Rothamsted Report for 1963

Chemistry Department

G. W. Cooke

CHEMISTRY DEPARTMENT G. W. COOKE

The Department was delighted by the award to R. G. Warren of the O.B.E.

D. S. Jenkinson and A. C. D. Newman transferred to Pedology Department; J. K. Coulter and Marie Blakemore were appointed to the staff.

G. W. Cooke led the United Kingdom Delegation to a Conference on the Development of Fertilisers in Asia and the Far East held in Bombay in November. He also visited Malaya in March at the invitation of the Rubber Research Institute. R. K. Cunningham attended a Symposium held in Ireland on Potassium in Relation to Grassland at the invitation of the International Potash Institute.

R. K. Cunningham was awarded the Ph.D. Degree of London University. P. D. Salt obtained the Licentiateship of the Royal Institute of Chemistry.

The following visitors joined the Department: Mr. J. Deist (South Africa), Dr. I. P. Garbuchev (Bulgaria), Mr. I. G. Iordanou (Cyprus), Mr. T. Kubota (Japan), and Mr. M. D. Webber (Canada).

Organic Manures, Soil Structure and Nutrient Uptake

Work on organic manures, described in recent Reports, emphasised that their effects on crops are mostly from the nutrients supplied. However, with some horticultural crops, farmyard manure (FYM) has additional effects that may be related to changes in soil physical conditions. In other work we have attempted to relate laboratory measurements of easily soluble nutrients with nutrient uptake in the field. One cause of variation in such correlations has been differences between the structure of the same soil in different years. For these reasons we are trying several ways of altering soil structure in attempts to distinguish between the nutrient and physical effects of organic manures that may contribute to differences in yield. We are also testing the effect on uptake of nutrients of changing the volume of soil available to roots, because improving structure increases the internal volume of soil.

Farmyard manure experiments at Woburn. In previous years FYM and fertilisers tested on Stackyard Field at Woburn gave equal yields of sugar-beet roots and sugar, provided enough fertiliser was given; the top/root ratio was increased by fertiliser. In 1963 globe beet and "intermediate" carrots were grown instead of sugar beet. The relative performance of the fertilisers and FYM was the same for globe beet as for sugar beet; early growth was the same, and the best fertiliser treatment gave 11·0 tons of bulbs/acre and the FYM 10·7 tons/acre. There was an extra 1·2 tons of tops/acre with fertiliser. Carrot roots with FYM (27·5 tons/acre) were a little heavier than with fertiliser (26·2 tons); tops at the time of lifting were

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almost identical (10·2 and 10·4 tons/acre respectively), although at singling time the tops on FYM plots were twice the size of those grown with fertilisers, and even 4 weeks before harvest the tops of the carrots grown with FYM were larger. The reason for this better earlier growth with FYM is not known. There was no difference in the time of germination or in the number of carrot seedlings, both treatments gave an almost perfect stand.

In this series of experiments a new site has been used each year to try to confine the comparison between FYM and fertiliser to nutrient effects and to avoid changes in soil structure that occur with repeated applications of bulky organic manures. The germination of globe beet is particularly sensitive to seedbed conditions, and the soil used in Stackyard Field is not ideal for the crop. In the 1963 experiment germination was less uniform than with carrots, but was no better with the single application of 15 tons/acre of FYM than with fertiliser. (Johnston and Warren)

Improving soil structure at Woburn. The old Permanent Wheat and Barley Experiments in Stackyard Field (discontinued in 1927) were on a light sandy loam which became acid during the course of the experiments; chalk was given several times from 1955 to 1957 to raise the pH to 6. The soil compacts easily and seedbed tilth is destroyed by rain, so that permeability is lessened and run-off occurs. The condition of the seedbed between sowing and germination depends on weather during this period. Between 9 and 12 in. deep the soil is less permeable to water than it is above or below; mechanical analyses of the soils from the three depths do not account for this difference, which is probably caused by the tractor wheel compressing and smearing the soil at the bottom of the furrow during ploughing. Two plots in the old cereal experiments received moderate rates of FYM, but the remainder of the sites has received no bulky organic material other than cereal stubble and roots since 1876. The soil contains very little organic matter (0·5–0·6% organic C) and the sites are well suited for studies on the effect of organic matter on soil structure. Ways of improving the physical condition of the soil were tested in three experiments in 1962 and 1963. Basal dressings of inorganic fertilisers were given.

The first experiment tested subsoiling and liming to pH 7, and on subplots of these main treatments the following materials were tested as soil improvers: peat, dead bracken (ground finely and also tested in 6-in. lengths), coir fibre, gypsum, sodium alginate and a hydrolysed polyacrylonitrile soil conditioner (CRD.189). The bulky organic materials were applied at 4 tons/acre, the others at 10 cwt/acre, and all were dug in during March. Alternate rows of sugar beet and globe beet were sown in April. Rain on the fresh moist seedbed destroyed most of the crumb structure. The globe beet failed as very few seedlings penetrated the hard cap that formed in dry weather after the rain. There were enough sugar-beet seedlings to give a 5-in. spacing at the first thinning and there was a satisfactory crop at harvest. The mean yield of sugar-beet roots was 17·1 tons/acre, sub-soiling increased it by 1·8 tons, but liming had no effect. The coarse organic materials, coir fibre and bracken, lowered yields by

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1–1·5 tons/acre, but fine peat gave an increase of 1 ton; other materials had no effect.

The experiment continued on the same site in 1963, when new dressings were given only on the peat, sodium alginate and soil conditioner (CRD.189) plots. (To compensate for the nutrient effect of Na in the sodium alginate an equivalent dressing of NaCl was given to all other plots.) Peat was tested at 30, 60 and 90 cwt/acre. In contrast with 1962 the materials were worked into the soil down to 3 in. during seedbed preparation and not dug in. Globe beet was sown. The weather after sowing was similar to 1962, rain was followed by a hot dry period and germination was poor on plots that were not treated in 1963. Treating the seedbed with CRD.189, sodium alginate, and the largest amount of peat, greatly increased germination. Although thinning diminished the differences in plant number between treatments, yield of roots was much increased by these three treatments. (Table 1.)

TABLE 1

Effects of soil conditioners on number of seedlings and yield of globe beet at Woburn in 1963

Soil treatment	Number of seedlings (thousands/acre)		Yield of bulbs (tons/acre)
	Before singling	After singling	
None	80	47	4·3
CRD. 189	279	110	7·3
Sodium alginate	209	98	6·1
Peat ⎰ 30 cwt	107	61	5·7
Peat ⎱ 60 cwt	136	78	6·0
90 cwt	182	94	6·5

The effects of three amounts of peat, applied on the seedbed and dug in, on germination and yield of globe beet were measured in another experiment, which will be continued to build up several levels of soil organic matter. Experiments on soil conditioners must be repeated in several seasons, as weather during germination influences the size of the effects. In this experiment coarser and harder seedbed tilth favoured germination on the untreated plots and peat applied to the seedbed at 62·5 cwt/acre increased number of seedlings by only 30%. After singling, plant numbers per acre were the same with and without peat, but seedbed peat increased the yield of bulbs from 5·6 to 7·4 tons/acre. Peat dug in (at 62·5 and at 125 cwt/acre) had no effect on germination or yield.

In a third globe-beet experiment, seedbed dressings of CRD.189, sodium alginate and a rubber latex emulsion were tested alone and with a seedbed dressing of peat. The seedbed was prepared later than for the other experiments; only a little rain fell soon after sowing, and the improvements in germination caused by CRD.189, sodium alginate and peat were less than in other experiments (Table 2.) All treatments were given during seedbed preparation, except the latex emulsion, which was diluted with water and applied immediately after sowing (applying the latex this way *destroyed* some of the soil crumbs and, where peat was not given, germination and yield of roots were less than on untreated plots). Peat was best and increased yield by 2·5 tons/acre, CRD.189 had no effect, sodium

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alginate increased yield by 1 ton and latex decreased it by 1·5 tons. Adding CRD.189, sodium alginate or latex along with peat did not improve its performance. The harmful effect from watering latex emulsion on untreated soil was avoided where peat was given.

TABLE 2

Effects of soil conditioners on numbers of globe beet seedlings and yield at Woburn in 1963

Treatment	None	CRD.189	Sodium alginate	Latex
Numbers before singling (thousands/acre)				
None	149	187	190	78
Peat	190	187	227	165
Numbers after singling (thousands/acre)				
None	83	93	107	55
Peat	106	92	101	90
Yield of bulbs (tons/acre)				
None	8·2	8·1	9·1	6·7
Peat	10·7	10·3	11·1	10·6

Improvements in germination and yield on the Woburn soil from applying CRD.189, sodium alginate and peat depend on weather from sowing time to germination. With wet weather CRD.189 was best, but only peat was successful when it was drier. CRD.189 seems to produce a stable and open seedbed structure which is ideal in moist weather but may allow too much water to be lost in dry weather. Peat could not give such a stable structure as CRD.189, but provided more moisture around the seed in dry germination periods. (Johnston and Warren)

Experiments with synthetic rubber latex. The latex tried in the preceding work was tested more extensively in other work at Rothamsted and Woburn. Peas and globe beet were sown and latex emulsion was watered on immediately after. On the clay loam at Rothamsted there was heavy rain before the last germination count and, altogether, 6 in. fell during the experiment; at Woburn 3·2 in. fell, all in light showers. At Rothamsted latex quickened germination of peas, but at harvest there were more plants on untreated plots. Yields and height of peas harvested after 7 weeks and of beet at 10 weeks were increased by latex. Latex improved germination and yield of globe beet at Rothamsted without affecting final plant number. At Woburn latex improved germination of globe beet, but gave only small increases in yields of seedlings (taken 10 weeks after sowing). The water-stable aggregates in soil samples taken from the top inch, 1 month after harvesting the seedlings, were increased by 20% at Rothamsted, and by 30% at Woburn. (Williams)

Improving Docking soil. In a microplot experiment on light soil from an area where sugar beet suffer from "Docking disorder" (Gibbs, *Plant Path.* (1959), **8**, 93–94) applying either a synthetic soil conditioner (CRD.189) or FYM increased sugar-beet yields by 30%. Peat and coir

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fibre did not increase yields. Adequate N, P, K and Mg fertilisers were given to all plots, and extra water was applied when needed. CRD.189 and FYM increased uptake of N, P and K and % P and % K in the beet. These effects, and those on yield, seemed to reflect physical conditions not connected with water or nutrient supplies. (Hoyt)

The effect of soil condition and volume on nutrient uptake and root growth.
Uptake of nutrients is influenced by the total amounts present, by their mobility (which determines whether nutrient can move to root), and by the extent and intensity of root growth. Experiments are being done to understand more about how root growth and crop nutrition are influenced by the structure and "useful volume" of soil.

Adding peat to coarse sand had no effect on penetration by roots of oat seedlings growing in tubes in the glasshouse; in a 3-day test vermiculite added to the sand increased penetration five times. The nature of the roots was also changed by adding peat or vermiculite; peat gave poorer, and vermiculite better top growth than sand alone. These differences in root penetration were related to the force needed to push a fine wire into the growing media, but not to other physical measurements, including pore size distribution. Roots penetrated more easily in wide than in narrow tubes, confirming the suggestion of Wiersum (*Plant & Soil* (1957), **9**, 75–85) that it is the rigidity of pore spaces in soil, rather than their actual size or continuity, that affects root growth.

In a glasshouse experiment with oats, soil volume was varied by growing the plants in pots of different depths. P uptake/litre of soil increased as soil depth decreased, apparently because roots were more concentrated in the smaller volumes. Uptake/litre increased most rapidly with decreasing depth in soils rich in P. The effects of P concentration on changes in uptake, caused by change in soil depth, were not because high concentration and large soil volume gave an excess of P; dry matter response to added P was greatest in the largest volumes of soil. In contrast, N uptake/litre of soil was constant and independent of volume of soil containing little N; because of its mobility, only the amount of nitrate mattered and differing root intensities both took up most of the N present. At the larger amount tested, N supply was no longer a limiting factor, P concentration then controlled growth and the uptake of N/litre of soil decreased as volume increased in the same way as P uptake decreased. In the deep pots, the larger N dressing provided more than was needed, and apparent dependence of N uptake/litre on root intensity was related only to differences in growth caused by phosphate. Uptake of P and K, both of which are not mobile in soil, depend on root intensity and soil volume and on placement of nutrient relative to root surface. In contrast, where the supply of nitrate, a mobile ion, does not exceed the needs of the crop the amount present can be taken up irrespective of soil volume or of its position in relation to roots.

In other experiments aggregates of various sizes were sieved from a bulk of soil. Maximum yield of ryegrass was from soil finer than 2 mm. Size groupings of 1–2 mm and 1–10 mm were next in order of yield, 4–5 mm and 7–10 mm gave least grass. (Cornforth)

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Soil properties in relation to aggregate stability. A series of 190 British soils, differing widely in mechanical compositions, organic matter contents and past histories, were used to study properties that may be associated with the stability of aggregates. Most of the tests used have been described (Williams and Cooke, *Soil Sci.* (1961), **92**, 30–39). Surface soils from grassland were all stable, irrespective of mechanical composition or % organic carbon. In other soils instability (measured by loss in pore space on slaking in water) was well related to % N and % C in soil and to water-holding capacity. The stability of aggregates to water was closely related to their stability to mechanical pressure. Bulk and absolute densities of soil, loss on ignition and permeability to water after slaking were not well related to water stability. The forces needed to split cylinders of soil formed by first mechanically slaking wet soil and then air-drying it were closely related to the amounts of clay in soils having 2% or less of organic carbon; correlation was much less close in soils with more organic matter. Generally the stability of naturally formed aggregates is dominated by the form of organic matter present rather than its total amount, whereas the strength of clods formed by slaking and mechanical pressure is determined mainly by mineral composition of soil (particularly clay content) and far less by the organic matter content. (Williams)

Decomposition in Soils of Chlorophyll-type Compounds

Work on the decomposition of chlorophyll-type compounds began with the hope that measurements of these substances might identify soils containing freshly added plant residues. Following the degradation of well-characterised organic groupings present in plants also helps to understand how plant materials decay in soil and organic matter accumulates.

Chlorophyll-type compounds occur in both woodland and agricultural soils, their synthesis by soil micro-organisms has not been detected, and most must come from higher plants. Much is added by ploughing in grass or legumes; smaller amounts come from straw and leaves in which chlorophyll is partly decomposed before reaching the soil. An important secondary source is animal droppings, though FYM usually contains little of these compounds.

Tissue enzymes decompose chlorophyll in fresh plant material deposited on or in the soil. At 25°C in the laboratory ryegrass in a humid atmosphere lost 90% of chlorophyll-type compounds in 4 days; leaves of other species behaved similarly. This enzyme action is stopped by comminution, freezing, desiccation and waterlogging. Compounds that escape decomposition by tissue enzymes are decomposed mainly by micro-organisms; acid also converts chlorophyll to pheophytin. Aerobic micro-organisms in soil decompose chlorophyll-type compounds rapidly; they act quickest in neutral and alkaline soils and at 50–60% of water-holding capacity; they are checked by low temperature. Chlorophyll was decomposed very slowly in soils below pH 4, suggesting that soil fungi are ineffective. Rate of decomposition was little affected by the species and quantity of leaves deposited in the soil.

The decomposition of individual chlorophyll-type compounds in soil

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followed a general pattern with a wide range of plant tissues and soil conditions. Chlorophyll *a* decomposed more rapidly than chlorophyll *b*, pheophorbide is usually present in very small quantities, and chlorophyllide was found only in intact tissues. Pheophytin is the most generally abundant compound in the soil (except for chlorophyll itself in the early stages of decay), suggesting that it resists decomposition most.

Arable soils contain enough chlorophyll-type compounds for differences in content to be detected, but the total is usually very small. Under long-established grassland, the amount is considerable. Animal droppings are rich in chlorophyll-type compounds which leach into the soil. This is probably the reason for the compounds being plentiful in the top inch of soil under grazed grass—equivalent to the amount in 1 ton/acre of fresh grass; the amount in the next 5 in. decreases sharply with depth, but was equivalent to that in a further ton of fresh grass. Soil under ungrazed grass had about two-thirds as much of these compounds as soil under grazed grass. (Hoyt)

Field and Laboratory Experiments with Nitrogen Fertilisers

Alternative nitrogen fertilisers for spring barley. Previous comparisons of calcium and sodium nitrates with ammonium sulphate gave some results difficult to explain, particularly the striking superiority of sodium nitrate reported last year. In 1963 calcium, potassium and sodium nitrates were broadcast over the seedbed and compared with ammonium sulphate; all the experiments were on soils over Chalk, but only two were calcareous. Sample cuts at, or shortly after, ear emergence measured yield and the amounts of N, K, Na and Mg contained in this green barley. At this stage

TABLE 3

Mean yields of green barley and of grain in five experiments in 1963

N given (cwt/acre)	Without N	Ammonium sulphate	Calcium nitrate	Potassium nitrate	Sodium nitrate
		Green barley (cwt/acre of dry matter)			
0·35	27·3	45·6	44·4	46·6	44·6
0·70		49·3	51·1	48·7	51·2
		Barley grain (cwt/acre at 15% moisture content)			
0·35	21·2	28·9	30·4	30·6	30·6
0·70		32·8	33·7	33·2	33·5

results were similar with all fertilisers, but ammonium sulphate produced less harvested grain than did the three nitrate salts (Table 3). The amounts of N, K, Mg and Na in the green barley were little affected by the form in which N was given, except that Na was much increased by $NaNO_3$. Conversely, K content was increased little by PK fertilisers or by KNO_3. The green barley contained much more K than was found in mature grain plus straw in earlier work; uptakes of K, Na and Mg were greatly increased by N because of its large effect on yields. (Widdowson, Penny and Williams)

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Comparisons of solid nitrogen fertilisers with solutions. In a pot experiment done in February–March Italian ryegrass was grown in Rothamsted clay loam and in light loam from Woburn and given the equivalent of 200 lb N/acre as ammonium sulphate or as calcium nitrate before sowing and again after the first cut was taken; both fertilisers were used as solids and as solutions containing $3\cdot2\%$ N. Applied before sowing, solid ammonium sulphate gave more dry matter than the solution on the clay loam soil, and less on the light loam. Solid calcium nitrate produced more grass than the solution on both soils. The differences between N taken up by grass given solids or solutions were very small. Applied after the first cut, solid ammonium sulphate and a solution gave similar yields on the heavy soil, but on the light soil the solution gave more; N uptake was similar from solid and solution. Calcium nitrate gave significantly more grass on the clay loam than on the sandy loam, perhaps because high concentration of NO_3^-ions damaged the crop in the lightly buffered soil. Dry matter yields and N uptake were less on both soils with calcium nitrate given in solution than with the solid.

In another pot experiment in May, with Italian ryegrass grown in Rothamsted clay loam, 56 and 112 lb N/acre as ammonium sulphate and as calcium nitrate were compared as solids and solutions containing $1\cdot8\%$ N. Applied before sowing, dry matter yields and N uptake were the same with solid and dissolved ammonium sulphate at both rates and with calcium nitrate at the half rate. At the full rate, yield was less with calcium nitrate in solution than as solid, although the N uptakes were the same. Applied after the first cut, dissolved ammonium sulphate gave slightly less grass than the solid at both rates, but N uptakes were the same; solid and liquid forms of calcium nitrate gave similar yields. Residual effects measured on the second and third cuts were the same for solids and solutions.

These glasshouse experiments were done to try to explain some of the differences found in earlier field experiments comparing N applied as solids and solutions. No consistent pattern emerged. As in the field experiments, any general advantage is with solid forms, and gains from using solids are a little greater with a nitrate than with ammonium sulphate. (Nowakowski and Jephcott)

Insoluble nitrogen fertilisers. There is continued need for nitrogen fertilisers that act more slowly than nitrates and ammonium salts and so lessen losses by leaching and denitrification. Possible materials that have been suggested or tested in other countries recently are urea nitrate, oxamide and crotonylidene di-urea (CD-urea). These were compared with ammonium sulphate for ryegrass grown in pots. Fertilisers applied at two rates ($0\cdot25$ and $0\cdot50$ g of N/pot) were mixed with one-quarter of the soil in the pot. (Pots contained either 2,000 g of Rothamsted clay loam or 2,400 g of sandy loam from Woburn.) Oxamide and CD-urea were also tested when *broadcast* in a layer about 1 in. below the seed, and when *placed* in this layer at 6 points with $0\cdot25$ g N/pot and 12 with $0\cdot50$ g.

At $0\cdot25$ g N/pot the early growth of grass was not harmed, but both urea nitrate and oxamide at the double rate caused damage, particularly on the

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light soil. Ammonium sulphate, urea nitrate and oxamide produced the same yield of dry matter, much more than was produced by CD-urea. These results suggest that CD-urea will supply nitrogen very slowly over a prolonged period, but the likely total recovery cannot yet be estimated. The different methods of applying oxamide and CD-urea did not affect rate of uptake by the grass. (Gasser and Jephcott)

Inhibiting the nitrification of ammonium salts. Another possible way of lessening losses of nitrate by leaching and denitrification is by applying an ammonium salt and inhibiting its microbiological transformation to nitrate, which C. A. I. Goring (*Soil Sci.* (1962), **93**, 211–218 and 431–439) reported can be done by 2-chloro-6(trichloromethyl)-pyridine, the nitrification inhibitor "N-Serve" (registered Trademark of Dow Chemical Company). Field experiments at Rothamsted and Woburn in 1962–63 tested the effects of "N-Serve" on the nitrification and movement of ammonium sulphate either broadcast on the soil surface or sown in rows during November (early at Woburn, late at Rothamsted). Soil samples were taken in spring (March at Woburn, May at Rothamsted) to measure the amount of mineral-N in the surface layers (down to 36 in. at Woburn and to 18 in. at Rothamsted) and its distribution between ammonium and nitrate forms. After taking samples, the soil was lightly cultivated and ryegrass was sown. Untreated ammonium sulphate was applied to the seedbed to compare with the autumn dressings. The grass was cut twice, dry matter yields and nitrogen contents were measured.

More ammonium from untreated ammonium sulphate was nitrified than from that treated with "N-Serve". When broadcast on the soil surface nitrification was retarded more by the double rate of "N-Serve" (2% of the weight of N applied) than by the half rate. When the fertiliser was placed in the soil both rates of "N-Serve" retarded nitrification equally.

Of the N applied in autumn at both Rothamsted and Woburn, least was recovered by the grass from the untreated ammonium sulphate, and most from the treated fertiliser placed in the soil; even so, less was recovered than from spring-applied ammonium sulphate.

A greater proportion of the total fertiliser-N was in the second cut of grass from plots given untreated ammonium sulphate in autumn than from plots given treated fertiliser in autumn or untreated in spring, indicating that earlier nitrification allowed NO_3-N from the untreated fertiliser to be washed deeper down. (Gasser and Penny)

Fertiliser Placement Experiments

With increasing mechanisation of arable farming, the value of combine-drilling fertilisers for cereals and of placement for other crops is being questioned. Many farmers have found that applying fertiliser separately before sowing or planting, especially with a "spinning-disc" distributor giving a wide swathe, speeds spring work. Early planting is often needed to get good yields in the dry parts of England. Experiments were therefore planned to obtain more information on the gains from special methods of applying fertilisers.

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Combine-drilling PK and NPK fertilisers for barley. In the experiments testing several nitrogen fertilisers (page 44) broadcasting was compared with combine-drilling a compound supplying 0·5 cwt P_2O_5 and 0·5 cwt K_2O/acre. Table 4 shows the PK fertiliser increased yields at both harvests, more so when combine-drilled than when broadcast, particularly at the half rate of N.

TABLE 4

Mean yields of green barley and of grain, from broadcasting or combine-drilling PK fertiliser in 5 barley experiments in 1963

N applied* (cwt/acre)	PK fertiliser		
	None	Broadcast	Combine-drilled
	Green barley (cwt/acre of dry matter)		
0·35	41·5	43·8	47·3
0·70	46·7	49·1	49·5
	Grain (cwt/acre at 15% moisture content)		
0·35	26·8	27·9	29·8
0·70	29·9	32·1	33·5

* As ammonium sulphate.

Four other experiments compared grain yields from two compound fertilisers, containing 20% N, 10% P_2O_5 and 10% K_2O (20–10–10) and 10% N, 10% P_2O_5 and 10% K_2O (10–10–10) respectively, applied to give 0·3, 0·6 or 0·9 cwt N/acre. At each rate of N the second fertiliser supplied twice as much P_2O_5 and K_2O/acre as the first. Each was tested broadcast (over the ploughing) and combine-drilled. Two experiments were on clay loams, one on Chalk and the other on sand-and-gravel. Combine-drilled 10–10–10 checked early growth much more than did 20–10–10 supplying the same quantity of N; this check was severe with the medium dressing, and very severe with the largest (0·9 cwt N, P_2O_5 and K_2O/acre). This

TABLE 5

Mean yields from four barley experiments comparing two compound fertilisers broadcast and combine-drilled in 1963

	Grain yields (cwt/acre at 15% moisture content)	
Without fertiliser	19·5	
Fertiliser tested	20–10–10	10–10–10
At 0·3 cwt N/acre		
Broadcast	26·2	26·6
Combine-drilled	28·2	30·1
At 0·6 cwt N/acre		
Broadcast	31·6	33·8
Combine-drilled	35·0	36·5
Half broadcast } Half combine-drilled }	33·8	34·1
At 0·9 cwt N/acre		
Broadcast	34·1	34·6
Combine-drilled	36·8	35·8
One-third broadcast } Two-thirds combine-drilled }	35·7	35·6
Two-thirds broadcast } One-third combine-drilled }	35·9	34·9

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obvious damage decreased with time and disappeared by harvest, except on the sand-and-gravel. Table 5 shows that each fertiliser gave more grain when drilled than when broadcast (except with the largest dressing of 10–10–10 on the sandy loam), and the gain from drilling was greatest with the smallest dressing of 10–10–10 and with the medium dressing of 20–10–10; so, under these conditions, 0·3 cwt P_2O_5 plus 0·3 cwt K_2O/acre were the best quantities for combine-drilling. The experiments also suggest early growth was damaged much more by K than by N, and that 20–10–10 was an adequate fertiliser for barley grown on these soils only when it was combine-drilled. (Widdowson and Penny)

Placement of large fertiliser dressings for potatoes. One experiment in 1962 and two in 1963 tested an NPK fertiliser (13% N, 13% P_2O_5 and 20% K_2O) at 5, 10 or 15 cwt/acre, applied in three ways: broadcast and worked in by rotary cultivator, broadcast over the seedbed and placed in two bands (one at each side of the seed). Broadcasting and working-in had

TABLE 6

*Mean yields of total tubers (tons/acre) from three potato experi-
ments comparing three methods of applying fertiliser*

Without fertiliser		7·9	
Fertiliser applied (cwt/acre)	5	10	15
On ploughing and cultivated in	11·2	13·1	13·8
On seedbed	11·4	12·4	13·6
In two side-bands	11·6	11·9	11·1

little effect on early growth, and placing in bands was safe at 5 cwt/acre, but at 15 cwt checked growth badly; dressings broadcast on the seedbed had intermediate effects on early growth. Table 6 shows that fertiliser broadcast and worked-in increased yields the most at 10 and 15 cwt/acre, but at 5 cwt/acre placement was best. (Widdowson and Penny)

Fertiliser Experiments on Grassland

Grazed Reference Plots at Rothamsted. In 1959 an experiment was started in Highfield, on a very old sward containing little clover, to test fertilisers on grazed grass; a preliminary account is in our Report for 1961 (p. 50). From 1961 to 1963 cages (each 1 yard square) were used to protect the

TABLE 7

*Mean annual yields of dry grass (cwt/acre) from the Rothamsted
Grazed Reference Plots 1961–63*

Annual nitrogen manuring (cwt/acre)	Phosphate and potash manuring			
	—	P	K	PK
None	55·0	62·1	57·6	69·2
As ammonium sulphate				
1·5	84·1	99·3	87·1	98·5
3·0	—	—	—	100·7
As calcium nitrate				
1·5	76·3	93·3	92·1	103·1
3·0	—	—	—	108·2

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grass from grazing and so to measure yields in four periods each of 2 months; at the beginning of each period 0·375 or 0·75 cwt N/acre (i.e., total dressings of 1·5 or 3·0 cwt N/acre/year) was applied as ammonium sulphate or calcium nitrate. Table 7 shows that yields were increased much more by phosphate than by potash, but there was a positive PK interaction except when ammonium sulphate was given. Applying 1·5 cwt N/acre in the year increased yields by almost one-half, but giving twice as much N increased yields only a little more. At 1·5 cwt N/acre ammonium sulphate and calcium nitrate behaved similarly, but at 3 cwt N/acre calcium nitrate was better. (Widdowson and Penny)

Nitrogen and potash fertilisers for grass. An experiment was started at Rothamsted in 1958 to find out how much K fertiliser was needed by grass manured with increasing amounts of N. Responses to 0·3, 0·6 or 0·9 cwt N/acre/cut (as "Nitro-Chalk"), and to 0·3 or 0·6 cwt K_2O/acre/cut (as muriate of potash) in factorial arrangement were measured. Responses to superphosphate (measured only at the heaviest N and K manuring) were small. Results from 1958 to 1961 described in our Report for 1961 (p. 49) showed little yield response to K fertiliser. In spring 1962 cocksfoot (S.37) was sown and the fertiliser treatments continued unchanged. Table 8 summarises results from 1958 to 1963. In 1958 and 1959 K fertiliser did not

TABLE 8

Results of an experiment testing N and K fertilisers on Italian ryegrass (1958–61) and on cocksfoot (1962–63)

	1958–63		1963 only	
Fertiliser treatment (cwt/acre/cut)	Total yield of dry grass (cwt/acre)	Total K taken up (cwt/acre)	Mean % K in dry grass	Easily soluble K* in surface soil in November (mg K/100 g)
Without N or K fertiliser	143	4·0	2·52	6·6
0·3 N plus				
0·0 K	352	8·5	1·58	4·3
0·25 K	360	10·4	2·42	4·9
0·50 K	359	11·5	3·11	11·1
0·6 N plus				
0·0 K	436	10·1	1·46	4·0
0·25 K	468	12·5	1·94	4·7
0·50 K	481	14·8	2·62	6·4
0·9 N plus				
0·0 K	463	10·3	1·25	3·8
0·25 K	491	13·4	2·09	5·1
0·50 K	506	15·9	2·67	7·1

* Extracted with 0·3N-HCl.

increase yields at any cut. In 1960 (after reseeding) it increased yields at the first cut, but not subsequently in 1960 or in 1961. In 1962 (again after reseeding) K greatly increased yield at the first cutting, but had little effect at the second; however, in 1963 K consistently increased yield at each cutting. After growing grass intensively for five years, K reserves in the soil were so depleted that in 1963, for the first time, a shortage of available

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K limited growth for a whole year. The grass grown on plots not given K fertiliser, but which received 0·6 or 0·9 cwt N/acre/cut, removed altogether more than 10 cwt of K/acre between 1958 and 1963 (Table 8). This exceeded the most K applied by any treatment during this period (8·5 cwt K/acre). The mean % K in cocksfoot given N in 1963 was almost halved unless K was given too; applying 0·5 cwt K/acre/cut maintained % K in the grass slightly above that in the grass receiving neither N nor K. At the third and fourth cuttings in 1963 grass on three plots showed the bronzing associated with severe K deficiency; it contained less than 1% K in dry matter. There was less K soluble in 0·3N-HCl in the surface soil in autumn 1963 than in autumn 1961; so it seems that 0·5 cwt K/acre/cut will not maintain adequate soil reserves when this field grows grass heavily manured with N. (Widdowson, Penny and Williams)

Experiments with Phosphate Fertilisers

Residual and cumulative effects. Three year's results from the long-term experiments at Rothamsted were summarised in last year's Report (p. 53). In 1963 there were no significant differences between years from the different forms of phosphate applied at 3 cwt P_2O_5/acre in 1959; on average of the different forms tested, residues produced increases of 1·47 tons of potatoes, 9·5 tons of swedes and 4·1 and 5·7 cwt/acre of barley grain and straw respectively in 1963. Corresponding increases/acre in 1963 from the immediate and residual effects of 0·5 cwt P_2O_5/acre given annually since 1960 were 1·55 tons of potatoes, 12·5 tons of swedes and 2·9 cwt of barley grain and 6·1 cwt of straw. Results for barley are unreliable because of lodging and damage by birds; residues from the large dressings given in 1959 are still as effective for potatoes as the immediate and residual effects of annual dressings of 0·5 cwt P_2O_5/acre, but not for swedes. (Mattingly)

We found (*Rothamsted Report* for 1960, pp. 63–64) that residues from Gafsa rock phosphate and basic slag—but not superphosphate—accumulate in an acid sandy soil in the Forestry Commission's Research Nursery at Wareham in Dorset. Soil taken in 1963 was used in a pot experiment with ryegrass. Total yield of dry grass without phosphate was 3·3 g/pot; residues from basic slag and Gafsa rock phosphate produced totals of 13·1 and 13·5 g respectively, whereas superphosphate residues gave only 8·4 g.

Residues from both insoluble phosphates produced greater yields than those from superphosphate, particularly at the 3rd and 4th cuts. Labile (isotopically exchangeable) P, measured from the $^{32}P/^{31}P$ ratio in the crop, increased steadily during growth on soils with rock phosphate or basic slag residues, but not with superphosphate residues. This, and large P uptakes in the later cuts, suggest that residues from both fertilisers (known to accumulate in the sand fraction of the soil) are slowly dissolved during such greenhouse experiments. The same experiment compared other soils from the same nursery containing residues either from superphosphate or from bracken hop-waste compost (which contained about two-thirds as much total P as was applied by superphosphate). The values of the residues

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from the composts, relative to residues from superphosphate, were different in each experiment, perhaps because of differences in management in the field. But the labile P in all the soils containing compost residues did not increase during cropping. This suggests that organic P in residues from the composts was not mineralised in the greenhouse in 4 months in these very acid soils (pH in $0.01 M\text{-}CaCl_2 = 3.6\text{--}5.2$); the effects of liming these soils on mineralisation is now being examined. (Mattingly, Benzian and Jephcott)

Valuing phosphate fertilisers in glasshouse experiments. Potassium metaphosphate and magnesium ammonium phosphate made in three granule sizes (<0.18 mm, $0.5\text{--}1.0$ mm and $1.0\text{--}2.0$ mm) were compared with powdered triple superphosphate (<0.18 mm) in greenhouse experiments with kale, oats and ryegrass. A commercial sample, said to be magnesium phosphate, (with 37.8% P_2O_5) was also tested. Ryegrass was cut twice. At the first cutting, 32 days after sowing, all fertilisers except powdered magnesium ammonium phosphate produced significantly less grass than equivalent triple superphosphate. There were no significant differences between yields of oats or kale receiving powdered triple super or these fertilisers in any granule size. Fertilisers differed much more in their effect on P uptake than on yield. Uptake from powdered potassium metaphosphate was consistently less than from triple superphosphate. Except at the first cut of grass, more P was taken up from *granular* metaphosphate than from equivalent superphosphate. This agrees with results with ryegrass grown in microplot field experiments (*Rothamsted Report* for 1962, p. 52), which showed greater P uptake from metaphosphate (in $0.5\text{--}2.00$-mm granules) than from equivalent granular single superphosphate. Uptake by each crop from powdered magnesium ammonium phosphate was almost equivalent to that from powdered triple super; larger granules of this material however, acted slower than triple super, particularly with ryegrass. P uptake by each crop from the powdered commercial sample of magnesium phosphate was consistently less than from triple super. Approximate "triple superphosphate equivalents" of the other fertilisers, averaging rates of application, were:

Potassium metaphosphate

<0.18 mm	74
$0.5\text{--}1.0$ mm	123
$1.0\text{--}2.0$ mm	117

Magnesium ammonium phosphate

<0.18 mm	96
$0.5\text{--}1.0$ mm	102
$1.0\text{--}2.0$ mm	102

"Magnesium phosphate" (powder)	53

They are based on mean P uptakes by kale, oats and two cuts of ryegrass (total uptakes were similar for the three crops). (Blakemore and Mattingly)

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Potassium Manuring of Sitka Spruce Seedlings

In late summer Sitka spruce seedlings, grown with soluble potassium fertilisers on the leached sandy Wareham soil, often develop typical discolorations associated with K-deficiency. In the presence of a basal dressing of "Nitro-Chalk", superphosphate and kieserite, four rates of KCl were tested either as a *single* dressing before sowing or as a *divided* dressing (half before sowing and half in late June). The single application doubled height and dry matter (with only small differences between rates) (Table 9); divided dressings gave a further increase of 10–20%. By contrast, the

TABLE 9

*Yields, potassium-deficiency symptoms and potassium in crop
(tops + roots) of one-year Sitka spruce seedlings at Wareham
Nursery in 1963*

(Low rate = mean of 4·5 g and 9 g K/sq. yd. High rate = mean of 13·5 g and 18 g K/sq. yd)

	Height (in.)	Dry matter (mg/ plant)	Visual colour score*	K in dry matter (%)	K in crop lb/acre	K in crop % re-covery
K applied						
None	0·7	85	6	0·31	4·7	—
All in March						
Low rate	1·4	160	5	0·44	11·9	18
High rate	1·6	167	4	0·48	14·2	8
Half in March, half in June						
Low rate	1·7	195	1	0·68	23·6	34
High rate	1·7	196	0	0·92	32·2	20

* 0 = no discoloration.

single dressings improved seedling colour only slightly, but the divided K applications prevented deficiency symptoms and considerably increased % K in the plants, the high rate trebling it. Although in 1963 seedling growth at Wareham was below average, numbers, which were not affected by treatment, were large (1,640 seedlings/sq. yd), and total dry matter produced was comparable with long-term averages. Uptake of K (lb/acre) ranged from 4·7 for no-K plots to 32 for plots receiving the high rate divided.

In a small trial, seedlings with severe K-deficiency symptoms grown on plots manured with 9 g K/sq. yd (as KCl) in March, had their green colour restored by a single September top-dressing of KCl (4·5 g K/sq. yd); % K in the plants was increased from 0·4 to 1. (Benzian)

The Effect of Fertilisers on the Composition of Crops

Cation–anion relationships in crop nutrition. Last year's Report (p. 45) showed that the ratio (R) of sum of the cations : sum of the anions in Italian ryegrass was related to % N, but not to % K, and that NO_3^- was the main anion and K^+ the main cation taken up by the grass. This R–% N relationship depended on the form of N taken up; curves showing the relationship for grass grown in the greenhouse and in the field, although the same shape, did not coincide. This may mean that, for one plant species,

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there is not a single R–% N relationship but rather a family of curves, perhaps depending on soil temperature, light intensity, water tension, as well as conditions of drying and storing of soil. Therefore pot experiments were done under glass in 1963 with Italian ryegrass grown in Rothamsted clay loam, to test the effect of these factors on ion uptake and R–% N relationships.

The first experiment showed the R–% N relationship was influenced by soil temperature. With equal % N, R values were smallest at 11° C and greatest at 28° C; the increase at higher temperatures is apparently caused by the grass taking up a greater proportion of divalent cations than of other ions.

The same experiment was used to test the effect of soil temperature, and form and level of N on growth and chemical composition of Italian ryegrass. The grass was grown in Rothamsted clay loam kept at 11° C, 19·5°C and 28°C. Six levels of N (0–500 ppm) were tested as NH_4-N or NO_3-N (ammonium salts were treated with "N-Serve" to inhibit nitrification (p. 46)). Tops grew best at 19·5°C and roots at 11°C. At 19·5°C yields of tops grown with NO_3-N were most at 100 ppm of N, and with NH_4-N at 200 ppm. Increasing NO_3-N above 100 ppm greatly decreased yield of tops, but increasing NH_4-N did not. Tops were larger with NO_3-N than with NH_4-N at low levels of N, but smaller at higher levels. Root weights were similar with both forms of N, but, whereas the roots were well distributed throughout the soil with NH_4-N, with NO_3-N they were mainly confined to the upper half of the soil. Form of N greatly influenced the composition of the grass. Increasing NO_3-N greatly increased % Ca and % Mg and decreased % P, % Cl and % S; increasing NH_4-N decreased Ca. Per cent N was larger with NO_3-N than with NH_4-N. Raising the soil temperature greatly increased % Ca and % Mg, but had little influence on the concentrations of N, P, S, Na and K; % Cl was always largest at 11°C. (Nielsen and Cunningham)

The effects of chloride on potatoes. Potatoes were grown in 1963 at Rothamsted at two levels of chloride (0 and 240 lb of Cl/acre) in the presence and absence of two levels of NH_4- or NO_3-N (0 and 90 lb N/acre). All treatments received per acre, 168 lb of P_2O_5, 336 lb of K_2O, 190 lb of Ca and 110 lb of S, using mixtures of the following fertilisers: triple superphosphate, potassium sulphate, potassium chloride, potassium nitrate, calcium nitrate, urea, calcium sulphate and calcium carbonate; the chloride ions were increased without increasing a co-ion, by replacing carbonate ions.

TABLE 10

The effect of chloride and sources of nitrogen on potatoes

	Without N		With ammonium-N		With nitrate-N	
	Without Cl	With Cl	Without Cl	With Cl	Without Cl	With Cl
Fresh yield (tons/acre)	9·0	9·8	12·2	12·7	12·3	12·7
% dry matter	21·1	18·9	19·8	18·7	19·7	18·4
Dry matter yield (tons/acre)	1·89	1·85	2·43	2·37	2·41	2·35
% ware (1½ in. riddle)	92	94	95	96	95	96

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Yields of fresh and dry tubers were much increased by both forms of N (Table 10). Although chloride increased fresh weights of tubers by about $\frac{3}{4}$ ton/acre in the absence of N, and by $\frac{1}{2}$ ton in the presence of N, it had little effect on dry weights; tubers given much chloride were a little larger and had smaller % dry matter than those without chloride. (Cunningham)

The effect of nitrogen fertilisers on barley composition. In the experiments testing four forms of nitrogen on barley (p. 44) part of the crop was harvested at ear emergence and the content of N, K, Na and Mg was determined. Most differences in uptake of these elements caused by the different sources of N were very small when 39 lb N/acre were given, but much larger with 78 lb. 4–7 lb more N was taken up from the nitrate fertilisers than from ammonium sulphate. Ammonium-N depressed uptake of both K and Na. Applying sodium nitrate depressed uptake of K, but doubled the amount of Na in the barley. (Widdowson, Penny and Williams)

The effects of N and K on soluble carbohydrates in grass. In the experiment with cocksfoot grown on Harwoods Piece (p. 49), which tests 0·3, 0·6 and 0·9 cwt N/acre and 0·3 and 0·6 cwt K_2O/acre, N considerably decreased total soluble carbohydrates in grass, because the fructosan content was less (Table 11). Increasing the level of K had no effect on the soluble carbohydrate content. (Nowakowski)

TABLE 11

Effects of N fertiliser on soluble carbohydrates in cocksfoot
(% in dry matter)

	Soluble sugars	Fructosan	Total soluble carbohydrate
Without N	6·3	13·0	19·3
With N fertiliser (cwt N/acre/cut)			
0·3	7·6	6·8	14·4
0·6	7·9	2·0	9·9
0·9	6·8	1·2	8·0

The effect of soil temperature and N fertiliser on nitrogen fractions and soluble carbohydrates in Italian ryegrass. Grass from the pot experiment testing three soil temperatures and six levels of N (p. 53) was fractionated. Total-N, total soluble-N and nitrate-N were much more, whereas amide-N (particularly asparagine) and α-amino-N were much less in grass given NO_3-N than in grass supplied with NH_4-N. These differences increased with increasing amounts of applied N. At higher soil temperatures total soluble-N and nitrate-N increased considerably, but amide-N (particularly asparagine) decreased irrespective of the form of N supplied. Total soluble carbohydrate in the grass decreased with increasing level of N, and this decrease was greater in grass with NH_4. At all levels of applied NH_4-N total soluble carbohydrate in the grass was less at higher soil temperatures; but, with NO_3-N, higher temperature lessened total soluble carbohydrate only at the smallest level of applied N. (Nowakowski, Cunningham and Nielsen)

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Nitrogen in Soils

A chemical test for mineralisable-N in soils. The work to develop a chemical test for mineralisable nitrogen described in last year's Report (p. 61) was concluded. The material dissolved by Ba(OH)$_2$ contained polysaccharides, probably of bacterial origin. The amount of polysaccharides in the extracts from a range of soils correlated roughly with the non-nitrate-nitrogen content of the extracts. The polysaccharides were determined colorimetrically as "glucose" by comparing the colour developed when the Ba(OH)$_2$ extract was treated with the anthrone reagent for hexoses with that developed by treating a solution containing a known amount of glucose with this reagent. Thirty-six soils taken from field experiments testing N fertilisers on barley (Gasser, *J. Sci. Fd Agric.* (1961), **8**, 562–573) were used. The amounts of "glucose" and N extracted by Ba(OH)$_2$ from these soils were correlated with barley yields (Table 12).

TABLE 12

Correlation coefficients between soil measurements and the yields of barley grown without nitrogen fertiliser

	1957	1958	1959	All years
No. of soils	6	13	17	36
Mineral-N, fresh soil	0·55	0·83	0·60	0·63
Δ mineral-N, air dry soil stored 12 weeks	0·35	0·72	0·77	0·68
% total N in soil	0·83	0·73	0·73	0·72
Ba(OH)$_2$-soluble "glucose"	0·69	0·88	0·84	0·83
Ba(OH)$_2$-soluble non-nitrate N	0·45	0·60	0·78	0·70

Correlation coefficients between yield and total N in the soil, Δ mineral-N, and the mineral N originally present in the soil, are also in Table 12. For 1957, 1958 and 1959 combined, Δ mineral-N, total N and Ba(OH)$_2$-soluble N were well correlated with yields. The amount of mineral-N in the fresh soil gave the poorest correlation, and "glucose" dissolved by Ba(OH)$_2$ the best.

Last year's Report (p. 62) stated "Ba(OH)$_2$ extracts more nitrogen from a soil with a pH below 6·3 than from a soil with the same capacity for releasing nitrogen but with a pH above 6·3". The ratio

$$\frac{\text{``Glucose'' dissolved by Ba(OH)}_2}{\text{Nitrogen dissolved by Ba(OH)}_2}$$

is less for soils below pH 6·3 than above pH 6·3: this explains, at least in part, why the correlation between "glucose" and yield was better (Table 12) than that between Ba(OH)$_2$-soluble-N and yield.

Because the results given in this and last year's Report were all obtained on soils that had been stored air-dry for up to five years, a separate experiment on four contrasted soils was done to examine the effects of air drying and storage on the amounts of Ba(OH)$_2$-extractable-N and "glucose". On average, *air-drying* increased Δ mineral-N by 112%, nitrogen dissolved by Ba(OH)$_2$ by 18%, and "glucose" dissolved by Ba(OH)$_2$ by 51%. When the soils were *stored* air-dry for six months Δ mineral N increased by 13%, Ba(OH)$_2$-soluble-N by 14% and "glucose" by 13%. Although these

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averages conceal individual differences in the behaviour of the four soils, they show that storage has relatively little effect on the amount of material dissolved by $Ba(OH)_2$, once soil is air dried. As correlations between results obtained by the $Ba(OH)_2$ "glucose" method and the behaviour of crops are better than those obtained by the ordinary incubation method (which is very similar to methods developed in many other laboratories and used in advisory work), the new method seems to merit more extensive testing by research and advisory workers. (Jenkinson)

Isotopic exchange of fixed ammonia. Work on the isotopic exchange reactions between NH_4-hydrobiotite and ^{15}N-labelled NH_4Cl solution was extended to other NH_4-treated minerals. NH_4-treated illite contained 41 me $NH_4/100$ g; 35 me NH_4 was exchangeable with KCl and 34 me was isotopically exchangeable, showing that almost all the exchange sites were equally accessible to NH_4^+ and K^+. As with hydrobiotite, only very small amounts of isotope were in the fixed ammonium fraction (not exchangeable with KCl).

Five size fractions were used in exchange experiments with World vermiculite, to discover if particle size influenced KCl and isotopically exchangeable fractions. KCl-exchangeable NH_4 increased from 9 me/100 g for the largest particles (500–150 μ) to 39 me/100 g for the smallest (<12 μ). NH_4, isotopically exchanged after 13 days, increased from 8 me/100 g to 38 me/100 g; the difference, (KCl-exchangeable NH_4)—(isotopically exchangeable NH_4), was 1 me/100 g, independent of particle size. The fixed NH_4, which varied little with particle size (100–110 me/100 g), contained a small amount of isotope.

All the isotope-exchange experiments done show that less than 1% of the fixed NH_4 exchanges after 13 days, so that the thermodynamic "active mass" in ion exchange must be very small. It is therefore unrealistic to use total fixed NH_4 in expressing by mass-action quotients the affinity of the mineral for NH_4 relative to any other ion. However, previous work showed that, when a mineral containing fixed NH_4 was shaken with NaCl solution, NH_4 ceases to move from mineral to solution after 3 days, when an apparent equilibrium was reached; successive treatments of this type eventually removed all fixed NH_4 from the mineral. Therefore, to estimate the active mass of mineral NH_4 at each point in this exchange sequence, the equilibrium solution was labelled with ^{15}N, and the subsequent distribution of isotope allowed the active mass of NH_4 to be calculated. The first experiments showed that the active mass was so small that only very approximate values could be calculated, giving mass action quotients in the range 0·2–1; using total fixed NH_4 the values (*Rothamsted Report* for 1962, p. 61) are in the range 0·001–0·006. (Newman)

Phosphorus in Soils

Effects of farmyard manure and rape cake on the solubility of soil P. On slightly calcareous arable soils at Rothamsted, farmyard manure (FYM) and rape cake dressings increase the *solubility* of soil P (measured in $0·01 M$-$CaCl_2$) as well as the *amount* of soluble P. Where superphosphate

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and FYM were applied to separate plots on Barnfield for about 100 years, FYM increased the concentration of P in $CaCl_2$ extract, relative to the increase in total P, five times more than superphosphate did (Table 13). Chemical differences between the P compounds in FYM and in super might

TABLE 13

The effects on total and soluble soil phosphate of dressings of
farmyard manure and superphosphate on Barnfield

	Total P (mg/100 g)	P soluble in $0.01M$-$CaCl_2$ (g mol/litre $\times 10^{-6}$)	P soluble in $0.5M$-$NaHCO_3$ (mg/100 g)
Without FYM or super	67	0.5	1.8
Increase from			
Superphosphate	55	2.6	5.1
FYM	59	12.3	6.8
FYM + superphosphate	121	21.9	12.7

account for some of this difference, but not for all. When super and FYM are applied together the increased solubility is greater than the sum of the separate effects, indicating that substances in FYM increase the solubility of the superphosphate residues in the soil. Rape cake increased solubility three times more than superphosphate.

The increases in $CaCl_2$-solubility of P in the Barnfield soil result from the accumulation from annual applications over a long period and do not show how solubility changes with age of residues. In the Exhaustion Land Experiment P residues are 50–100 years old and the solubility of P on the FYM plots there is now only twice that on the superphosphate plots. Differences between the two forms of P in the soil therefore persist for a long time. The immediate effects of a single dressing of each material on P solubility in Rothamsted soil have not yet been compared, but at Woburn the ratio of the solubilities is greater than 5. The great solubility of P in the FYM plots at Rothamsted probably accounts for it moving below plough depth; only where FYM is applied can extra P be detected below the ploughed layer.

In comparing the effects of fertilisers and organic manures (including green manures) on productivity, the effect of organic matter on the solubility of soil P must be considered in addition to soil-structure effects, and the amounts and forms of the nutrients added by the organic materials. At Woburn 13 applications of 30 cwt/acre of straw, given in alternate years, did not alter the solubility of soil P; we have no similar information for Rothamsted, or for other forms of organic matter.

The effect of the differences in the solubility of soil P in $CaCl_2$ solution between the FYM and NPK fertiliser plots on yield and uptake of P by mangolds and sugar beet on Barnfield cannot be determined accurately because the two kinds of manuring supply different amounts of N and K. Uptakes of P from the two sources are, however, not very different, so the two crops seem to be insensitive to these large differences in solubility of soil P, perhaps because both treatments supply more than they need; other crops might behave differently. $CaCl_2$-soluble P measures an intensity but the amount of P dissolved by $0.5M$-$NaHCO_3$ indicates better the *capacity*

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of the soil to supply P from its reserves. On Barnfield, Broadbalk and Hoosfield, $NaHCO_3$ solution extracts 9–11% of the extra total soil P derived from either superphosphate or FYM. In contrast to the solubilities in $CaCl_2$ solution, the soil P dissolved from FYM and superphosphate plots by $NaHCO_3$ solution differs little on Barnfield; values are 6·8 and 5·1 mg P/100 g of soil for FYM and super plots respectively, where the two manures are applied together the solubility (12.7) shows their effects are additive. Sugar beet and mangolds may therefore depend more on capacity rather than intensity factors associated with soil phosphate. (Johnston and Warren)

The effects of forms of N on growth and P uptake by ryegrass grown on calcareous soils. In previous work (*Rothamsted Report* for 1961, pp. 53–54) more P was taken up by ryegrass from calcareous soils (containing 0·8–2·5% $CaCO_3$) given $(NH_4)_2SO_4$ than when given $NaNO_3$. One highly calcareous soil derived from Jurassic limestone, and another from Chalk, were used in a glasshouse experiment testing $Ca(NO_3)_2$, $NaNO_3$, NH_4NO_3 and $(NH_4)_2SO_4$ at two rates, with and without added P (as monocalcium phosphate). Table 14 shows mean effects of the four forms of N as totals

TABLE 14

Total yields and N and P uptakes by ryegrass grown with four nitrogen fertilisers on calcareous soils

Nitrogen fertiliser	Yield of dry matter (g/pot)	N uptake (mg/pot)	P uptake (mg/pot)
Calcium nitrate	3·38	115	3·73
Sodium nitrate	3·51	114	4·06
Ammonium nitrate	3·70	125	4·09
Ammonium sulphate	3·82	126	4·28
Standard error	0·042	1·8	0·057

for four cuts of grass. Yields and P uptakes were significantly greater from soils receiving $(NH_4)_2SO_4$ than from those receiving $NaNO_3$; yields and uptakes from $Ca(NO_3)_2$ were less than from $NaNO_3$, and from NH_4NO_3 were less than from $(NH_4)_2SO_4$. The form of N applied had less effect than reported previously, probably because $(NH_4)_2SO_4$ did not lessen the pH of these highly calcareous soils which also contained more P than the soils used previously. Yields without P were less, and with P larger on the Limestone than on the Chalk soil; this agrees with results in last year's Report (pp. 62–63)—soils from hard limestone have smaller phosphate capacities than those from softer limestones. (Chona and Mattingly)

Potassium in Soils

The value of potassium reserves in British soils. The mechanical compositions of 40 soils, collected by B. W. Avery and others in the Soil Survey, were determined, including the percentage of fine clay ($<0·2\ \mu$) in the clay fraction ($<2\ \mu$). Previous work (*Rothamsted Report* for 1959, pp. 45–46) suggests that the percentage of fine clay ($0·1–0·3\ \mu$) in the soil is related to the rate of release of K from non-exchangeable reserves. The percentages

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of clay finer than $0.2\,\mu$ in the total clay fractions of these soils were approximately related to the geological origin of the parent material. Soils derived from Jurassic and Cretaceous clay formations contained much more fine clay than those from both earlier and more recent sediments. The potassium-releasing capacities of this wide range of soils is now being related to their proportions of fine clay and to other properties. The pK–$\frac{1}{2}$pCa values, $-\log\frac{(K)}{(Ca)^{\frac{1}{2}}}$, (*Rothamsted Report* for 1956, p. 57) of these soils were measured 1 hour after adding KCl solutions of strength $2.5 \times 10^{-5}M$ to $10^{-2}M$ to suspensions of soil in $10^{-2}M$-CaCl$_2$ solution. From these measurements, the change in pK–$\frac{1}{2}$pCa caused by the exchange of 1 millimole of K/g of clay in the soil was calculated; it is inversely proportional to the capacity of the soil to buffer changes in the K content of the exchangeable cations in the soil clay. The origin of the parent material seems to have little influence on this "capacity". (Talibudeen)

Exchangeable potassium in soils. The desorption of exchangeable K by electrolyte solutions from arable soils having exchangeable $\frac{K}{Ca}$ ratios <0.1 was examined using various soil : solution ratios. Air-dried soils released up to 50% more K to $0.01M$-CaCl$_2$ and to M-NH$_4$Cl than did soils pre-wetted overnight at soil : water ratios several times field capacity. Pre-wetting at about field capacity gave smaller values of exchangeable K. Increasing the time of exchange from $\frac{1}{2}$ minute to 2 days released more K at small soil : solvent ratios (minimum 1 : 25), but at large ratios (maximum 1 : 400) K exchange was most after $\frac{1}{2}$ minute, remaining unchanged up to 2 days.

The lyotropic series of K exchange with competing cations at small soil : solvent ratios was $0.03M$-NH$_4^+$>$0.01M$-Mg^{++}>$0.03M$-Na$^+$>$0.01M$-Ca^{++}, but at high dilutions the order was $0.03M$-Na$^+$>$0.03M$-NH$_4^+$>$0.01M$-Mg^{++}>$0.01M$-Ca^{++}; in both series the difference between the end members was two-fold or more. In batch extraction with more concentrated solutions at a soil : solution ratio of 1 : 100, the lyotropic series was $1.0M$-Na$^+$>$0.10M$-Ca^{++}>$1.0M$-NH$_4^+$. Decreasing the concentration of the exchanging cation from $1.0M$ to $0.03M$ increased the exchangeable K measured by the NH$_4^+$ ion, which collapses the "inter-layer" space in expanding micas. The reverse effect was obtained with Mg^{++} (which does not collapse the inter-layer space) when its concentration in the extracting solution was decreased from $0.1M$ to $0.01M$. Similar experiments on K-saturated Wyoming bentonite, Montana vermiculite and Willalooka illite showed that pre-wetting time, and the concentration of the exchanging cation, had little effect on exchangeable K. These experiments show that pre-treatment of soils, the proportion of K in the total exchange capacity and the nature and concentration of the exchanging cation may all have important effects on measurements of exchangeable K in soils. (Deist and Talibudeen)

K/Rb ratios in soil : solution exchange studies. Work described in last year's Report (p. 63) was repeated on four soils of different mechanical

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and mineralogical compositions using five levels of Rb. "Exchangeable K" values at equilibrium, calculated as before, decreased with increasing Rb levels and were always much greater than K exchangeable to $1·0M$-ammonium acetate. Thus only part of the Rb removed from solution by the soil is governed by the Ratio Law. With increasing Rb levels, increasing amounts (but decreasing proportions) of Rb were specifically adsorbed by the soil very rapidly. Subsequent changes in the K/Rb ratio in solution are directly related to exchange on to internal surfaces within the soil. The K in the soil in equilibrium with the Rb remaining in solution after rapid adsorption has occurred was calculated by the Ratio Law and found to increase with increasing Rb concentration to a maximum; this value was equal to the ammonium acetate-extractable K. With the most added Rb the "adsorbed" Rb was directly related to clay content, but when little was added the same amount of Rb was adsorbed by all the four soils. (Deist and Talibudeen)

Ratios of K/Rb taken up by perennial ryegrass and white clover. Rb and K uptakes by both crops grown in sand culture were measured at 24, 31 and 54 days' growth in a half-strength Hoagland solution containing $0·003M$ (K + Rb) chlorides at six K/Rb ratios from 2·5 to 200. Potassium was analysed by flame photometry and Rb radiometrically as [86]Rb. Tops and roots were analysed separately and distribution factors $k_d = \dfrac{(K \div Rb)\ \text{plant}}{(K \div Rb)\ \text{solution}}$ were calculated. All k_d values were close to 1, indicating that there was no large discrimination by either crop between these ions. Ryegrass had a slight preference for Rb (mean $k_d = 0·96 \pm 0·01$), whereas clover did not differentiate between the two ions ($k_d = 1·02 \pm 0·01$). The K/Rb ratio in solution had little effect on the ratio in the plant at the $0·003M$ (K + Rb) level. K was preferentially transported to the clover tops only during early growth (the first 24 days); k_d for the whole plant (both crops) increased by 5% between 24 and 31 days and then remained constant up to 54 days. Between different K/Rb ratios in solution, between the 2 species and between tops and roots the largest differences in the observed K/Rb ratios in the plant were at 24 days. Potassium in the seed had no effect on the k_d values for the two species. At K/Rb ratios <5, plant growth was retarded. These results suggest that in solution and sand cultures Rb is a suitable tracer for K, especially when plants are grown for long periods. (Deist and Talibudeen)

The K/Rb ratio was measured in successive monthly cuts of ryegrass grown in 6 mixtures of sand with soil from Sawyers Field at Rothamsted. Soil : sand ratios ranged from 0·5 to 4 and the mixtures were pre-treated for 3 days at field capacity with 1·6 microequivalents of Rb as ^{86}Rb/100 g soil. Dry matter yield increased with the logarithm of the soil : sand ratio, linearly in the first cut, curvi-linearly in the second and to a maximum at ratios of 2 and 4 in the third cut. The yield of K rose to a maximum in all cuts at soil : sand ratios of 2 and 4. The cumulative yields of dry matter, K and Rb rose approximately linearly with time. K : Rb ratios increased with, and were linearly related to, log (soil : sand ratio) in the first and second cuts. K : Rb ratios in the first cut were always greater than those in

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the second cut by a constant amount; this difference may have been because the tops from the first cut contained more K. The experiments show that maximum yields of dry matter and K can be obtained at soil : sand ratios >2; decreasing the ratio to $\frac{1}{2}$ decreased yields of dry matter and of K by a fifth; they also show that K diffuses more slowly than Rb from soil particles to plant roots in this "unmanured" soil of pH 5·2. (Talibudeen and Weerasekera)

Natural Radioactivity and Total Potassium in Soils

Previous experiments (*Rothamsted Report* for 1962, pp. 67–68) were repeated this year on 15 test soils from England and Wales. Geiger–Müller (GM) counting gave % K in 6 soils not significantly different from total % K determined chemically. In 5 soils, where the % K values by GM counting were on average 28% more than the chemically determined values, thorium contents of the soils measured by γ-ray spectrometry successfully accounted for the difference. In the remaining soils an average difference of 33% between the "chemical" and "GM" values for % K was decreased to 19% by allowing for thorium contents. Presumably the difference that remains is caused by uranium, but none of the low energy ($<1·4$ MeV) γ-emissions from the uranium family could account for it. We cannot measure high-energy emissions in a reasonable time with our 44 cm $\times$ 50 cm NaI(Tl) crystal.

Thorium contents were estimated by measuring the integrated emission from the 1·53 and 2·62 MeV emissions from ThC′ and ThC″ respectively. The average counting time for a "thorium-equivalent" of 0·35% K (in soil) was 200 minutes, this gave a standard error of $\pm 2·5\%$ on the net count-rate of the sample. GM counting required an average counting time of 100 minutes for a soil with 1% K (S.E. $\pm 1·3\%$). These counting times are inversely proportional to the square of the standard error of the measurement and to the size of the detector crystal. (Talibudeen)

The Effect of Beryllium on Kale and Grass

Investigations of crop failures on two shallow soils were described last year (pp. 55–60). Both soils were unusual in having detectable levels of beryllium soluble in 0·5N-acetic acid. The Lincolnshire soil had 0·2 ppm of soluble Be and the Hertfordshire soil 0·08 ppm. There is very little published information on the effects of Be on crops, or on its uptake, though toxicity symptoms in culture solutions are recorded (Romney, Childress and Alexander, *Science* (1962), **135**, 786–787). A glasshouse experiment was done to see whether "thousand head" kale and S22 rye-grass took up Be from these two soils and from a sand culture. Three levels of Be (0, 0·4 and 40 ppm of Be in the culture media) were tested as $BeSO_4.4H_2O$. Adequate basal dressings of all nutrients were given.

In sand culture both kale and ryegrass established badly, and with 40 ppm of Be the seedlings were extremely stunted, and died prematurely. In the soils all the plants grew well and looked normal, except that with 40

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ppm of Be kale leaves tended to curl backwards. The experiment lasted 57 days, grass was cut twice in this time and kale was harvested at the end. In both soils fresh and dry matter yields both of kale and of grass were significantly increased by the Be treatments by 12–25%. We have no explanation for this unexpected result. H. H. Le Riche determined Be in the crops spectrographically. Kale on the Lincolnshire soil contained <0.2 ppm and 0.26 ppm beryllium in the dry matter of plants receiving the two rates of application. Kale on the Hertfordshire soil that received the large rate of Be contained 0.47 ppm. Grass samples contained less, and these are being examined further.

The performance of the crops in the *soils* with added beryllium differed from the *sand culture* and from results in water-culture, where 5 ppm Be stunted growth. It seems that added Be is immobilised by these soils, $BeSO_4$ supplying 200–500 times as much as is soluble in acetic acid extracts of these soils produced no leaf symptoms, and did not restrict root growth. Both soils were light, contained only 5% of clay (<0.002 mm) and silt, and were slightly calcareous with pH (in water) >7. Presumably heavier soils would immobilise Be even more. As the solubility relationships of Be added to acid soils were not studied, it cannot be assumed that the dressings used will have no effect on crops grown on all soils. (Williams)

Apparatus and Experimental Methods

Mass spectrometer. The equipment continues to show good reproducibility with standard samples of pure ammonium salts, so that occasional discrepancies with experimental materials must be attributed to contamination during experiments or during sample preparation, and to the variability of the normal isotopic ratio in materials from different sources. The "Technical Meeting on the Use of Isotopes in Soil Organic Matter Studies" held in Brunswick in 1963, showed that these discrepancies are widely experienced. Contamination during NH_3 distillation described in last year's Report (p. 68) has now been largely eliminated. Apparently NH_3 is chemisorbed on cold glass surfaces, so that any system in which NH_3 comes in contact with cold glass will hold it up. A silver tube surrounded by a cooling jacket is now used to condense the steam-distilled NH_3, and there is very little contamination. Because three corrections are now made to the mass spectrometer readings, calculating the results takes increasingly more time. In conjunction with J. H. Rayner (Pedology Department) a programme was written that enables the % ^{15}N to be calculated on the Elliot 402 computer. (Newman)

Measuring cation-exchange capacity of soils by a rapid radio-tracer method. A modified semi-micro method using ^{45}Ca-labelled calcium salts to determine the negative charge on soils succeeded with 12 soils. The soil need not be weighed accurately, and the total time for measurements on batches of soils is $\frac{1}{2}$ hour/soil. The negative charge on acid soils could be determined at the soil's own pH, and also at neutrality, by using ^{45}Ca-labelled $CaCl_2$ and calcium acetate solutions. Cation exchange capacities were read

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from a calibration curve without computation. (Talibudeen and Weera-sekera)

Reducing nitrate by a zinc–ferrous sulphate mixture. The $Zn–FeSO_4$ method for measuring nitrate in soil has been selected as most suitable after examining the amounts of Zn, $FeSO_4$ and MgO required for complete reduction. Using $Zn–FeSO_4$ for reducing nitrate to ammonia was first proposed by Salle (*Ann. Chim. anal.* (1910), **15**, 103–105). The method was adopted by the Association of Official Agricultural Chemists (U.S.A.) to determine nitrate in fertilisers containing no organic matter, calcium cyanamide or urea, and current details are given in their *Official Methods of Analysis* (1960). The reduction is done in $2N$-NaOH, but this solution is too alkaline for soil extracts and decomposes organic nitrogen. Substituting MgO for NaOH was successful. A complete chemical explanation of the role of Zn in the mixture used to reduce nitrate has never been given. With a very large excess of $FeSO_4$, and no Zn, full reduction can be obtained, but the reaction is slow even at boiling point. We have never obtained complete reduction with Zn alone; but with 0·4 g powdered Zn and 0·4 g $FeSO_4.7H_2O$ ground together, 100 μg of NO_3-N are reduced and distilled as ammonia in 5 minutes. Past failures with $Zn–FeSO_4$ (originally devised as a macro-method) were probably because the macro-method was transferred directly to micro-method conditions without establishing how much reducing mixture was needed and the proportion of the two constituents. (d'Arifat and Warren)

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