ROTHAMSTED RESEARCH

# Rothamsted Experimental Station Report for 1965

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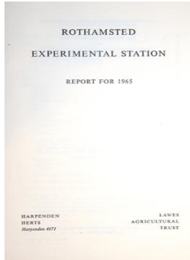
ROTHAMSTED
EXPERIMENTAL STATION
REPORT FOR 1965

## Chemistry

### G. W. Cooke

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# CHEMISTRY DEPARTMENT

G. W. COOKE

Two valued members of the department retired, R. G. Warren after 42 years service, and F. J. Seabrook after 54. Barbara M. Jephcott and J. K. Coulter left, J. D. D. Mitchell and F. G. Hamlyn were appointed.

G. W. Cooke visited Bulgaria at the invitation of the Bulgarian Academy of Sciences, and Malaya at the invitation of the Rubber Research Institute. J. K. Coulter visited Guinea at the request of F.A.O., and the Sudan at the request of the World Bank. J. K. R. Gasser was seconded to the Ministry of Overseas Development for five weeks to join a Technical Mission to Brazil.

I. S. Cornforth was awarded the Ph.D. degree of London University.

Professor W. H. Patrick from Louisiana State University and Mr. Wang Keun Oh from Korea both worked in the Department for five months.

## Soil Classification and Fertility

In continuing the work described last year designed to relate kind of soil to its fertility, experiments were done to see how soil characteristics of the kind that influence classification affect root growth; other new experiments attempted to measure the maximum yields of crops grown on contrasted soil types.

**Soil factors and root development.** Plots of Sitka spruce, Norway spruce and Japanese larch transplants were grown on three sites on different parts of a slope at the Wareham forest nursery. At the end of the growing season the roots of all species at two sites were almost completely confined to the 8-in.-deep cultivated (Ap) horizon. Most roots only just entered the top inch of the $A_2$ horizon, where even the strong tap root of Japanese larch then turned horizontally. Norway and Sitka spruce behaved similarly in 1964. The $A_2$ horizon is almost pure sand with no cracks, and its bulk density (1·49 g/cc) may be so large as to prevent roots from penetrating. Hidding and Van den Berg (*Proc. 7 int. Congr. Soil Sci.* (1960) **1**, 369) showed that roots do not penetrate sands with less than 40% pore space, i.e., bulk density of 1·56. Another reason may be that the $A_2$ horizon is often waterlogged, for pits dug soon after heavy rain showed water flowing laterally through the $A_2$ over the top of the impermeable $B_{humus}$ horizon. At one site without any $A_2$ horizon, which was probably destroyed by deep digging, Japanese larch roots penetrated 30 in.

The shallow rooting imposed on small trees by these soils has the practical advantage that they can be lifted easily with whole root systems; but for other crops such an impermeable layer may be detrimental. Water probably flows through the $A_2$ after most showers, and soluble fertilisers may be washed down the slope, so interfering with experiments.



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The distribution of sugar-beet roots was measured at Broom's Barn (in co-operation with P. B. H. Tinker and O. Talibudeen) on an experiment laid out in a logarithmic design (*Rothamsted Report* for 1964, p. 51). The plants were spaced from 36 to 7 in. apart and were grown with and without NPK fertiliser. Rooting depth was examined in three ways: $^{32}P$ was placed at two depths, monoliths were excavated on a "nailboard", and the moisture-extraction pattern was determined with a neutron meter. Plants spaced 36 in. apart did not take up $^{32}P$ placed 2 ft deep at any of the sites. (At two sites in one plot plants took up P placed 4 ft deep, but excavating showed this was a disturbed site.) Plants spaced 22 in. apart took up P placed 2 ft deep from all four sites in the plot given NPK fertiliser, but from only one out of four sites in the unfertilised plot; on two sites out of eight at this spacing (one fertilised, one unfertilised) plants removed P from 4 ft. At two out of four sites in the fertilised plot, and three out of four sites in the unfertilised, plants spaced 13 in. apart removed P from 2 ft deep; at five sites out of eight (two fertilised, three unfertilised) they removed P placed 4 ft deep. At the 7 in. spacing P was taken up at five out of six sites (three fertilised, two unfertilised) from 2 ft, but at only one site out of six from 4 ft deep.

In a supporting experiment the growth of sugar-beet roots was measured by injecting $^{32}P$-labelled potassium phosphate solutions 20 cm deep in three concentric rings of 10, 20 and 30 cm radius, around a 6-weeks-old healthy sugar-beet plant in a fertilised plot. Labelled phosphate in leaf samples showed peaks at 4 and 6 weeks after injecting, suggesting that lateral roots 20 cm deep had extended 10 cm from the stem after 2½ months-growth, and 20 cm after 3 months.

Excavating soil monoliths, with the roots retained on a "nailboard", showed that the widest-spaced plants had very "fangy" roots in the fertilised plots. Beet grown more closely in the fertilised plots, and at all spacings in the unfertilised plots, were better shaped. The close-spaced plants in undisturbed soils have a more intensive and deep root system. Where the soil had been disturbed even the most widely spaced plants had extensive root systems down to the maximum depth excavated (3 ft). At the widest spacing in undisturbed soil the tap roots turned sideways on reaching the compact chalky-clay layer approximately 2 ft deep. At the close spacing the sugar beet had an intensive system of very fine roots, which followed every crack and worm hole to more than 36 in. deep in this horizon, which had a bulk density of 1·70 g/cc and was so compact that it had to be dug out by a crow-bar.

Rain was such that there was no long period of moisture deficit, so the neutron meter could not be used to estimate where the roots had extracted water.

The widely spaced sugar beet had shallow roots, and closer spacing encouraged deeper rooting until the plants were so close together (7 in.) as to remain small, when deep rooting was less common. Similar results were obtained with cabbages in the dry year of 1964 (*Rothamsted Report* for 1964, p. 51), when deeper rooting could be explained by the large moisture deficits. No such prolonged deficits occurred in 1965, but perhaps even temporary shortages of moisture encouraged the roots to go deeper. The



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experiment showed that even the widest-spaced plants made an extensive deep-root system where the soil was easy to penetrate. (J. K. Coulter)

**Soil volume.** The effect of soil volume on plant growth was studied with sugar beet at Broom's Barn and cabbages at Woburn. The size of sugar beet increased from the closest to the widest spacings in both fertilised and unfertilised plots; NPK fertiliser had little effect on size at the closest spacing, but at spacings more than 9 in. fertilisers increased root size, and even at the widest spacing their average weights were 2·2 lb more in the fertilised plot (5·4 lb) than in the unfertilised (3·2 lb). Sugar percentage (17·0) was greatest in plants spaced 22 in. apart in both fertilised and unfertilised plots and least in those 36 in. apart. Potassium percentage in the roots increased slightly with increasing spacing, and sodium greatly (from 0·39 to 1·08% in the unfertilised plots and from 0·51 to 1·64% in the fertilised plots). Amino-N also increased greatly with increased spacing. The concentrations of the most mobile nutrients increased most with increased spacing, which slightly decreased dry matter of the roots.

The cabbages in the experiment at Woburn were transplanted late and grew badly; without fertiliser they did not grow at all, even at the widest spacings. This contrasts with the results with cabbages at Rothamsted in 1964, and with sugar beet at Broom's Barn in 1965, where widely spaced plants were of normal size without fertilisers. The Woburn soil so lacks nutrients, particularly N, that the plants cannot get enough to grow even when they can exploit a large volume of soil. (J. K. Coulter)

**Maximum productivity.** Crops grown on different soils were given adequate basal dressings of P and K but various amounts of N, and the dry matter they produced was measured. Barley, grown at three sites on the top, the middle and the bottom of a slope at Saxmundham, was harvested green. The basal dressing of 3 cwt/acre 15–10–10 compound fertiliser was given before sowing and plots were top-dressed with 0, 1, 2 or 3 cwt/acre N. The crops on all plots top-dressed with 2 or 3 cwt/acre N, except at the bottom of the slope, lodged badly. Dry matter averaged 7,800 lb/acre with basal fertiliser only, and only at the bottom of the slope was it increased greatly by additional N. This site yielded the least dry matter (7,300 lb/acre) with the basal dressing only and the most (9,700 lb/acre) with the 3 cwt N/acre. The percentage N in the crop increased from 0·99% with basal fertiliser to 1·99% with the 3 cwt N/acre top-dressing. On average, the crop contained 77 lb N with basal fertiliser only and 179 lb N with the top-dressing of 3 cwt N/acre. The recovery of added N (assuming that recovered from the basal dressing remained constant) averaged 46% from the 1 cwt N/acre top-dressing and 30% from 3 cwt/acre N. (J. K. Coulter)

At Wareham nursery perennial ryegrass was sown in plots of 1 sq yd with basal dressings of magnesium, ammonium phosphate and potassium metaphosphate. When 2 in. high the grass was top-dressed with "Nitro-Chalk" to supply amounts of N ranging from 0 to 320 lb/acre at each occasion. Similar dressings of N and a basal dressing of 107 lb/acre K were given after the first cut. Fertilisers were not given after the second cut,



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but were after the third, as after the first. The rainfall of 14·5 in. during the experiment was supplemented by 5 in. of irrigation (this need was calculated from preceding rainfall). Four cuts were taken, the first on 21 June, the last on 3 November. Dry-matter yields were increased by N dressings up to 672 lb/acre (given in three applications), but not beyond, and 960 lb/acre N depressed yield slightly. The largest total dry matter yield from the four cuts was 10,500 lb/acre. The amount of N applied had little effect on percentage K in grass at the first, second and fourth cuts; K was not applied before the third cut, and its percentage in grass fell from about 1·8 with the smallest N dressing to 1·3 with the largest. The largest yields removed 230 lb/acre K, nearly three-quarters the amount applied as fertiliser. The sodium concentration in the grass increased with increasing dressings of N, and was particularly large, about 0·5%, in the third cut on plots given much N for earlier cuts. Altogether about 40 lb/acre of Na was recovered by grass dressed with the most N; some of this must have come from rain, for the top 6 in. of Wareham soil contains only about 35 lb/acre of exchangeable Na. The N in the first cut ranged from 1·95% on plots without N to 5·34% on those with the largest amount, and grass from these latter plots contained free nitrate. Most N was recovered (41%) from plots given 576 lb/acre N. (J. K. Coulter)

Seedbeds and transplant beds of Sitka spruce had basal fertiliser dressings of magnesium ammonium phosphate plus potassium metaphosphate, and ten incremental dressings of "Nitro-Chalk", ranging from none to a total of 60 g N/sq. yd (about 640 lb N/acre). The seedlings were 1·1 in. high on "no N" plots, 2·4 in. with the "low N" range, 2·6 in. in the middle range and 2·1 in. with most N. The corresponding values for transplants were: 6·3, 7·9, 7·5 and 6·7. The most dry matter produced by seedlings was 470 g/sq yd (5,000 lb/acre) and by transplants 450 g/sq yd (4,800 lb/acre). N in both seedlings and transplants ranged from 0·6% on the "no N" plots to 1·3 with the largest dressings. Ancillary tests showed that there was no response to the 5 in. of irrigation water supplied. (Benzian)

## Soil Physical Conditions and Nutrient Uptake

The use crops make of nutrient reserves in soils, and crop responses to fertilisers, depend on characteristics of soil profiles and on properties that determine how much of soil and subsoil is explored by roots. Recent work has included experiments where cereals were grown without ploughing, measurements of bulk density and pore space at Saxmundham (where compact subsoils interfere with both root growth and water penetration) and developments to our method of measuring the stability of soil aggregates.

**Growing cereals without ploughing.** The herbicide paraquat leaves no active residues in soil, so weeds and the remains of a previous crop can be killed with it and a new crop sown immediately afterwards. The possibility of eliminating ploughing and seedbed cultivation has obvious attraction, and it could also affect soil management and crop nutrition. When a ley is ploughed before sowing an arable crop the thin layer of soil where struc-



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ture is improved by the ley (usually no more than 3 in. deep) is buried and the arable crop may be sown on unimproved subsoil. Ploughing and cultivating speed the loss of organic matter from soil, and omitting these operations may conserve organic matter and alter the supply of nitrogen to the crop. Two possible disadvantages are that, unless soil is ploughed, phosphorus and potassium fertilisers are not easily incorporated in seed-beds, and should the soil become too compact, root growth may be impeded and more fertiliser needed to replace nutrients that would otherwise be taken from the soil.

A field experiment started in 1964 on a 10-year-old ley compared spring wheat sown after ploughing and conventional cultivations with the use of paraquat spray to kill the ley followed by various cultivations before sowing. One treatment was direct drilling of seed into the killed sward ("sod seeding"). This was a failure, because the grass grew again strongly, perhaps because the sward was badly poached by cattle before it was sprayed. In plots rotovated after spraying some grass grew, and yields were less than on the ploughed plots. Plots sprayed before ploughing yielded slightly less than unsprayed plots.

In 1965 the experiment was repeated with spring barley using the same treatments on the same plots (except that spring and autumn applications of the herbicide were compared). Early on, almost all the weeds and grass in the stubble seemed to have been killed, but couch grass (*Agropyron repens*) and annual grasses soon appeared in the sprayed plots; the sod-seeded plots yielded considerably less than ploughed plots, particularly those given little or no nitrogen fertiliser (Table 1). The crop lodged severely, which probably explains the depression in yield by nitrogen on

**TABLE 1**

*Effects of method of sowing and rate of nitrogen fertiliser on wheat and barley yields*

| | Yield of grain (at 15% moisture) in cwt/acre | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Spring wheat, variety Opal, 1964 | | | | Barley, variety Maris Badger, 1965 | | | |
| Cwt N/acre | 0 | 0·3 | 0·6 | 0·9 | 0 | 0·3 | 0·6 | 0·9 |
| *Cultivation treatment* | | | | | | | | |
| Normal: ploughing, disking, etc. | 33·3 | 38·8 | 40·2 | 45·2 | 39·1 | 37·4 | 36·6 | 36·4 |
| Paraquat spray followed by: | | | | | | | | |
| Normal ploughing, etc. | 30·4 | 36·4 | 39·2 | 43·6 | 37·5 | 36·2 | 36·7 | 37·1 |
| Rotovating and seeding | 25·9 | 33·6 | 33·7 | 37·8 | 33·5 | 34·9 | 34·0 | 35·0 |
| Sod-seeding | 9·3 | 12·5 | 14·5 | 17·7 | 16·0 | 22·0 | 28·8 | 25·5 |
| *Standard errors* | | | | | | | | |
| Horizontal comparisons | ±1·10 | | | | ±1·15 | | | |
| Vertical comparisons | ±1·57 | | | | ±1·24 | | | |

the ploughed plots. Other factors apart from weed competition may have reduced yields on the sod-seeded plots. At drilling the ground was too dry for sod-seeding and the seed was not sown deeply enough (in contrast to 1964, when the ground was wet and sod-seeding was satisfactory but the ploughed plots could not be sown with the same drill). Also, much seed on the sod-seeded plots was eaten by birds, for the old stubble provided more



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cover than on the ploughed plots. In the very different conditions of the two years sod-seeding failed because grass weeds were not killed by the herbicide, and in neither year could the nutrition of crops grown without conventional cultivations be studied. Effects on the soil fauna are described in the Report of the Entomology Department (p. 189). (Bolton)

**Bulk densities of Saxmundham soils.** Table 2 shows the bulk densities of soil samples taken from the Rotation I experiment described in the Report for 1964 (p. 230) and from an adjacent grassed headland, using a special core sampler that left the samples undisturbed.

The land under winter wheat in 1965 had never been ploughed more than 7 in. deep, and the samples showed a plough pan. Land under barley and sugar beet in 1965 was ploughed deeper (10 in.) for the first time in autumn 1964, and topsoil and subsoil were incompletely mixed. Samples from the headland showed that structure was improved down to 12 in. by grass that had probably been undisturbed for 60 years. Except from under old grass, roots were not found deeper than 9 in.

The bulk densities of the soils under barley in 1965 were large (1·60 or more), and showed little effect from annual dressings of 6 tons/acre of FYM given on plot 1 for 65 years. Presumably, effects that may have existed were obliterated by the deeper ploughing (as they were on the area under sugar beet in 1965). The cores taken from land where winter wheat had grown had the largest bulk densities (1·74 on plot 40 that has NPK fertiliser each year). Bulk density was smaller and pore space larger with FYM than with NPK fertiliser each year.

**TABLE 2**

*Bulk densities and pore space in soils of Saxmundham Rotation I Experiment*

(Data are for oven-dried soils)

| Plot No | Continued manuring | Bulk density (g/cc) 0–3 in. | 3–6 in. | 0–6 in. | Total pore space (%) 0–3 in. | 3–6 in. | 0–6 in. |
|---|---|---|---|---|---|---|---|
| | | Spring barley in 1965 | | | | | |
| 6 | None | 1·57 | 1·67 | 1·62 | 37·7 | 33·7 | 35·7 |
| 10 | NPK fertiliser | 1·62 | 1·73 | 1·67 | 35·7 | 31·3 | 33·7 |
| 1 | FYM | 1·60 | 1·60 | 1·60 | 35·7 | 35·7 | 35·7 |
| | | Winter wheat in 1965 | | | | | |
| 36 | None | 1·49 | 1·69 | 1·59 | 40·9 | 32·9 | 36·9 |
| 40 | NPK fertiliser | 1·76 | 1·64 | 1·74 | 30·2 | 34·9 | 32·5 |
| 31 | FYM | 1·57 | 1·49 | 1·53 | 36·9 | 40·1 | 38·5 |
| | Old grass headland | 1·08 | 1·17 | 1·13 | 52·8 | 48·9 | 50·8 |

Bulk density of soil under the grassed headland was much less, and pore space about one-third larger, than under cereals. Bulk density about 1·60 seems to restrict root growth on this soil. The subsoil (6–12 in. deep) under winter wheat, which had never been disturbed by cultivations, and had a bulk density of 1·71, was devoid both of roots and cracks roots might have penetrated. In contrast, the headland subsoil with a density of 1·53 contained many roots.

The winter wheat in 1965 grew well without N fertiliser, suggesting that



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it might have taken up nitrate leached from the surface and stored in the subsoil, but analyses of deeper cores showed no accumulation of mineral-N ($NH_4$—N + $NO_3$—N). (Williams)

## Reference Plot Experiments

The long-term reference plot experiments at Rothamsted (*Rothamsted Report* for 1964, p. 64) and Woburn (*Rothamsted Report* for 1964, pp. 63–64) are useful for relating crop growth and yield, and fertiliser responses, on the two kinds of soil.

**Rothamsted.** The experiment was started in 1956 and concluded its second rotation in 1965. The crop sequence of barley, clover–ryegrass ley, potatoes, wheat and kale was maintained, and responses to all combinations of N, P and K fertilisers were measured on each crop; additional plots measured increases from FYM (applied for potatoes and kale) with and without NPK fertiliser. There are similar tests on an adjacent strip of permanent grass. Mean yields from the second five-year rotation were slightly less than from the first with wheat and barley, slightly greater with potatoes and kale and considerably greater with the ley. Permanent grass yielded much less in the second 5-year period. N, P and K affected the yields of the five crops similarly in the two periods. Table 3 shows that N fertiliser greatly increased the total yields of wheat, kale, permanent grass and barley, P the yields of kale and the ley, and K the yields of the ley, potatoes and wheat. The largest increases in yield were from K (ley and potatoes), and the next largest from P (to kale) and K (to wheat). Ley and potatoes were the most critical test crops for K and kale for P; all except the potatoes and ley were good test crops for N. (Widdowson and Penny)

**TABLE 3**

*The ranges and differences between crops in responses to N, P and K fertilisers at Rothamsted, 1961–65*

| | Increases in yield* (cwt of total dry matter/acre) | | | | | |
|---|---|---|---|---|---|---|
| Response to | 50–40 | 40–30 | 30–20 | 20–10 | 10–5 | 5–0 |
| Nitrogen | — | — | Wheat | — | — | — |
| | — | — | Kale | — | — | Ley |
| | — | — | Grass | — | Potatoes | — |
| | — | — | Barley | — | — | — |
| Phosphorus | — | Kale | Ley | Potatoes | — | Grass |
| | — | — | — | Barley | — | — |
| | — | — | — | Wheat | — | — |
| Potassium | Ley | Wheat | — | — | Grass | — |
| | Potatoes | — | — | Kale | Barley | — |
| | — | — | — | — | — | — |

* Yields of wheat and barley are of grain plus straw.

**Magnesium deficiency at Woburn.** The value of these experiments for following the removal from soil of plant nutrients, and showing how deficiencies are caused, was shown at Woburn, when for the first time leaves of sugar beet in some of the plots were chlorotic. Leaf analyses



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confirmed the cause as magnesium deficiency, and showed that leaves from the FYM plots contained much more Mg than leaves from plots given only NPK fertilisers. Giving K fertilisers annually decreased the magnesium content of the leaves and increased the visual leaf symptoms. Some results are shown in the table below: (Bolton)

*Per cent Mg in dry matter of sugar-beet leaves at Woburn in 1965*

| | | Fertiliser | | |
|---|---|---|---|---|
| | | NPK | None | |
| With FYM | | 0·41 | 0·48 | |
| | | Other fertilisers | | |
| | NP | N | P | None |
| Without K fertiliser | 0·27 | 0·37 | 0·30 | 0·27 |
| | NPK | NK | PK | K |
| With K fertiliser | 0·11 | 0·16 | 0·20 | 0·22 |

## Cereal Experiments

The fertiliser dressings given to cereals have increased greatly in the last 20 years. Yates and Boyd (*Outl. Agric.* (1965) **4**, 203–210) showed that the average nitrogen dressings for wheat grown in arable areas increased four-fold between 1943–45 and 1962, and for barley nearly three-fold. As the current average dressings of nitrogen approach those thought to be optimal, it is important that the amounts used should be adjusted to suit the fertility of individual fields. (Much of the yield lost by lodging is because too much N is given to cereals on soils that have reserves derived from recent periods under herbage crops or from organic manures used for roots.) Also, both the form of nitrogen fertiliser and its timing should be appropriate to soil, crop and season. In the 10 years from 1952 to 1962 the amounts of phosphate used in arable areas increased from 0·22 to 0·29 cwt $P_2O_5$/acre for wheat and from 0·24 cwt to 0·29 cwt for barley. The potash used increased much more than this, from 0·12 to 0·34 cwt $K_2O$ for wheat, and from 0·16 to 0·40 cwt for barley. The average amounts of P and K fertiliser used at present are "maintenance" dressings; they supply no more K but rather more P than good crops remove. The main problems with P and K manuring of cereals are: (1) to identify the relatively few poor soils that need much larger dressings of P; (2) to make sure that enough K is supplied in the rotation; (3) to assess the gains from drilling seed and fertiliser together. Our cereal experiments attempt to get information on these problems.

Soil-borne pests and diseases cause much loss of yield where cereals are grown frequently, and they affect the need for fertilisers. We have therefore initiated field experiments with small plots to test the effect on yield of partially sterilising the soil, and to examine the interactions of sterilisation, nitrogen fertiliser and watering.

**Forms and amount of nitrogen for spring barley.** Four experiments in 1965 were made on soils over Chalk (two calcareous) to compare ammonium



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sulphate with calcium nitrate. Each fertiliser was broadcast to give 0·4 or 0·8 cwt N/acre on the seedbed and was tested with and without additional top-dressings of 0·4 cwt N/acre (aggregate dressings were 0·4, 0·8 or 1·2 cwt N/acre). These eight nitrogen tests were made in all combinations with and without potassium (0·5 cwt/acre $K_2O$ combine-drilled) and with and without sodium (3 cwt/acre agricultural salt (sodium chloride) broadcast on the seedbed). Additional plots measured the response to phosphate (0·5 or 1·5 cwt $P_2O_5$/acre combine-drilled).

Combine-drilled potassium checked early growth at three and broadcast sodium at two of the four centres, but phosphate greatly improved early growth on the two calcareous soils.

**TABLE 4**

*Mean yields from four barley experiments in 1965*
*(cwt of grain/acre containing 15% moisture)*

Yield without nitrogen fertiliser 20·8

| N applied, cwt/acre | | Form of nitrogen | |
|---|---|---|---|
| To seedbed | Top-dressing | Ammonium sulphate | Calcium nitrate |
| 0·4 | 0·0 | 28·6 | 32·3 |
| 0·8 | 0·0 | 35·4 | 38·8 |
| 0·4 | 0·4 | 36·7 | 39·8 |
| 0·8 | 0·4 | 39·0 | 40·1 |

Calcium nitrate gave larger yields than ammonium sulphate in each experiment and in three-quarters of the total comparisons (Table 4). Applying 0·4 cwt N/acre to the seedbed and 0·4 cwt N/acre in May gave slightly larger yields than applying 0·8 cwt N/acre to the seedbed; the gains were similar for both N-fertilisers, so nitrate-N applied to the seedbed could not have been lost by leaching. Applying 1·2 rather than 0·8 cwt N/acre increased yields significantly at only one centre in this wet year. Combine-drilled potassium decreased yields slightly in three of the four experiments. At the other centre the barley gave only a little response to potassium and then only when nitrogen was given. Agricultural salt had no effect at two centres, but slightly increased yield at the other two. Phosphate increased yields sizeably on the two calcareous soils and slightly on the other two. (Widdowson and Penny)

**Comparisons of broadcasting and drilling NPK fertilisers.** Four experiments compared yields from three NPK fertilisers; these were 22–11–11 (% N: % $P_2O_5$: % $K_2O$ ratio = 2 : 1 : 1) and two forms of 18–18–18 (ratio = 1 : 1 : 1), one contained potassium chloride and the other potassium nitrate. Each fertiliser was applied to give 0·45 or 0·90 cwt N/acre and was either broadcast over the ploughed land or combine-drilled. With 0·9 cwt N/acre, divided dressings (part broadcast and part combine-drilled) were also tested. Two experiments were on Clay-with-Flints, one on a chalky loam and the other on a gravelly loam. On the two light soils where barley was sown in February early growth was not checked by combine-drilling, but it was on the two heavier soils sown in April.



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Yields from the three fertilisers (Table 5) were not significantly different at any centre. Drilling gave slightly larger yields than broadcasting at three of the four centres, the mean gain being 1·7 cwt grain/acre at both rates of

**TABLE 5**

*Mean yields from four barley experiments comparing broadcasting and drilling three NPK fertilisers in 1965 (cwt/acre of grain containing 15% moisture)*

Yield without fertiliser 23·6

| | Fertiliser tested | | |
|---|---|---|---|
| | 22–11–11 | 18–18–18 (K from KCl) | 18–18–18 (K from $KNO_3$) |
| At 0·45 cwt N/acre: | | | |
| All broadcast | 35·8 | 35·0 | 35·5 |
| All drilled | 37·6 | 36·8 | 37·0 |
| At 0·90 cwt N/acre: | | | |
| All broadcast | 39·5 | 40·4 | 38·5 |
| Three-quarters broadcast, One-quarter drilled | 41·2 | 40·3 | 39·6 |
| Half broadcast, Half drilled | 40·9 | 41·4 | 40·8 |
| All drilled | 41·4 | 41·5 | 40·5 |

manuring. Applying half broadcast and drilling the remainder gave almost the same yield as drilling the whole dressings. (Widdowson and Penny)

**Effects of growing one-year leys on yields of following winter wheat.** The experiment made at Rothamsted (*Rothamsted Report* for 1962, p. 50) was repeated on a heavy clay-loam over Oxford Clay at Woburn; a test of K fertiliser on the ley was included. Three kinds of ley, ryegrass (S.22), red clover (Dorset Marl) and mixtures of the two were undersown in 1963. The leys were cut twice for silage in 1964, then ploughed and winter wheat sown. The effects of varying nitrogen and potassium were tested on both crops (Table 6). The leys responded little to potassium, but greatly to nitrogen. Applying 2·0 cwt N/acre to pure ryegrass produced 50% more dry matter/acre than was obtained from pure clover leys. Wheat grown without N-fertiliser yielded much more after clover than after ryegrass;

**TABLE 6**

*Yields of leys grown in 1964 and of the wheat that followed in 1965*

| | Type of ley | | | | | |
|---|---|---|---|---|---|---|
| | Clover | Clover–ryegrass | | Ryegrass | | |
| N to ley (cwt/acre) | 0·0 | 0·0 | 1·0 | 0·0 | 1·0 | 2·0 |
| Yields of dry grass in 1964 (cwt/acre) | 59·8 | 69·5 | 89·9 | 48·1 | 88·5 | 94·1 |
| Yields of wheat grain in 1965 (cwt/acre containing 15% moisture) | | | | | | |
| From nitrogen (yields averaged over K test on ley and K test on wheat) | | | | | | |
| Without nitrogen | 31·6 | 27·2 | 21·8 | 21·5 | 20·1 | 28·2 |
| With 1·0 cwt N/acre | 38·3 | 37·3 | 36·2 | 36·4 | 34·9 | 34·6 |
| From potassium (averaged over N test on wheat and K test on ley) | | | | | | |
| Without potassium | 33·4 | 33·0 | 28·9 | 28·9 | 27·3 | 30·6 |
| With 2·4 cwt $K_2O$/acre | 37·7 | 32·1 | 29·2 | 30·6 | 28·8 | 33·2 |



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this difference was diminished, but not eliminated, by applying 1·0 cwt N/acre to the wheat. Applying 2·4 cwt $K_2O$/acre to the wheat consistently increased yields, but more after clover than after the other leys, and so did not change the advantage from the clover. (Widdowson and Penny)

## Effects of Formalin on the Yields of Spring Wheat

The experiment started in 1964 at Woburn (*Rothamsted Report* for 1964, p. 65) was continued in 1965 on the third consecutive wheat crop. Formalin freshly applied for the 1965 crop was tested in all combinations with formalin applied in 1964. The test of Nabam was discontinued.

**TABLE 7**

*Mean effects of formalin, of water, and of nitrogen on yields of spring wheat in 1965*

(cwt/acre of grain and straw containing 15% moisture)

| | Formalin in 1964 | | Formalin in 1965 | | Nitrogen, cwt/acre | | | Extra water | |
|---|---|---|---|---|---|---|---|---|---|
| | Without | With | Without | With | 0·6 | 1·2 | 1·8 | Without | With |
| Grain | 21·4 | 19·1 | 12·2 | 28·3 | 16·0 | 22·4 | 22·3 | 20·3 | 20·1 |
| Straw | 29·4 | 26·0 | 19·4 | 36·1 | 22·9 | 29·3 | 31·0 | 27·5 | 28·0 |

Table 7 shows that plots treated with formalin in 1964 yielded less than untreated plots. By contrast, plots treated with formalin in 1965 greatly out-yielded untreated plots. Responses to nitrogen were sizeable, to water negligible.

Table 8 shows that plots not treated with formalin in either year yielded only 13·8 cwt grain/acre, even when given 1·8 cwt N/acre; plots treated only in 1964 yielded 3·1 cwt more. The largest yield (35·8 cwt/acre) was on plots treated in 1965 only, and exceeded that in comparable plots treated

**TABLE 8**

*The effects of formalin and nitrogen on spring wheat in 1965*

(cwt/acre of grain containing 15% moisture)

| | Formalin in 1964: Without | | Formalin in 1964: With | |
|---|---|---|---|---|
| | Formalin in 1965 | | Formalin in 1965 | |
| N applied cwt/acre | Without | With | Without | With |
| 0·6 | 6·6 | 29·1 | 8·8 | 19·6 |
| 1·2 | 10·5 | 35·8 | 16·5 | 26·7 |
| 1·8 | 13·8 | 32·6 | 16·9 | 25·8 |

in both years by 9 cwt/acre. Maximum yield in 1964 was 37·2 cwt/acre. D. B. Slope and T. D. Williams measured the incidence of take-all fungus and cereal root eelworm on the plots, with results (see p. 127 and p. 149) that explain the effects of formalin.

Effects of formalin were also measured at Rothamsted, where take-all and eelworm are less damaging than on the lighter Woburn soil. Experiments were made on two fields with contrasting cropping history, Little



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Knott, which was ploughed from grass in 1943 and has grown cereals in 19 of the following 21 years, and Pastures, which was ploughed from 10-year-old grass and sown to spring wheat in 1964. Each experiment measured the effects of formalin with and without N-fertiliser. Table 9 shows

TABLE 9

*The effects of formalin and nitrogen on yields of spring wheat at Rothamsted in 1965*

(cwt/acre of grain containing 15% moisture)

| | Little Knott field Formalin | | Pastures field Formalin | |
|---|---|---|---|---|
| | Without | With | Without | With |
| N cwt/acre | | | | |
| 0·0 | 17·0 | 23·9 | 33·6 | 35·9 |
| 0·5 | 28·3 | 34·9 | 32·7 | 28·5 |
| 1·0 | 26·6 | 35·4 | 24·1 | 25·1 |
| 1·5 | 26·2 | 32·5 | 18·5 | 21·7 |

that formalin considerably increased yield on Little Knott almost independently of the amount of N applied, but not on Pastures, where it had no consistent effect. The experiments also illustrate vividly the difficulty in giving general advice on nitrogen manuring. Without formalin, as in practice, 1·0 cwt N/acre increased yield on the old arable field by about 10 cwt/acre, whereas on the field ploughed from grass it *decreased* yield by this amount. G. A. Salt sampled the crops for cereal diseases, and his results (p. 128) explain why formalin increased yields in Little Knott but not in Pastures. It is noteworthy that, given the most appropriate treatment of formalin and nitrogen fertiliser, maximum yields on each field were the same. (Widdowson and Penny)

## Potato Experiments

Recent experiments in England and Wales by the N.A.A.S. (Boyd & Dermott, *J. agric. Sci., Camb.* (1964) **63**, 249–263) show that potatoes usually respond well to large fertiliser dressings and that, in particular, the responses to phosphate were greater than had been expected when the work began. Farmers fertilise potatoes generously; in the arable areas average dressings of nitrogen and phosphate increased by about one-quarter, and of potassium by about one-half in the ten years from 1952 to 1962. Many potato crops receive more fertiliser, particularly nitrogen, than can be justified. However, turning fertiliser into potatoes is profitable, and the amount of extra yield needed to justify an increase in the fertiliser dressing is often less than can be measured precisely in experiments. For these reasons it is difficult to persuade farmers to use less or to adjust the dressings to fit their soils and farming system more closely. Early work on placing fertilisers for potatoes is obsolete, as it was done with much smaller dressings than are now used, so further experiments have been done to devise safe methods of using large dressings and to measure their residual effects on following crops.



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The results from three early experiments were summarised in the *Rothamsted Report* for 1963, p. 48; two more have now been done in each of the last two years, and the results of all are summarised in Table 10.

TABLE 10

*Mean yields of total tubers (tons/acre) from seven potato experiments comparing three methods of applying fertilisers*

| | | | |
|---|---|---|---|
| Yield without fertiliser | | 7·3 | |
| | Fertiliser applied (cwt/acre of 13–13–20*) | | |
| | 5 | 10 | 15 |
| Broadcast: | | | |
| On ploughing and worked-in | 11·1 | 13·2 | 14·7 |
| On seedbed | 11·2 | 13·0 | 14·2 |
| Placed in sideband | 12·2 | 13·3 | 12·5 |

* 13% N, 13% $P_2O_5$, 20% $K_2O$.

Three were on Clay-with-Flints, two on Oxford Clay and two on Chalky Boulder Clay. Fertiliser greatly increased yields, and there was a worthwhile additional increase from broadcasting, though not from placing, 15 rather than 10 cwt/acre of the compound fertiliser (13–13–20) used. This manuring (2·0 cwt N, 2·0 cwt $P_2O_5$ and 3·1 cwt $K_2O$/acre) is much larger than is currently recommended, but was justified in these experiments when correctly applied. Both methods of broadcasting gave similar yields with 5 or 10 cwt/acre of 13–13–20, but not with 15 cwt/acre, when early broadcasting (on the ploughing) was usually the better method. Placing in bands beside the seed was the best method of manuring in four experiments with 5 cwt/acre of fertiliser, and in two experiments with 10 cwt. With 15 cwt/acre, placing beside the seed was always inferior, presumably because it checked early growth, so broadcasting is to be preferred on soils needing large dressings.

**Effects of planting density.** One experiment in 1964 and one in 1965 compared yields from potatoes (grown on the flat) spaced 14 in. apart in rows 14 in. or 28 in. apart. Total yield was increased each year by doubling plant number, but the difference was independent of the amount of fertiliser applied. The yield of saleable tubers (over 1½ in. riddle) was decreased by more than 1 ton/acre by doubling plant number in 1964, but was little affected in 1965. In 1964 fertiliser greatly increased yield (6·9 tons/acre with normal and 5·9 tons/acre with twice normal plant numbers). By contrast, in 1965 fertiliser decreased yields (by 1·2 tons/acre with both plant numbers); the reason for this decrease was an early and severe attack of potato blight, which was not controlled by spraying, and so the tops were killed on 11 August. (Widdowson and Penny)

## Long-term Experiments with Potassium and Magnesium Fertilisers and Limestone

Two experiments testing factorial combinations of potassium and magnesium fertilisers were cropped in 1965 with barley at Rothamsted and with sugar beet and potatoes at Woburn. The barley showed only a small



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response to potassium, in contrast to the previous large responses with ryegrass, clover and potatoes. In contrast again, barley responded to magnesium, whereas the previous crops had not. At Woburn potatoes and sugar beet gave large responses to potassium fertilisers and smaller but significant responses to magnesium. There was no evidence of interactions between potassium and magnesium responses.

Long-term liming experiments, started at Rothamsted and Woburn in 1962, were cropped with beans each year until 1965, when barley was grown. At Rothamsted the yield of barley increased with liming up to a pH of 5·8 only, whereas at Woburn it increased up to pH 7·3. At Rothamsted the yields on the unlimed plots (pH values 4·8–5·1) were uneven both between and within the plots; at the lowest pH (4·8) there was almost a complete crop failure, and the range of yields without lime was from 6–19 cwt grain/acre. At pH 5·1 yield ranged from 29–43 cwt/acre. (Bolton)

## Forms of Nitrogen Fertilisers

Most nitrogen in British fertilisers is nitrate or ammonium salts, and these two forms have often been compared in the last 10 years. Much less urea is used; it has some disadvantages and is often less efficient than ammonium or nitrate when used as a straight fertiliser, especially as a top-dressing (Gasser, *Soils Fertil.* (1964) **27**, 175). It is not known whether urea is also less efficient when it supplies some or all of the nitrogen in compound fertilisers, and this was tested. Other experiments tested materials that supply nitrogen more slowly than inorganic fertilisers; partly this work is intended to see whether slow-acting fertilisers increase the proportion of a nitrogen dressing used by crops, and partly to develop materials that imitate the way organic matter in soils supplies nitrogen slowly as it decomposes.

**Urea in NPK fertilisers.** Experimental fertilisers (with % N : % $P_2O_5$ : % $K_2O$ ratios of 2 : 1 : 1) were obtained containing four different proportions of urea to ammonium nitrate; expressed as a percentage of the total N in the mix, urea was 100, 66, 33 and 0. Two groups of these four fertilisers were made. The first contained triple superphosphate and muriate of potash, and the second mono-urea phosphate and muriate of potash. (In the second group the balance of the nitrogen was added in the proportions shown above, so all these mixes contained some urea.) Two experiments (on Lower Greensand soils) compared yields of barley with the fertilisers, each combine-drilled to give 0·5 or 1·0 cwt N/acre. Much rain fell in the week after sowing, and the drilled fertiliser checked early growth only a little, but fertiliser containing all its nitrogen as ammonium nitrate did so most. An experiment on the same soil compared yields of kale with broadcast dressings of the same fertilisers supplying 1·25 or 2·50 cwt N/acre. The double rate checked growth and decreased plant number; differences between fertilisers were small, but mixes containing all ammonium nitrate checked growth most. The yields of neither barley nor kale differed consistently between eight fertilisers.

The amount of fertiliser nitrogen recovered by the kale was measured in



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samples taken in June and at harvest and by barley at harvest. In June all fertiliser increased N-uptake, and the various forms did not differ significantly. All the sources of fertiliser-N applied in the spring significantly increased uptake by the crops at harvest; although uptakes from the fertilisers tested differed by amounts that were nearly significant, there was no regular pattern of difference between fertilisers with different proportions of urea and ammonium nitrate. On average, kale recovered 54% of the N applied at 1·25 cwt/acre and 43% of the N applied at 2·5 cwt/acre. (Gasser, Penny and Widdowson)

**Granulated oxamide.** Oxamide $(CONH_2)_2$ is sparingly soluble in water. It is not manufactured for use as a fertiliser, but seemed a useful experimental material, because the rate at which it dissolves can be controlled by varying the size of the granules used.

Ryegrass was grown in pots containing three contrasted soils to compare ammonium nitrate with oxamide in several particle sizes, a powder (less than 1 mm) and granules of 2–4 mm, 4–6 mm, 7–9 mm and 9–11 mm diameter were tested. The powdered oxamide and the smallest granules (2–4 mm) behaved like ammonium nitrate and had no further effect on growth of grass after 120 days from sowing. The intermediate granules (4–6 mm) produced as much dry matter initially as the rapidly acting forms and continued to increase yields until 260 days after sowing; they also gave the largest total yields between 100 and 260 days. The largest granules increased yields less early on, but the grass produced dry matter at an almost constant rate from 50 days after sowing to 300 days, when the experiment ended. Grass with 7–9-mm granules produced as much total dry matter as with 4–6-mm granules; grass with the largest granules (9–11 mm) produced slightly less, but at 300 days after sowing both of the large granules were still increasing yield. (Gasser and Jephcott)

In a field experiment ammonium nitrate and three types of oxamide (powder, 2–4-mm and 7–9-mm granules), supplying 100 and 200 lb N/acre, were applied to ryegrass sown in early April, and cut in June, August and October. Ammonium nitrate and powdered oxamide increased yields most at the first cutting, the two granulated oxamides most at the second and third cuttings. The total dry matter produced by the ryegrass over the season was increased similarly by all fertilisers supplying 200 lb N/acre, but with 100 lb/acre less was produced from the large granules. At the first cutting the grass had taken up most fertiliser nitrogen from ammonium nitrate and least from the large granules of oxamide. At the third cutting grass recovered most nitrogen from the granulated oxamides, but the total recovery for the three cuts was greatest from ammonium nitrate, and least from the large granules of oxamide. (Gasser and Penny)

Although oxamide behaved in the way predicted from its physical properties, it did not increase the efficiency with which grass used nitrogen to produce dry matter. Clearly, however, it is useful for slowing the action of nitrogen and for discovering whether usual N-fertilisers are inefficient because they are very soluble and lost by leaching or denitrification before the crops can use them. It also simulates the slow action of "natural" forms of nitrogen in soil. (Gasser)



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**Losses of nitrogen during the nitrification of ammonium salts in acid sands.** Ammonium sulphate and calcium nitrate both containing excess $^{15}N$ were applied to four acid sandy soils. Two soils were from old arable fields and two from grassland; they were selected so that one of each pair was about pH 5 and the other about pH 6 (in water). One set of each soil was incubated for 6 weeks at 21° C in large glazed earthenware pots with the nitrification inhibitor 2-chloro-6-(trichloromethyl)-pyridine and another without an inhibitor, and the mineral-N was determined at intervals. The total-N was determined at the start and after 6 weeks. The atom excess $^{15}N$ in the mineral-N extracted from soils treated with ammonium sulphate was determined after 0, 3 and 6 weeks, and at 0 and 6 weeks in the total-N of all the soils given N-fertiliser. Other soil samples were incubated in closed flasks, where the air was replaced by a mixture of helium and oxygen; nitrogen was added as ammonium, as nitrite and as nitrate, some samples were sterilised by $\gamma$-irradiation.

In the large pots much added nitrogen was immobilised at first, but some was remineralised during the second half of the incubation. Measuring the excess $^{15}N$ in the mineral-N extracted from soils treated with ammonium sulphate showed that proportionately less $^{15}N$ than $^{14}N$ was remineralised during the second half.

Measuring the total-N in all the soils at 6 weeks showed that labelled-N had been lost from the two grassland soils. The incubations in closed flasks gave similar results; little nitrogen or oxides of nitrogen were evolved from the arable soils, the grassland soils lost as much as in the large pots.

Nitrite was added to all soils and to samples of the two grassland soils sterilised with $\gamma$-radiation; oxides of nitrogen were evolved from all the soils and nitrogen from the grassland soils, whether sterile or not, showing that losses occurred by a chemical, not biological mechanism. There was no loss from the soil given nitrate instead of nitrite.

After 6 weeks incubation the soil remaining in each jar was halved to provide duplicate pots and sown with ryegrass. A similar series of pots with the same treatments (but with unlabelled fertilisers) was also prepared from the soil that had been stored slightly moist and at 21° C; these were sown with ryegrass that was cut after 42 days and again after 71 days. The total-N content of grass and soil, and the excess of $^{15}N$, showed nitrogen was not lost from soils treated with ammonium while the grass grew, but some was lost from the grassland soils treated with nitrate. The nitrification inhibitor decreased yields of grass at the first cutting on grassland soils treated with ammonium, but increased them on soil treated with nitrate. This suggests that changing the proportions of nitrate to ammonium by adding the inhibitor alters the growth rate and yield of grass. (Gasser, Greenland and Rawson)

## Phosphate Fertilisers

Experiments with phosphate fertilisers examine the direct, residual and cumulative effects of kinds of phosphate that differ greatly in solubility in water and in other physical and chemical properties. The purpose is to



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compare existing fertilisers with possible replacements, and to try to improve the small short-term efficiency of phosphate fertilisers.

Previous glasshouse experiments with potassium metaphosphate and magnesium ammonium phosphate (*Rothamsted Report* for 1963, p. 51; for 1964, p. 55) tested small granules ($<2$ mm) on an acid soil (pH 5·7). The same fertilisers have now been tested in a factorial experiment using ryegrass grown in large pots (holding 5–6 kg of soil) on three soils with pH values 4·4, 6·9 and 7·5 (in $0 \cdot 01M$-$CaCl_2$). Ryegrass was cut six times to assess the relative rates of release of P from fertiliser applied as powders ($<0 \cdot 18$ mm) and as granules 2–3 mm and 4–5 mm diameter. Table 11 shows changes in percentage superphosphate equivalents (calculated from P uptake from the powder) during the experiment. On both soils superphosphate equivalents at the first cut decreased rapidly with increasing granule size. At pH 4·4 the value of the larger granules of the three fertilisers to the grass increased rapidly during its growth, relative to the standard powdered fertiliser. On the calcareous soil (pH 7·5) all granules,

**TABLE 11**

*Percentage powdered triple superphosphate equivalents of granular fertilisers from an experiment on ryegrass*

(Values are means of 3 rates of application and are calculated from P uptakes)

| Fertiliser | Granule size (mm) | Sawyers (pH 4·4) 1st cut | Sawyers (pH 4·4) Cuts 1–3 | Sawyers (pH 4·4) Cuts 4–6 | Pegsdon (pH 7·5) 1st cut | Pegsdon (pH 7·5) Cuts 1–3 | Pegsdon (pH 7·5) Cuts 4–6 |
|---|---|---|---|---|---|---|---|
| Triple superphosphate | 2–3 | 80 | 93 | 107 | 15 | 36 | 50 |
| | 4–5 | 47 | 75 | 92 | 13 | 23 | 39 |
| Potassium metaphosphate | <0·18 | 36 | 52 | 97 | 77 | 95 | 127 |
| | 2–3 | 27 | 82 | 132 | 9 | 51 | 81 |
| | 4–5 | 10 | 41 | 120 | < 0 | 34 | 58 |
| Magnesium ammonium phosphate | <0·18 | 70 | 87 | 90 | 78 | 104 | 125 |
| | 2–3 | 23 | 67 | 124 | 7 | 23 | 54 |
| | 4–5 | 9 | 37 | 108 | < 0 | 18 | 47 |

including the water-soluble granular triple superphosphate, were much less effective for later cuts of grass than were granules on the acid soil or powdered fertilisers on the calcareous soil. These results with larger granules (2–3 mm) agree with previous ones (*Rothamsted Report* for 1963, p. 51) with smaller granules of potassium metaphosphate. Uptake of phosphorus from granular metaphosphate *on an acid soil* significantly exceeded uptake from the fertiliser as a powder at the last three cuts. However, in a calcareous soil more phosphorus was taken up by grass from *powdered* potassium metaphosphate at all stages of its growth than from granules. (Blakemore and Mattingly)

An experiment using microplots was started on an acid soil (Sawyers II field at Rothamsted) to measure the rate of action, and the residual and cumulative values of these three phosphorus fertilisers. Comparing fertilisers that supply more than one nutrient is difficult when all nutrients are sparingly soluble and large basal dressings of N, K and Mg, adjusted to



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allow for those in the tested fertilisers, were applied. The fertilisers supplied 24 and 48 lb/acre of P, and two sizes of granules (<1 mm and 2–5 mm) were tested. The treatments included some where half the phosphorus was applied in one form and half in another; one tested all three fertilisers applied simultaneously—triple superphosphate, potassium metaphosphate and magnesium ammonium phosphate. Early potatoes were grown, followed by radish. Responses to phosphate were large, and all the combinations of fertilisers, applied as powders, increased yields of potatoes by 4–5 tons/acre (averaging rate of application). There were very large effects of granule size, and granular triple superphosphate produced nearly 2 tons/acre *more* tubers than powdered triple superphosphate. Yields from all other granular products, including mixtures containing triple superphosphate, were less by amounts ranging from 0·6 to 3·8 tons/acre than from the corresponding powdered fertiliser.

Yields of radish were increased by 6–7·5 tons/acre by the residues from the powdered fertilisers. Residues from granules produced slightly larger responses (7–9 tons/acre). (Mattingly, Penny and Blakemore)

**Residual and cumulative effects of phosphate fertilisers at Rothamsted.** Experiments on residual effects of phosphorus fertilisers were described in the *Rothamsted Report* for 1964 (p. 63). Table 12 gives the mean yields of potatoes, barley and swedes in 1965 as averages of the two experiments. As previously, there were only small increases in yields of barley from cumulative or residual dressings of phosphate. The most interesting result was the very large response by potatoes to the residues of all fertilisers given 6 years before; the mean increase in yield (2·4 tons/acre) was equal to that from the cumulative annual dressings which have now supplied half as much phosphorus as the residues. (Mattingly)

**TABLE 12**

*Residual and cumulative effects of phosphate fertilisers at Rothamsted*

| | Annual dressings (cwt $P_2O_5$/acre) | Mean yields per acre in 1965: Potatoes (tons) | Barley grain* (cwt) | Swedes (tons) |
|---|---|---|---|---|
| No P | | 14·4 | 34·0 | 6·6 |
| Superphosphate annually, 1960–65 | 0·25 | 16·8 | 36·2 | 21·6 |
| | 0·50 | 18·7 | 35·0 | 23·0 |
| Residues from 3·0 cwt $P_2O_5$ given in 1959 (mean of 7 fertilisers) | 0 | 16·8 | 35·3 | 18·5 |

* 85% dry matter.

## Slow-release Fertilisers for Conifer Seedlings

The two experiments described last year (pp. 55–7) were continued during 1965, when spring and early summer rainfall and leaching losses were less than in 1964. Responses to potassium for both height and dry matter were larger than in 1964. Table 13 shows that the standard soluble PK compound (made from superphosphate and potassium chloride), which was no better than superphosphate alone in 1964, trebled plant height in



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1965, and that considerable further improvement was obtained by supplementing the PK compound with summer top-dressings of potassium nitrate. The slow-release fertiliser—potassium metaphosphate—was again superior to the soluble PK compound. Seedlings grown with any of the PK fertilisers contained similar % P, but % K increased in the same order as in 1964, i.e., PK compound alone, potassium dihydrogen phosphate, potassium metaphosphate, PK compound plus potassium nitrate.

**TABLE 13**

*The effects of P and K fertilisers on 1-year Sitka-spruce seedlings at Wareham in 1965*

| | Rates applied (g. element/ sq yd) P | K | Height (in.) | Dry matter of tops (mg/plant) | Colour score* | P % (in dry matter) | K % (in dry matter) |
|---|---|---|---|---|---|---|---|
| No fertiliser | 0 | 0 | 0·4 | 27 | Severe | 0·19 | 0·28 |
| Superphosphate only | 9 | 0 | 0·5 | 35 | Severe | 0·28 | 0·20 |
| PK compound (from super + KCl) | 9 | 9 | 1·4 | 117 | 2 | 0·22 | 0·32 |
| Potassium dihydrogen phosphate | 9 | 12 | 1·1 | 84 | 1 | 0·23 | 0·57 |
| PK compound + $KNO_3$ | 9 | 15 | 1·7 | 158 | 0 | 0·21 | 1·12 |
| Potassium metaphosphate | 9 | 12 | 1·6 | 131 | 0 | 0·21 | 0·70 |

* For the purple and yellow discoloration typical of K-deficiency (0 = no discoloration.)

A second experiment compared magnesium ammonium phosphate at rates 1, 2 and 4 plus potassium chloride with the "standard fertiliser" consisting of "Nitro-Chalk" superphosphate, potassium chloride and kieserite. (Rate 1 supplied as much phosphorus as the "standard fertiliser".) To avoid the potassium deficiency caused in 1964 by early leaching, all four treatments were supplemented by summer top-dressings of potassium nitrate. A fifth treatment consisted of a compost made from bracken and hop-waste used in conjunction with "standard fertiliser". The plants grown with magnesium ammonium phosphate (differences between rates were small) were all larger than those grown with "standard fertiliser", but did not quite equal those with standard fertiliser plus compost. (Benzian, Bolton and Mattingly)

## The Effects of Fertilisers on the Composition of Crops

**Potassium concentrations and protein.** The role of potassium in plants is not fully understood; most people think it is not primarily associated with protein synthesis, but that when it is deficient *cytoplasm* breaks down and leaves die early. When this happens protein is rapidly hydrolysed and simpler nitrogenous compounds accumulate. American workers recently showed that K-fertilisation had no effect on protein concentration in grass 4 weeks old, but considerably increased it at 6 weeks old. They suggested that a nitrogen–potassium imbalance can change the organic composition of herbage, but may or may not affect yield.

In an attempt to find the minimum amount of potassium needed in grass to maintain the protein content, a field experiment was laid down



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on Stackyard field at Woburn, where the soil initially contained 79 ppm of exchangeable K. All plots had 25 lb P/acre and 100 lb N/acre (as ammonium nitrate). Potassium was given as potassium chloride at 0, 60, 120, 180 and 240 lb K/acre. Cocksfoot and meadow fescue were grown and cut four times, after each cut dressings of nitrogen were repeated. Potassium fertiliser did not increase dry-matter yields significantly, or affect the protein concentration in the grass. The failure to reproduce results reported by other workers (e.g. Cummings and Teel (1965), *Agron. J.* **57**, 127) probably means the soil initially contained too much exchangeable K and that more was released during the season. Even at the last cut, the grass not given potassium contained more than is thought to indicate deficiency.

**TABLE 14**

*The effect of potassium fertiliser on the chemical composition of grass from the Woburn Reference Experiment*

(Mean values for 3 cuts in each year)

| | 1964 | | 1965 | |
|---|---|---|---|---|
| | Without K fertiliser | With K fertiliser | Without K fertiliser | With K fertiliser |
| Yield (cwt/acre) of: | | | | |
| Dry matter | 16·7 | 20·8 | 18·7 | 25·4 |
| Protein | 1·94 | 2·13 | 2·38 | 2·63 |
| % in dry matter: | | | | |
| K | 1·00 | 2·14 | 0·90 | 2·72 |
| N (total) | 2·19 | 1·92 | 2·47 | 1·97 |
| N (as protein) | 1·88 | 1·62 | 2·05 | 1·64 |
| C | 42·2 | 42·8 | 43·6 | 42·6 |
| Yield (cwt/acre) of: | | | | |
| Nitrogen | 0·37 | 0·40 | 0·46 | 0·50 |
| Carbon | 7·1 | 8·9 | 8·2 | 10·8 |

The permanent grass on the Reference Experiment at Woburn (p. 45) is deficient in potassium where none is applied, and yields are increased by K-fertiliser. Samples of herbage of all cuts in 1964 and 1965 were analysed, and Table 14 shows mean results with three cuts. Both plots receive 168 lb N after each cut and 25 lb P/acre each year; the test dressing of K is 185 lb/acre. Grass grown without K-fertiliser contained proportionately more total nitrogen and protein nitrogen than grass given potassium. However, the uptake of nitrogen and the protein yield per acre were hardly affected by the potassium. The carbon concentration also was not affected, and the increase in yield from potassium reflected the increase in carbon fixed photosynthetically. In grass containing from 1·0 to 3·0% K the equilibrium between protein-nitrogen and total nitrogen was unaffected by potassium fertiliser, and 83–85% of the total nitrogen in the plant was protein. Whatever mechanism is responsible for restricting the growth of grass deficient in potassium, it seems unlikely to be associated with the distribution and uptake of nitrogen. (Nowakowski)

**Effects of nitrogen and potassium concentrations in conifer seedlings on frost damage.** Top-dressings of nitrogen and potassium were applied to conifer seedbeds at Wareham Nursery so late in the season that nutrient concentra-



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tions were increased in the seedlings without further increasing their growth. Frost damage during December, in the form of needle browning, was decreased by increasing % N in Sitka spruce and Western hemlock and was almost eliminated by increasing % K in Sitka spruce (Table 15).

**TABLE 15**

*Nitrogen and potassium concentrations in seedlings of Sitka spruce* (Picea sitchensis) *and Western hemlock* (Tsuga heterophylla) *in relation to frost damage*

| *Experiment A* | N concentration (% in dry matter) Low | N concentration (% in dry matter) High | Score for frost damage* N% Low | Score for frost damage* N% High |
|---|---|---|---|---|
| Sitka spruce | 0·94 | 1·78 | 2·2 | 1·2 |
| Western hemlock | 0·79 | 1·99 | 2·8 | 2·2 |

| *Experiment B* | N concentration (% in dry matter) Low | N concentration (% in dry matter) High | K concentration (% in dry matter) Low | K concentration (% in dry matter) High | Score for frost damage* N low K low | N high K low | N low K high | N high K high |
|---|---|---|---|---|---|---|---|---|
| Sitka spruce | 0·82 | 1·58 | 0·42 | 1·01 | 3·4 | 1·0 | 0·0 | 0·5 |

* The higher the score the larger the number of seedlings damaged by frost.

Sitka-spruce seedlings at Kennington Extension Nursery, and on the Reference Plots at Woburn (see *Rothamsted Report* for 1961, pp. 51–52), on "no K" plots showed browning resembling the symptoms of the "low K" seedlings at Wareham, though much more severe. Seedlings on plots given potassium were almost completely free from symptoms. (Benzian)

## Nutrients in Soils

Much of our work on nutrient reserves in soils is done to develop better methods of measuring the soluble fraction plants can use, to distinguish between different crops in their abilities to use the reserves and to follow changes in the soluble fractions caused by cropping, weather and season. All of these are important when soil analyses are used to predict the fertiliser needed to achieve maximum yields, or to balance the gains and losses caused by manuring and cropping.

**Changes during one year in soluble nutrients in different soils and under different crops.** From May 1963 to April 1964 soluble nutrients were measured in soil samples taken monthly from plots having none, PK and NPK fertilisers in the Reference Experiments (p. 45) at Rothamsted and Woburn. Phosphorus, potassium and magnesium concentrations in equilibrium extracts of the soils made with 0·01*M*-calcium chloride solution were measured; exchangeable P was determined with an anion-exchange resin. Samples were taken under five arable crops growing in rotation, and under permanent grass.

Concentration of both P and K varied from month to month, but there was also a seasonal pattern of change, and under most crops they were greatest in spring. This pattern was caused by applying fertiliser, uptake by crops and by the reactions that tend to restore equilibria between the forms



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of a plant nutrient in soil. In both soils soluble P and K were usually maximal in the spring of 1963 and were minimal just after the crops had been harvested; concentrations gradually increased during winter, and by spring of 1964 had mostly reached the original maxima. The size of crop grown affected the results; concentrations of both P and K in equilibrium extracts of NPK-treated plots fell below those of the PK-plots because the larger crops grown with N fertiliser took up more P and K. Herbage crops containing legumes were exceptions, as PK-treated plots yielded well because the clover fixed N. Minimum concentrations of P and K in the $CaCl_2$ extracts occurred later under crops (kale, sugar beet and ley) that grew during late summer and autumn than under cereals or potatoes.

The P concentrations in $CaCl_2$ extracts changed proportionately more at Rothamsted than at Woburn; in contrast, exchangeable P varied little at Rothamsted but did greatly in the light Woburn soil.

The differences between maximum and minimum P and K concentrations were large enough to be very important practically. Soluble P and K commonly varied by two or three times during the season, and maximum concentrations in a few plots were four or five times larger than the minima. Maximum amounts of exchangeable P were commonly twice the minima, and some were three times greater.

Seasonal changes in concentrations of Mg in $CaCl_2$ extracts of soils were small. Ratios of the ion concentrations $\frac{K}{\sqrt{Mg}}$ were larger at Rothamsted than at Woburn, but at both sites they depended largely on the amounts of K dissolved.

Measurements on soil taken at four times during the year from the Rotation I experiment at Saxmundham varied as at Rothamsted and Woburn in concentrations of P and K in $CaCl_2$ extracts. Amounts fell when crops were growing and increased again in winter. Concentrations of sodium in the solutions were larger in NPK-treated plots (where N was supplied as $NaNO_3$); they decreased during the year, presumably because of leaching and uptake by crops. Trends in nutrient concentrations were less regular at Saxmundham than at Rothamsted and Woburn. Sampling more often than once in 3 months is needed in such work. (Garbouchev)

**Changes in phosphate potentials during cropping and storage.** We reported last year that the monocalcium phosphate potentials of cropped soil ($\frac{1}{2}$pCa + $pH_2PO_4$) did not change appreciably during 3 months in moist aerobic conditions. Measurements after 6 and 12 months confirmed that the potential of a cropped soil from Barnfield did not change. But the phosphate concentration and potential of Woburn soils increased during prolonged storage (Table 16). Small variations in the potential of the Rothamsted soil mostly reflect changes in pH and not changes in P concentration. In contrast, the pH of Woburn soil remained almost constant, but the P concentration increased steadily with time, so that values for $\frac{1}{2}$pCa + $pH_2PO_4$ decreased.

This continuous decrease in the values of ($\frac{1}{2}$pCa + $pH_2PO_4$) has been observed consistently in experiments with limed soils from Woburn and with mixtures of Woburn and Rothamsted soils. When an acid Woburn



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soil and a calcareous Rothamsted soil were mixed, and stored moist, and aerobic, the pH values remained nearly constant after 1 day, but phosphorus concentrations increased for many weeks. The increase in P in such mixtures seems partly because phosphate is released from the calcium

**TABLE 16**

*Changes in pH, phosphorus concentration and monocalcium phosphate potential in cropped soils after moist, aerobic storage*

| Storage (months) | Rothamsted (Barnfield, plot 4·0) | | | Woburn (Butt Close, Irrigation Experiment, plot 95) | | |
|---|---|---|---|---|---|---|
| | pH | P concn (x$10^{-6}M$) | $\frac{1}{2}$pCa + $pH_2PO_4$ | pH | P concn (x$10^{-6}M$) | $\frac{1}{2}$pCa + $pH_2PO_4$ |
| 0 | 7·66 | 0·49 | 8·19 | 7·24 | 1·93 | 7·29 |
| 1 | 7·70 | 0·47 | 8·25 | 7·25 | 2·14 | 7·25 |
| 3 | 7·82 | 0·50 | 8·30 | 7·37 | 2·97 | 7·18 |
| 6 | 7·82 | 0·40 | 8·40 | 7·20 | 3·83 | 6·97 |
| 12 | 7·87 | 0·49 | 8·36 | 7·21 | 5·27 | 6·83 |

carbonate in Rothamsted soils. However, this mechanism does not explain satisfactorily the increases in P concentration observed when Woburn soils are treated with pure calcium carbonate, and also when the pH is raised by adding calcium and magnesium salts during cropping. The increases in P concentrations are tentatively attributed to the continuous slow solution of phosphate compounds, perhaps iron and aluminium phosphates that hydrolyse at pH values $>7·0$. (Webber and Mattingly)

## Cations in Soils

**Distribution and rate of release of cations from mechanical fractions of soil.** The total amounts of cations (K, Na, Ca and Mg) in the four major mechanical fractions of soil (defined by the International scale) were determined on six British soils and four soils from Malaya. Table 17 shows the range of total cations in the different fractions of the British soils after removing exchangeable cations with 0·25*N*-hydrochloric acid.

**TABLE 17**

*Total amounts of cations in mechanical fractions of six British soils*

| | K | Na | Ca | Mg |
|---|---|---|---|---|
| | Range of values in mg/100 g of soil | | | |
| Coarse sand | 100–560 | 20–80 | 10–120 | 5–40 |
| Fine sand | 820–1,250 | 320–560 | 80–180 | 5–70 |
| Silt | 1,390–2,140 | 410–770 | 60–190 | 105–350 |
| Clay | 1,340–1,860 | 110–210 | 0–110 | 560–780 |

The soils from Malaya represent four of the major soil series found there; they contained fewer cations in all fractions than the British soils. Two latosols contained less than 50 mg/100 g of potassium and 10 mg/100 g of magnesium in the clay.

The rate the mechanical fractions released cations was measured in some of the soils by incubating with hydrogen-saturated ion-exchange resins for up to 43 days. As expected, the clay released cations much more readily than the larger fractions. Up to 30% of the total magnesium in the clay was



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released in 43 days, compared with about 10% of the total potassium and less than 3% of the total sodium. The silt fractions also released magnesium faster than potassium, relative to the total amounts present. (Bolton)

**Calcium as a plant nutrient for Sitka spruce.** Some of the concentrated fertilisers now commonly used contain little or no calcium, so calcium deficiencies in crops are more likely to occur than previously—especially on very acid soils. At Wareham nursery, on a site with pH values (in $CaCl_2$ solution) of 3·3–3·5, Sitka spruce seedbeds received increasing dressings of calcium (2½,5,10,20 g Ca/sq. yd) applied as calcium sulphate. The basal NPKMg manuring consisted of calcium-free fertilisers: ammonium nitrate ("Nitram"), potassium dihydrogen phosphate and kieserite. Seedling heights, which ranged from 1·5 in. on "no calcium" plots to 2·2 in. with the most calcium, followed the rates of dressing closely. pH values at the end of the growing season were unchanged, even by the largest calcium sulphate dressings. (Benzian and Bolton)

**Exchange equilibria of sodium.** Equilibria involved in sodium–calcium exchange were measured by equilibrating a selection of British soils with a range of 0·01*M*–$CaCl_2$ solutions containing amounts of sodium around the equilibrium value. Changes in exchangeable sodium ($\Delta$Na) were then plotted against the sodium activity ratio $\left(\frac{a_{Na}}{\sqrt{a_{Ca+Mg}}} \text{ or } AR_{Na}\right)$ in the equilibrium solution after shaking for 1 hour. A curvilinear relationship similar to that reported by Beckett (*J. Soil Sci.* (1964) **15**, 9) for potassium was found. Slopes of the linear part of the $\Delta Na/AR_{Na}$ graph were much less than the corresponding slopes for potassium, showing that the buffering capacity for sodium is less than for potassium.

The curved part of the $\Delta K/AR_K$ graph was interpreted by Beckett as showing exchange sites with a greater preference for potassium than the rest of the exchange capacity. The sodium curve can be similarly interpreted. Although the sites with a greater preference for sodium correspond to less than 1% of the exchange capacity, a large proportion of the exchangeable sodium in "natural" mineral soils was held at these "preferred" sites. Organic soils, most of whose exchange capacity is from their organic matter, gave no curvature of the $\Delta Na/AR_{Na}$ graph. (Bolton and P. B. H. Tinker)

## Cation Adsorption Isotherms of Soils and Clays

The release and retention of a cation by soil is mainly governed by the properties and amounts of minerals and organic matter in the clay and silt fractions, and by the other cations on the soil complex. Cation-activity ratios in the equilibrium soil solution reflect the thermodynamic status of the adsorbed cations, but do not exactly describe changes in the soil or the true activity of adsorbed ions, especially when nutrient cations are added or removed. Detailed studies of adsorption isotherms provide such information, although only systems containing two cations can be theoretically treated at present.



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Because exchangeable calcium predominates in most arable soils, K/Ca isotherms are important. Differences between the behaviour of potassium and sodium must be examined when sodium salts are used as fertilisers, especially on acid soils. Studying rubidium selectivity in competition with potassium helps us to understand the $NH_4^+/K^+$ relationship in soils because the rubidium and ammonium ions are very similar; it also defines conditions under which the rubidium-86 radioisotope can be used as a tracer for potassium in long-term experiments with soils.

K/Na adsorption isotherms at 25° C were obtained for five soils, and K/Rb and K/Ca isotherms for eight soils and for montmorillonite and vermiculite. In contrast with previous work (*Rothamsted Report* for 1964, p. 68), exchange equilibrium was approached by adding 0·01*N*-chloride solutions of Na, Rb or Ca to potassium-saturated soils and clays. After 8 days equilibration the suspensions were double-labelled, with $^{42}K$ and $^{24}Na$, $^{86}Rb$, or $^{45}Ca$. Isotopic equilibrium was reached within 5 minutes, and remained unaltered for at least 24 hours.

**Potassium/calcium exchange.** Isotherms for soils of the Cegin, Windsor and Dunkeswick series were obtained with samples that were initially K-saturated or Ca-saturated. They agreed only at large K-saturation values. At small K saturations isotherms obtained with soils initially saturated with K showed that these soils preferred potassium more than soils initially saturated with calcium. Similar hysteresis was also observed by Chaussidon (*Proc. int. Clay Congr., Stockholm* (1963) **1**, 195–201) on repeated wetting and air-drying of K–Ca saturated montmorillonite. Both sets of isotherms (from initial K-saturation and Ca-saturation) were identical for the other seven soils examined. The total exchangeable negative charge on all the Ca-saturated soils was between 10 and 30% greater than on their K-saturated forms, probably because the latter had collapsed inter-layer spaces which could be re-expanded by Ca-saturation. The total isotopically exchangeable K + Ca decreased with increasing K saturation, mainly because some $Ca^{2+}$ ions were trapped in the inter-layer space, but partly because of $K^+$ "fixation".

The activity coefficients of adsorbed calcium ($f_{Ca}$), calculated from a thermodynamic treatment of the isotherms, decreased sharply with increasing K saturation, but the activity coefficient of adsorbed potassium ($f_K$) increased up to 30–40% K saturation and then decreased as more potassium exchanged into the soil. At less than 35% K saturation $f_K$ probably became smaller because K was retained in structural cavities in the clay sheets; the decrease in $f_K$ above 35% K saturation is caused by the inter-layer space contracting in "expanding" clay minerals and so restricting the free access of ions to the bulk solution.

The standard free energies of exchange range for the ten soils from 1·1 to 3·4 kcal per mole (for "Cegin" and "Harwell" soils respectively), standard entropies from −3 to −20 e.s.u. and heats of reaction from −2 to −8 kcal/mole (for the Detchworth and Newchurch series respectively), i.e., there are considerable differences between soils in their selectivity for potassium and calcium ions.



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**Montmorillonite.** Two observations illustrate the extreme selectivity of Wyoming montmorillonite for $Ca^{2+}$ ions. Only a quarter of the exchangeable calcium in Ca montmorillonite could be displaced by three successive equilibrations (1 :30 soil: solution ratio) with 0·01*M*-KCl, and further treatment with this solution did not release more calcium. Again, K-montmorillonite exchanged for K about 30 me Ca from $CaCl_2$ solutions, and this could not be exchanged isotopically with $^{45}Ca$.

**Clinoptilolite in "Harwell" series.** Potassium selectivity was shown by a Harwell series soil from Halton, Bucks, whose coarse clay and silt fractions contain clinoptilolite, an "open" zeolite (*Rothamsted Report* for 1964, p. 74). Experiments on the rate of isotopic exchange of potassium (with $^{42}K$) showed that the self-diffusion coefficient of K in dilute suspensions of this soil (1: 30) increased from $3{\cdot}7 \times 10^{-13}$ cm² sec⁻¹ at 19% K saturation to $8{\cdot}3 \times 10^{-12}$ cm² sec⁻¹ at 35% K saturation; further K saturation, up to 50%, did not increase the self-diffusion coefficient. These results suggest that the presence of more exchangeable calcium increasingly obstructs the movement of potassium ions in structural holes in clinoptilolite, and that approximately a third of the total charge on this soil is contributed by this mineral, equivalent to 5·6% clinoptilolite in the soil.

**Potassium/sodium exchange.** Measurements on a new set of soils confirmed previous results (*Rothamsted Report* for 1964, p. 68) that potassium was selectively adsorbed but that the total negative charge on the soil was unaltered with increasing sodium saturation. A solution of 0·01*M*-NaCl was unable to exchange K or Ca ions out of some inter-layer space, but this could be done with *M*-NaCl and by isotopic exchange with $^{45}Ca$ in Ca-saturated soils.

The calculated activity coefficients of adsorbed cations at small saturation values were generally smaller for potassium than for sodium. However, the nature of the "activity coefficient : per cent saturation" relationship was remarkably similar for potassium and sodium and was unlike that for K/Ca isotherms, in which sharp changes occurred at critical saturation levels.

The standard free energies of exchange ranged from 0·9 to 1·3 kcal/mole, so differences in K and Na selectivity were smaller than with the K/Ca ion pair.

**Potassium/rubidium exchange.** K/Rb adsorption isotherms showed that all soils and minerals had a small but significant preference for Rb. The total negative charge of montmorillonite, and of soils from the Long Load and Harwell Series, remained constant over the whole isotherm. For the remaining six soils the charge was constant up to 80% Rb saturations decreasing continuously to a smaller value with Rb-saturated soil. With Montana vermiculite, total charge decreased continuously with increasing Rb saturation to a constant value above 40% Rb. The decrease in total charge of the soils, and of vermiculite, was caused by some of the adsorbed rubidium not being isotopically exchangeable.



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The rational selectivity coefficients (RSF) and the thermodynamic equilibrium constants for the reaction $RbX + K^+ \rightleftharpoons KX + Rb^+$ (where X is the cation-exchanger) were remarkably constant for all soils, montmorillonite and vermiculite. RSF-values for all materials were between 0·3 and 0·4 over the whole isotherm, compared with values between 2 and 13 for K/Na exchange and between 10 and 5,000 for K/Ca exchange. Calculations, made as for other ion pairs, show that the activity coefficients of adsorbed ions, $f_K$ and $f_{Rb}$, range only between 0·9 and 1·0 over the whole isotherm for all exchange materials. The standard free energies of exchange ranged from +400 to +700 kcal/mole (for the Dunkeswick and Bovey Basin Series respectively). (Deist and Talibudeen)

**Hydrogen/aluminium/calcium exchange in soils.** Unmanured soils from the Park Grass Experiment at Rothamsted and a liming experiment at Deer Park (Wexford, Ireland), and Wyoming montmorillonite, previously saturated with calcium ions, were equilibrated with $10^{-3}N$-chloride solutions of various (pH–$\frac{1}{3}$ pAl) values. The adsorbed hydrogen, aluminium and calcium were exchanged out by *M*-KCl and determined. Similar measurements were made on samples freed from organic carbon by prolonged treatment with cold "100 vol" hydrogen peroxide.

Nearly all the calcium was replaced by hydrogen and aluminium ions on all materials. With Al-free equilibrium solutions, appreciable amounts of aluminium were exchangeable—one-third, one-half and three-quarters of the cation exchange capacity for Deer Park soil, Park Grass soil and montmorillonite respectively. Soils free from organic carbon had the same *amounts* of adsorbed aluminium, but fewer adsorbed hydrogen ions and a smaller cation-exchange capacity. At large Al : H ratios in the equilibrium solution and pH values >3·8, exchangeable Al was adsorbed as a hydrolysed ion, of approximate composition $Al(OH)_2^+$ by the soils and $Al(OH)_2^+$ by montmorillonite. At a critical $H^+ : Al^{3+}$ ratio in the equilibrium solution the apparent hydrogen saturation of the exchanger was zero, probably because equivalent amounts of hydrogen and hydrolysed aluminium ions were adsorbed.

Calcium/aluminium exchange isotherms were obtained by adding solutions of $10^{-2}N$-$AlCl_3$ at different pH's labelled with "carrier-free" $^{45}Ca$ to soils and clays. The equilibrium pH and the Al, Ca and $^{45}Ca$ concentrations in the equilibrium solutions were measured, and the exchangeable calcium and aluminium on the exchanger calculated. Exchange isotherms relating the equivalent ion fraction of aluminium:

$$\left((\text{e.i.f.})_{Al} = \frac{\text{Al}}{\text{Al} + \text{Ca}}\text{; concentrations in equivalents}\right)$$

on the exchanger to that in the solution showed that all materials strongly preferred aluminium.

Isotherms at different pH values coincided, and those for Park Grass and Deer Park soils were similar. Aluminium was adsorbed preferentially in the order vermiculite ≫ Park Grass soil and Deer Park soil > montmorillonite > kaolinite. Soils from Park Grass and Deer Park preferred aluminium much less after removing their carbon.

Plotting log $\left(\frac{c}{c_0}\right)^2 \Big/ \left(1 - \frac{c}{c_0}\right)^3 \cdot c_0$ against log $\left(\frac{q}{q_0}\right)^2 \Big/ \left(1 - \frac{q}{q_0}\right)^3$ gave a line of unit slope for the untreated soils and clay minerals. ($c$ and $q$ are the normality of aluminium in solution and the equivalents of aluminium on the exchanger respectively, and $c_0$ and $q_0$ are the total normality and total adsorbed bases.) The exchange constants for aluminium by calcium were given by pK-values 3·0, 2·4, 2·2, 1·7 and 1·5 for Montana vermiculite, Park Grass soil, Deer Park soil, Wyoming montmorillonite and kaolinite respectively. (B. S. Coulter and Talibudeen)

## Apparatus and Experimental Methods

New equipment for analyses is being tested and adopted to replace older and more laborious methods.

**Nitrogen in crops.** The "Coleman Nitrogen Analyser" (Model 29A) was installed during the year, initially for determining N in plant materials. The Dumas method is used, and the sample is heated with copper oxide to reduce nitrogen compounds to nitrogen gas. To ensure complete reduction the issuing gases are passed through a "post-heater" packed with copper and copper oxide. The reaction products are swept through the Analyser by a stream of carbon dioxide, which is removed, together with other products of combustion, by passing the gas stream through potassium hydroxide solution before measuring the volume of nitrogen evolved. Samples have to be weighed into the combustion tubes, but once fitted to the Analyser, the combustion cycle is done automatically.

A normal time cycle of operations has been adopted with the upper and lower furnaces set at 700° C (these increase to 880° C during the combustion period) and the post-heater furnace at 580 °C. The combustion tube is packed with lightly ground copper oxide (M.A.R. grade). The-100 mg sample is introduced without using an aluminium boat. The nitrometer is filled with potassium hydroxide–barium hydroxide mixture as recommended by Vogel (*Elementary Practical Organic Chemistry* (1958), p. 648, London: Longmans Green). The carbon dioxide used is a special grade, containing little moisture or residual gases. The standard error of the method was 0·035% N or 2·20% of the mean value when calculated for over 40 duplicate samples containing from 0·90 to 2·80% N.

Increases in combustion and sweep times were unnecessary for good recoveries. Mixing cobalt oxide with the sample (recommended by Mazoyer, *Bull. Ass. fr. Etude Sol* (1964) No. 7/8, 282–287) was also unnecessary. A nomograph which takes into account temperature, pressure, weight of sample and a constant is used to give a factor that can be applied directly to the corrected volume of gas.

While setting up and checking these instruments the following practical details were found important:

Tubes must be carefully packed for reproducible results, with the copper oxide "tapped" to a uniform density. The sample must be at the recommended level, and not occupy more than a specified volume, otherwise premature combustion is likely. The aluminium boat was abandoned



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because it does not hold 100 mg of some types of plant material and it seemed responsible for occasional large results, probably because air was sometimes trapped. When the nitrometer was completely emptied and refilled it worked efficiently for about 1½ days, but then results with plant material became progressively larger. Emptying the nitrometer completely of the KOH mixture usually disturbed the mercury, which then had to be emptied and replaced. It was best to syphon off as much of the KOH mixture as possible each day (about 80%) and replace it with fresh solution, the KOH then remained efficient without having to replace the mercury.

Each instrument can do 30–32 determinations (blank + standards + unknown) in 8½ hours, and one assistant operates two instruments. When continuous operation cannot be maintained and the instrument cools extra blanks have to be determined. (Hamlyn)

**Flame spectrophotometer.** The Unicam SP900 flame spectrophotometer installed last year works well and was used for more than 6,000 analyses. Most were for calcium, magnesium and sodium, but potassium, rubidium and barium were also determined (most potassium measurements are made on other simpler flame photometers). New methods to suit the instrument were developed. (Salt)

**Estimating rubidium and potassium in the presence of each other.** The method of Dugenetay, Lubochinsky and Stolkowski (*J. Physiol., Paris* (1963) **55**, 523–532) was adapted for use with the SP.900 to determine rubidium in the presence of potassium. Rubidium in $2{\cdot}5 \times 10^{-2}$ molar potassium solutions (as KCl) was estimated in the range from $10^{-5}M$-Rb to $10^{-4}M$-Rb at a wavelength of 794·7 m$\mu$. This concentration of potassium enhanced rubidium emission, but background interference by potassium alone varied with its concentration. However, less than 1% error in the rubidium concentration measured was caused by the original potassium concentration of the test solutions. Concentrations of $2 \times 10^{-4}M$-Rb enhanced the emission of $10^{-4}M$ levels of K much more than observed by Dugenetay *et al* at 760 m$\mu$. Even $10^{-3}M$-Rb did not increase K emission fully. Similar results were obtained at the most sensitive K emission line (768 m$\mu$), so this wavelength was used. The following procedure was adopted for estimating K in the presence of Rb. The Rb concentration of a portion of the test solution was estimated and that in the remainder adjusted to a constant Rb concentration; the K concentration was then found from a K calibration curve with K standards containing this constant Rb concentration. A suitable concentration range was from $2 \times 10^{-5}M$-K to $2 \times 10^{-4}M$-K in the presence of $10^{-3}M$-Rb. (Salt)

**Determining total sulphur in plant material.** Cunningham's method (*Rothamsted Report* for 1961, p. 63) adapted for the SP900 worked at a concentration range from 2 to 20 ppm S (8·57 to 85·7 ppm Ba), 15 times more sensitive than the original method. Calcium (present as an impurity in the ammonium–E.D.T.A. solution used to dissolve the $BaSO_4$ precipitate) interfered with emission at the 553·6-m$\mu$ Ba line. Barium was



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therefore estimated at the less intense 513·9-mμ Ba line, which was free from calcium interference and was sensitive enough. (Salt)

**Atomic absorption spectrophotometry.** The apparatus we built (*Rothamsted Report* for 1964, p. 70) has been improved by balancing the temperature of the preheated air supply to the atomiser, and the rate solution is taken up. Sensitivity has improved, the efficiency of converting solution to aerosol has increased from 90 to 100%. The instrument is now used routinely to measure magnesium in extracts of crops and soils. (Rawson)

The SP920 attachment for the Unicam SP900 spectrophotometer allows measurements using the atomic-absorption principle to be made by this instrument. The normal range for magnesium is from 0·2 to 2·5 ppm using the SP900/920 as compared with 1–8 ppm by emission spectrophotometry with the SP900; concentrations as small as 0·05 ppm Mg are easily measured on the SP900/920. K, Na Ca, P, S and Fe at concentrations common in extracts of soil and plant ash interfered slightly. Aluminium and silicon much depressed magnesium values. An excess of calcium overcame aluminium interference, but a final strontium concentration of 500 ppm suppressed all observed interferences. The small burner head, normally used for emission measurements, could be used instead of the long-path length burner for atomic absorption measurements in the range from 1 to 10 ppm Mg. A lower instrument gain setting, and hence a more stable galvanometer reading, was obtained with atomic absorption as compared with emission for this concentration range for Mg. (Salt)

**Modification of Cambridge Recording DC Polarograph.** Incorporating a Cambridge "Univector" attachment in a Heyrovsky D.C. Polarograph, modified to produced AC recordings, increased the sensitivity of the original instrument several times. Cu, Cd, Ni and Zn can now be determined simultaneously with only 0·5 ppm in volumes ranging from 0·5 to 2·0 ml; the unmodified DC instrument failed to give measurable readings with such solutions. The instrument can be used up to 100 ppm of these four elements without diluting the sample solution; the limit of detection is about 0·05 ppm in the solution. Cu, Cd, Ni and Zn are extracted from solutions containing much alkaline-earth metals by diphenylthiocarbazone, which is better than precipitating with dithio-oxamide. Cobalt can interfere with the polarographic determination of zinc, but the extraction can be altered to avoid amounts of Co that affect the zinc peak. An advantage of the polarographic method is that the sample solution can be recovered and used again. (Williams)

## Radiometry

***Radioactive calcium-45.*** Dried films of $CaCl_2$ crystals, with and without $AlCl_3$, deliquesce rapidly in humid air and acquire varying and uneven thicknesses of water. Thin "*formvar*" films, normally used to protect such crystalline deposits, puncture to different extents under infra-red lamps. Thicker protective films, or films dried slowly, are unsatisfactory. Deposited samples of known weight per sq cm, prepared by these variants for



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Geiger–Muller (or scintillation) counting of radioactive calcium-45 in 0·01$M$-$CaCl_2$ (+$AlCl_3$), usually give inconsistent count-rates. Reproducible results were obtained when one drop of 0·01$M$-ethylene-diamine tetra-acetic acid in dilute (1 : 5) ammonium hydroxide was added to 0·5-ml portions of labelled $CaCl_2$ (+$AlCl_3$) solutions on counting planchettes and dried with infra-red heat. (B. S. Coulter)

***Simultaneous estimation of calcium-45 and potassium-42 by Geiger-counting.*** Aluminium planchettes, used for counting radioactive samples, fully absorb the 0·25-MeV β-radiation from radioactive calcium-45. Two closely matched end-window Geiger counters (2-in.-diameter thin mica windows) in a perspex–lead castle simultaneously measured the radioactive emissions on both sides of a planchette containing calcium-45 and potassium-42. These were recorded on two separate scalars. After applying a correction factor for differences in counting geometry, the count-rates of calcium-45 and potassium-42 were directly known.

Using planchettes of various thickness or supplementary absorbers, other weak β-emitters could be used with strong β-or $\gamma$-emitters in double-labelled experiments. (B. S. Coulter, Deist, Elsmere and Talibudeen)



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