreased by the presence of $10^{-3}M$ concentrations of citrate and diethyl-barbiturate ions; only that fraction of the labile soil phosphate which exchanges *slowly* is affected, and the effect is more definite with the diethyl-barbiturate ion. Citrate ions always increase the amount of labile phosphate in solution, and do so greatly at concentrations above $10^{-3}M$. Both ions speed up the process of isotopic exchange, but citrate is more effective than diethyl-barbiturate.

A group of calcareous soils containing varying amounts of total phosphorus were used to investigate the effects of different temperatures on measurements of isotopically exchangeable phosphate made in a suspension of soil in 0·02*M*–KCl solution. All the quantities measured (rate of solution of phosphate, equilibrium concentrations, labile phosphate and its components, and also rates of isotopic exchange) changed regularly for all soils as the temperature was increased from 25° to 35°. When using soils with high phosphorus contents these changes continued regularly up to 45°; however, in soils containing less phosphorus there were abnormal increases in labile phosphate, equilibrium concentration and rate of exchange at 45°, suggesting that a new and more labile phosphate phase was formed at this temperature. The new phase appears to be associated with the slowly exchanging component, as its rate of exchange increases ten times between 35° and 45°, which is double the rate of change in soils of high phosphorus status. This work is being continued to see whether the apparent alteration in the calcium phosphates is due to hydrolysis at the higher temperature or to the presence of KCl.

Other experiments on neutral soils have tested the effect on labile phosphate of varying both the cations present in the exchange complex and also the extracting solution. The amount of labile phosphate was usually affected only slightly by varying the cation, but sodium soils generally gave higher values. In two anomalous soils the labile phosphate in a sodium system was much higher than in a calcium system; this appeared to be due to the solution of organic phosphate. (Arambarri and Talibudeen.)

The isotopic exchange of calcium ions in aqueous solution with precipitated calcium carbonate was studied as a prelimary to investigating the absorption of orthophosphate ions by calcium carbonate. The kinetic features of the reaction are:

(i) a very fast exchange which is mostly complete after ½–1 hour;
(ii) a slow reaction which continues indefinitely.

The former is probably true surface exchange, whereas the latter may be due to exchange with layers deeper than the surface layer or may be the result of recrystallization. By assuming that the most frequently occurring crystal face in the calcium carbonate is the rhombohedral cleavage face (microscopic examination confirms this), it was calculated that there are two calcium atoms per 40·2 Å.². The specific surface calculated by using this figure is given below:

Ca concentration in solution, $M \times 10^{-4}$	Specific surface, M^2/g.
1·6	0·155
2·1	0·160
4·0	0·139

The specific surface calculated from the size analysis (determined by a sedimentation velocity method) was 0·076 m.²/g. The difference between the " geometric " surface and the exchange surface may be partly due to the shape of the particles (because the geometric surface is based on that of equivalent spheres) but as this shape factor is unlikely to be as large as 2, additional internal surfaces must be involved. The exchange surface is, of course, the most important quantity in studies of the adsorption of phosphate on calcium carbonate. (Newman.)

"Available" soil phosphate

Most methods of analysing soils to determine phosphate are empirical, and may fail if the extractant used dissolves phosphate which cannot be used by the crop grown. ^{32}P-labelled superphosphate was added to soils, which were then extracted with several conventional reagents to see whether they dissolved phosphate unable to exchange with labelled superphosphate. Total exchangeable phosphate ("A") values were measured for these soils in a greenhouse pot experiment on ryegrass. The acid reagents used (1 per cent citric acid, 0·5M-acetic acid, 0·002N-sulphuric acid and 0·3N-hydrocholoric acid) all gave much higher mean values for "available" P (27–32 mg. P/100 g. of soil) than the "A" values measured in the pot experiment (average value 19 mg. P/100 g. of soil). An acetic acid–sodium acetate buffer solution and a 0·5M-sodium bicarbonate solution at pH 8·5 gave mean values (19 and 17 mg. P/100 g. of soil respectively) which were closer to the "A" values determined in the pot experiment. Acid reagents dissolve more soil phosphate than is contained in the pool of latent phosphate crops can use. Two acid sandy soils derived from the Trias gave an extreme example of this effect; when they were extracted with citric acid nearly all of the inorganic phosphate was isotopically exchangeable, but in the greenhouse experiment little more than half was exchangeable. (Mattingly, Pinkerton and Close.)

It is very difficult to analyse satisfactorily by conventional methods for "available" phosphate when soils contain much free calcium carbonate. Several soils of the Sherborne Series derived from Oolitic Limestone were examined in joint work with Mr. R. D. Russell of the National Agricultural Advisory Service. The amounts of phosphate extracted from the soils by 0·5M-$NaHCO_3$ at pH 8·5 and the isotopically exchangeable phosphate were both closely related to the phosphate status of the soils measured in pot experiments. The phosphate concentrations of the soils measured in 0·01M-$CaCl_2$ solution were less useful. It appeared that responses to phosphate might be expected in soils containing less than 0·9 mg. P (soluble in bicarbonate solution) or having "A" values of less than 7 mg. P/100 g. of soil. (Mattingly and Close.)

Work on the Exhaustion Land and Four-Course Rotation experiments at Rothamsted showed that, even for soils with small amounts of calcium carbonate, acid extractants gave high values which did not agree with the performance of crops. Extracting these soils with sodium bicarbonate solution was satisfactory, and this method was also most suitable for examining the soils from the Agdell Experiment. The multiple cropping planned for Agdell in 1959, together with the proposed changes in the Barnfield Experiment, will provide excellent material for further tests on this and other methods. (Warren and Johnston.)

POTASSIUM IN SOILS

Removal of potassium by crops

When arable root and forage crops or grass are removed from land much potassium is carried away. When cropping of this kind is continued for long, soil potassium is depleted and must be replenished by manuring if crop yields are to be maintained. In the ley–arable experiments at Rothamsted, K-deficiency occurred in test crops following 3 years of either cut grass or lucerne. The crops grown in several recent years were analysed to provide a basis for applying the extra potassium needed to maintain both the K-status of the soils and the crop yields (Table 3). Supplementary dressings of potassium fertilizers, equivalent to the amounts of potassium removed by the leys, have now been applied since

TABLE 3

Amounts of potassium removed by the treatment crops in the Rothamsted ley–arable experiments

(Cwt. of K/acre/year)

	Mean values for 1954 and 1955		Mean values for 1956 and 1957	
Field (history)	Highfield (old grass)	Fosters Field (old arable)	Highfield (old grass)	Fosters Field (old arable)
Treatment cropping with leys				
Cut grass:				
Year 1	1·7	1·3	2·0	1·4
Year 2	1·1	1·3	2·2	2·0
Year 3	0·6	1·0	1·8	1·8
Lucerne:				
Year 1	0·7	0·7	0·7	0·5
Year 2	1·5	1·7	1·7	1·8
Year 3	1·1	1·2	1·3	1·8
Grazed ley:				
Year 1	1·1	1·0	0·8	0·6
Year 2	1·4	1·1	1·0	0·8
Year 3	1·3	1·0	0·6	0·6
Permanent cropping				
Reseeded grass grazed ...	1·0	1·0	0·8	0·6
Reseeded grass cut for hay and then grazed:				
Hay period	1·2	1·2	1·2	0·7
Grazed period	0·4	0·4	0·5	0·6
Permanent grass grazed ...	0·9	—	0·8	—
Permanent grass cut for hay and then grazed:				
Hay period	1·0	—	1·3	—
Grazed period	0·4	—	0·6	—
Arable rotation treatment				
Seeds hay	—	—	0·7	0·7
Potatoes:				
Without farmyard manure	—	—	0·7	0·8
With farmyard manure	—	—	1·2	1·1
Oats (grain + straw) ...	—	—	0·4	0·3

1956. The two pairs of years, 1954 with 1955 and 1956 with 1957, therefore compare K uptakes by the ley crops for two levels of K manuring. On average of the 2 years before supplementary potassium fertilizer was applied, the uptake of K by the cut grass grown on Highfield (the old grassland soil) decreased markedly with the age of the ley; there was only a small decrease on the old arable site, where the soil contained initially more readily soluble K than the old grassland soil. Applying extra K fertilizer in 1956 and 1957 prevented this fall in K uptake on the cut-grass plots. In the first period first-year lucerne removed less K than was taken up by first-year cut grass; uptake by lucerne was most in the second year and decreased in the third; the extra potassium given in the second period maintained the level of K uptake by third-year lucerne on the old arable soil but not on the old grassland soil. In contrast, where the leys were grazed the uptakes of potassium in the first period were very similar for all stages of the ley and for both soils. In the second period the uptakes by grazed ley decreased to about two-thirds of the previous values for both soils and all 3 years; this was due to lower yields and not to a fall in the potassium contents of the grass, which were maintained at about 3·5–4·0 per cent K (of dry matter) for the whole of the 4 years. Both cut grass and lucerne leys removed more potassium than the annual crops grown in the arable rotation.

The effects of the potassium deficiency which developed in the early years, and of the supplementary dressings which were given to correct the deficiency, have been measured on the test crops of potatoes (Table 4). In 1955, 1956 and 1957 the potatoes were grown following crops which had not received *extra* K; the cut grass and lucerne leys which preceded the 1958 potato crop had received extra K fertilizer to compensate for the greater uptake, but the grazed ley plots did not receive any extra K in any year. For the years 1955–57 the mean response by potatoes to potassium fertilizers in Highfield was 1·8 tons/acre where they followed lucerne and

TABLE 4

The responses of potatoes to dressings of potassium fertilizer in the ley–arable experiments at Rothamsted

	Preceding ley crop		
	Lucerne	Cut grass	Grazed ley
	Response to K fertilizer (tons of potatoes/acre)		
Highfield			
1955	1·34	1·67	1·07
1956	2·22	2·31	0·78
1957	1·84	1·78	0·60
1958 *	−0·30	−0·56	0·77
Fosters Field			
1955	0·65	0·95	0·34
1956	1·16	0·48	0·70
1957	1·26	0·29	0·48
1958 *	0·03	−0·43	0·77

* Supplementary K had been given to the plots which had grown lucerne and cut grass.

1·9 tons/acre where they followed cut grass, no supplementary K was given to these leys; following grazed ley the mean response was 0·8 ton/acre. In 1958 on plots where the lucerne and cut grass had received supplementary potassium the test dressings of potassium had no significant effects on yield. After grazed ley the potatoes gave the same response (0·8 ton/acre) in 1958 as was obtained on average of the earlier years. Many of the effects of potassium fertilizer on potatoes following grazed leys were not statistically significant, nevertheless the results are very consistent, and when all years are taken together they indicate a fall in potassium status on these plots. On Fosters Field the trends were similar to those measured on Highfield, although the actual effects were smaller, presumably because the old arable land contained more potassium at the beginning of the experiment than the old grass field. The supplementary dressings of potassium now given to the lucerne and cut-grass treatments appear to be stopping the drain on soil potassium. From 1958 onwards the potassium dressing given to the grazed ley has also been increased from a total of 1·2 cwt. K_2O/acre (for the 3 years) to 1·8 cwt.

The crops from the Woburn ley–arable experiment were similarly examined. Where no farmyard manure is given in the continuous arable rotation, and in the arable rotation which includes a hay crop, the amounts of K removed by the crops exceed the amounts added over the 5-year period of the rotation. Where farmyard manure is applied all rotations receive more K than is removed. (Warren and Johnston.)

Potassium fixation in Rothamsted and Woburn soils

Soil analyses showed that, when a fresh dressing of potassium fertilizer is added to the soil of the Exhaustion Land experiment, a large proportion is quickly converted to a non-exchangeable form. In laboratory experiments on slightly calcareous Rothamsted soil at least 80 per cent of the K present in a solution added to the soil was held in a non-exchangeable form; over a wide range of additions of potassium, from well below to well above the usual rates of applying K fertilizers, the amount fixed was proportional to the amount added. Acid Rothamsted soil, and slightly acid Woburn soil, both fixed only about half of the added potassium. The soils of the classical experiments will be analysed to see how much of the K added each year over long periods has been fixed. (Warren and Johnston.)

Availability of soil potassium

In many soils, particularly those low in exchangeable potassium, some fraction of the reserves of non-exchangeable potassium may be of value in crop nutrition. Pot experiments cropped continuously with perennial ryegrass are being used (with Close) to measure the rate of release of non-exchangeable potassium from a number of soils which are taken as standards in associated laboratory work on the value of cation-exchange resins for extracting potassium. The sodium form of "Amberlite IR-120" takes up approximately the amount of potassium that can be exchanged by leaching with neutral N ammonium acetate; the calcium resin takes up less and the hydrogen resin extracts considerably more potassium than is ammonium-exchangeable. The amount of non-exchangeable K extracted by H-resin in 14 days and the uptake of non-exchangeable K from the soil by 3 or 4 cuts of ryegrass grown in pot experiments agreed well. Some soils must be partially dispersed with sodium hexametaphosphate before adding the H-resin to obtain a sufficiently rapid reaction. The technique may be applied successfully to calcareous soils provided that wide ratios of resin to soil are used, together with a longer time of extraction; non-exchangeable potassium is released after the calcium carbonate has been dissolved by the resin, and from some calcareous soils quite large quantities may be extracted. In well-weathered soils most of the non-exchangeable K extracted by H-resin comes from the clay fraction: a soil overlying Malmstone was an exception, the 2–10-μ fraction releasing one-third as much K as the clay fraction. Extraction with H-resin for 14 days recovered at least 90 per cent of the potassium recently " fixed " by wet soils, but the results with soils that had fixed potassium on drying varied much more. H-resin extracted potassium which was not ammonium-exchangeable from certain minerals; dioctahedral micas released little of their non-exchangeable K to H-resin, but considerable quantities were released by trioctahedral micas. (Arnold.)

The amounts of exchangeable soil potassium and the amounts soluble in dilute HCl correlate satisfactorily with the K taken up by arable crops on the Exhaustion Land and on Agdell. Some of the potassium supplied by fertilizer dressings is held in a form not readily exchangeable; attempts were made to determine the amounts held in this way and their relation to exchangeable K. Repeated extractions with hot HNO_3 dissolved about ten times as much fixed fertilizer potassium as was exchangeable. For the grass crop grown on the Agdell experiment in 1958, the relationship between K uptake and exchangeable K levels in the soil was not satisfactory, and more work is needed to define the behaviour of different crops towards soil potassium. (Warren and Johnston.)

Potassium deficiency in spruce seedlings

Sitka spruce seedlings showing severe signs of potassium deficiency were tested for putrescine, but none was found. The purple colour of the leaves was due to an anthocyanin. (Jenkinson.)

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

Work has continued on the residues of P and K fertilizers which have accumulated in the soils of the Exhaustion Land and Agdell experiments from manuring.

The Exhaustion Land experiment

R. G. Warren showed (*Proc. Fertil. Soc.* 1956, no. 37) that the residues from P and K fertilizers applied before 1901 were useful to barley grown in the period 1949–53. In 1957 and 1958 this work was taken further by subdividing the old plots and superimposing tests of new dressings of P and K fertilizers on six crops (barley, spring wheat, potatoes, sugar beet, swedes and kale) which were grown side by side. All plots received a basal dressing of N fertilizer, basal P fertilizers were given when K was being tested and basal K was given where test dressings of P were applied. The increases in yields given by new additions of P and K fertilizers are stated in Table 5 for the six crops grown in 1957 and 1958.

TABLE 5

The increases in yields given by fresh additions of P and K fertilizers in the Exhaustion Land experiment

	Increase from new dressing of 1·0 cwt. P_2O_5/acre				Increase from new dressing of potassium fertilizer *			
Manuring in 1856–1901 period	No phosphate		Phosphate		No potassium		Potassium	
Year	1957	1958	1957	1958	1957	1958	1957	1958
	Increase in yield (per acre) of new test crops							
Barley (cwt. of grain) ...	6	15	0	5	1	0	0	1
Wheat (cwt. of grain) ...	2·5	10	0	2	0	1	0	0·5
Potatoes (tons of tubers)	8	8	4	5·5	6·5	5	4	3
Sugar beet (tons of roots)	3·5	4·5	0	2	0	3·5	0	0
Swedes (tons)	5	13	0·5	3	0	2	0	0
Kale (tons)	6	6	2·5	2	1	0	2·5	0

* 1·2 cwt. K_2O/acre for potatoes, sugar beet and kale; 0·6 cwt. K_2O/acre for cereals and swedes.

The weather in the first half of the two seasons differed; in 1957 there was a drought until July, and in 1958 it was wet. After early July in each year rainfall was above average. This difference in spring and early summer rainfall in the two years was reflected in the responses of barley and wheat to fresh dressings of phosphate. For both crops the increases in yield were much greater in the wetter season. In 1957 residues of phosphate in the soil resulting from manuring between 1856 and 1901 sufficed to grow full crops, and adding superphosphate did not increase yields. In the wet year (1958) barley grown with phosphate residues alone gave 5 cwt./acre of grain below the maximum yield obtained by applying superphosphate; similarly, wheat grown with P residues alone yielded 2 cwt./acre less than the maximum obtained by applying superphosphate. The greater responses to new dressings of phosphate measured in 1958 occurred because the cereals without fresh phosphate gave smaller crops than in 1957 and not because the treated crops yielded more. As there is no reason to consider that the chemical " availability " of the phosphate residues in the soil was less in the wetter than in the drier year, it is likely that the accessibility of the phosphorus differed, perhaps because root growth differed in the 2 years.

Potatoes, sugar beet and kale responded similarly in both years to new dressings of phosphate where these crops were grown on soil which received no phosphate from 1856 to 1901 (and none since). The mean yield of sugar beet in 1958 was 50 per cent greater than in 1957, kale gave a 25 per cent higher yield in the later year and potatoes gave similar mean yields in the two years. On the same soil the response of swedes to new dressings of phosphate was much greater in 1958 (13 tons/acre) than in 1957 (5 tons/acre); the mean yield of swedes in 1958 was double that obtained in 1957. The phosphate residues from the old manuring were sufficient for full crops of barley, wheat, sugar beet and swedes in 1957 but not in

1958. In 1958 the phosphate residues were equivalent to about one-half to four-fifths of the value of the new phosphate fertilizer dressing for these crops. For potatoes and kale the phosphate residues were inadequate in both years: each year the extra yield of potatoes from the residues was only half as great as the increase given by a new dressing of 1 cwt./acre of P_2O_5. For kale the corresponding extra yields in the 2 years were about two-thirds as great as the responses to new dressings.

On soil that received no potassium manuring between 1856 and 1901 (and none since) fresh dressings of potassium fertilizer greatly increased yields of potatoes in both years. In 1957 there was little or no increase in yield of the other crops grown due to fresh dressings of potassium; in 1958, however, new dressings of potassium also increased the yields of sugar beet and swedes; as in 1957, cereals and kale did not respond. On other plots that had received potassium between 1856 and 1901 barley, wheat, sugar beet and swedes obtained sufficient potassium in both years from the residues left in the soil. Potatoes, however, responded well to fresh dressings of potassium in both years, kale gave a moderate increase in yield in 1957 only. (Warren and Johnston.)

The Agdell experiment

R. G. Warren (*Rep. Rothamst. exp. Sta. for 1957*, p. 252) has described the soils of the Agdell experiment and summarized the immediate and residual effects of fertilizer dressings on crop yields up to 1957. Hitherto, information obtained on residual effects has been for the combined effects of the residues from P and K manuring; plans are now being made to separate the effects of the two nutrients for several crops in 1959. This work usefully extends that on the Exhaustion Land, because the levels of the residues from P and K manuring are higher on Agdell. In 1958 Italian ryegrass was sown on half of each of the Agdell plots. The grass was cut twice at silage stage and analysed (with the help of Widdowson and Williams). The amounts of P and K (in lb./acre) extracted in 1958 by the two cuts of grass were:

	P	K
From unmanured soil	5·5	105
From soil containing residues from PK manuring ...	19	205
Gain from residues	13·5	100

The *extra* amounts of P and K taken up by the grass from the plots containing PK residues were only a little greater than those taken up by the potatoes grown in 1957 (10 lb. of P and 95 lb. of K/acre). There was, however, a large difference in the *total* amounts of K removed by the two crops, which is not shown by the values for " gains from residues ". In 1958 grass grown on the " unmanured " plot extracted four times as much potassium as did the potatoes in 1957, but less than twice as much phosphorus. The greater extracting power of grass than of potatoes no doubt partly comes from a longer season of growth and from more complete " searching " of the soil by the grass roots. (Warren and Johnston.)

CATION-EXCHANGE CAPACITY OF PLANT ROOTS

There has recently been considerable interest in the cation-exchange capacity of plant roots. The literature suggests that the values recorded are relative rather than absolute, and the reactions at or on a root surface include diffusion and possibly chelation as well as simple exchange. The concept of an exchange capacity of roots may have some use in work on the uptake of cations. In preliminary investigations the exchange capacities of well-washed roots were determined in three ways: (1) The roots were allowed to take up barium, which was then displaced by acid. (2) Titration curves were obtained after the root material had reached equilibrium in a dilute HCl–KCl solution. (3) In a few experiments roots pre-treated with neutral dilute $CaCl_2$ solution were allowed to exchange with another $CaCl_2$ solution containing ^{45}Ca; rates of isotopic exchange were then determined by a scintillator counting technique. Values obtained by barium exchange were reproducible, and this method appeared to be more satisfactory than that involving titration of the roots. Rather few values were determined by using ^{45}Ca, but they agreed with those given by the barium exchange method. All three methods were used to obtain information on the roots of several crops.

Values given below for cation exchange capacities are in milli-equivalents/100 g. of dry root. The lowest value (1·7) was found with 2-year-old lucerne roots and the highest (75) with peas grown in pots. Perennial and Italian ryegrass, cocksfoot and timothy all gave similar values (20–28 m.e.q.) although some of the roots used were grown in pots and others were taken from the field. The range of values for wheat and barley from pots or the field was 12–16 m.e.q. In general, the values determined resemble those quoted by other workers except for red clover. Published information states that clover has an exchange capacity of 40–50 m.e.q., but four samples used in this work gave values of 13–16 m.e.q. For some of the crops measurements were made at several stages of growth. There was little change in cation-exchange capacity of wheat roots during spring and summer; with kale and clover the values decreased as the season advanced. The effects of fertilizers on cation exchange capacities of roots were not consistent. In field experiments the values for wheat and for permanent grass were not affected by nitrogen fertilization, but with newly sown Italian ryegrass in the field, and with barley grown in sand culture, nitrogen fertilizer increased the exchange capacities of the roots. Increases were also caused by phosphate manuring of perennial rye-grass grown on calcareous soil in a pot experiment. Exchange capacities of barley roots were influenced by variety and by applications of potassium fertilizer. This work will be continued to see whether cation-exchange capacities of roots can be related more closely to the uptake of nutrients by plants grown under controlled conditions. (Heintze.)

ANALYTICAL WORK

Determination of nitrogen in soils

The value of the Kjeldahl method for determining nitrogen in soils was studied by testing the effects of changes in the temperature of digestion, in the catalyst, and in the period of heating. For a range of soils containing from 0·03 to 2·7 per cent of N, the most important factor in Kjeldahl analysis was the temperature of digestion with sulphuric acid, which was controlled by the amount of potassium sulphate added. Under the conditions normally used for Kjeldahl digestion of soil there is little risk of loss of nitrogen due to consumption of sulphuric acid with consequent rise in the temperature of the digest. Selenium was the most effective catalyst for Kjeldahl digestion of soil. The method recommended by the Association of Official Agricultural Chemists gave much lower values than the other methods tested, but satisfactory results were obtained with this method when the period of digestion was increased to 5 hours. The values obtained by Kjeldahl analysis were not affected if the soils were pretreated with HF and H_2SO_4 (to release organic nitrogen and ammonium fixed by clay minerals) or with HI (to include compounds with N–N and N–O linkages). Kjeldahl methods modified to include refractory nitrogen compounds such as nicotinic acid and tryptophan gave the same results as the normal procedures, and it seems that soils contain little of such materials. The Kjeldahl methods normally used for soil analysis are satisfactory if digestion is continued for several hours. The period of digestion required can be decreased by adding more potassium sulphate. The results with micro-Kjeldahl procedures using 0·3–1·0 g. of soil ground to pass a 100-mesh sieve were highly reproducible and identical with those obtained by macro-methods using 5–10 g. samples of soil. (Bremner.)

Calcium in crops

When the EEL flame photometer is used to determine calcium in crops, anions which are present at similar concentrations affect the results. This interference is much decreased by " blanketing ", but with phosphate ions there is serious loss of sensitivity. J. Yofe and R. Finkelstein (*Anal. chim. Acta*, **19**, 1958, 166) showed that the lowering of the calcium emission caused by phosphate can be restored by adding lanthanum chloride when using a Beckmann D.U. spectrophotometer. This method can be applied to the EEL flame photometer, and the best results are obtained with a higher air pressure (15 lb./sq. in.) than is recommended for K (10 lb./sq. in.). Ten times as much lanthanum as phosphate (on an equivalent basis) is necessary and thirty times as much is tolerated. (Johnston.)

Potassium in soils

All naturally occurring potassium minerals contain the radioactive isotope ^{40}K, which provides about 0·01 per cent of all the K present. Soils have a little natural radio-activity from the isotope, and measurements were made to see whether it can be used to determine the total amount of soil K present, so that the customary tedious analytical methods, which involve destroying the silicate minerals, can be avoided. Soil samples ground to pass a 40-mesh sieve were packed in a M12 liquid Geiger–Müller counter, and packing density and counts per minute were measured. The method was calibrated against determinations made with mixtures of pure minerals and sand. The potassium contents of about twenty soils from Southern and Eastern England measured by counting were slightly higher than the values obtained by chemical analyses, perhaps because the soils contain small quantities of uranium and thorium. Discrepancies between results obtained by counting and by analysis were greater with soils formed from igneous rocks in Scotland and Wales. As the method is rapid and may prove very useful, the interference by other radioactive elements is being studied. (Rodriguez, Mattingly and Talibudeen.)

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