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# Report for 1971

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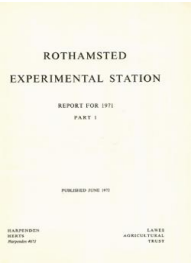
ROTHAMSTED
EXPERIMENTAL STATION

# Chemistry Department

## G. W. Cooke

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**Practical implications of the work**

A single injection of aqueous ammonia into pasture during spring gave yields as large as those from the same total amount of N as 'Nitro-Chalk' given in divided dressings before each cut, so when aqueous ammonia, applied as in our experiments, is cheaper, it can be expected to give yields as good as those from solids.

Liquid fertilisers supplying N, P and K cost as much as solids and have no advantages for barley unless they are cheaper to apply. Most liquids contain urea, which is liable to damage germinating seeds when combine-drilled, and when sprayed on the soil surface gives smaller yields than equivalent solid fertiliser. Injecting NPK liquid fertiliser away from the seed prevented urea being damaging, but the P and K were then too far away from the seed to benefit young plants. Shallower placement may make P and K more accessible without making urea harmful.

Damage from urea depends greatly on the weather after sowing, as do the risks of losing N by leaching, and of damage by disease. In two years out of five, rain at Saxmundham after sowing leached much nitrate applied early, and delaying the topdressings for barley until May increased yields. Choice of variety was important, too. Of the first varieties we grew, the short-strawed Deba Abed yielded consistently better than Maris Badger. Of the three we have grown recently Julia has yielded 25% (1970) and 75% (1971) more than Midas and Sultan, seemingly because these two suffered seriously from brown rust, especially in 1971, and Julia did not. Leaf diseases other than mildew seem the main reason for recent poor yields of barley in some of the Saxmundham experiments, for there was little gain from sterilising the soil, from fungicidal seed dressing to control mildew, or from doubling the nitrogen applied.

Compounds containing directly linked N and P have been suggested as fertilisers, and several such materials were roughly as effective as conventional fertilisers; only diamidophosphate was occasionally superior. These compounds cost much more than ordinary fertilisers to make, so are unlikely to be used, except, perhaps, in seed dressings or sprays.

Despite the much discussed benefits from increasing soil organic matter, most of our experiments fail to show any although we have had gains for unexpected reasons. In experiments with conifer seedlings and transplants that lasted 15 years, giving fertilisers only produced as large or larger plants as giving composts. There was no benefit from interrupting continuous conifer-growing and digging in a green crop every third year. The green crops had little effect on soil organic matter but annual compost dressings increased it by 70% at one site and 100% at the other; these 'improvements' did not produce better seedlings. However, at Rothamsted and Woburn both the damage to beans caused by using simazine at recommended rates, and its efficiency as a weedkiller, have depended on the amounts of soil organic matter. At Woburn simazine has diminished yields of crops on light soils with 1·5 to 2% organic matter, whereas on the heavier land containing 4 to 5% organic matter, it has neither damaged the crop *nor* killed the weeds. At Rothamsted also, where some plots on Barnfield receive only fertilisers and contain only 1·5% organic matter, simazine has seriously damaged the beans; other plots given FYM each year, contain 5% organic matter and simazine is safe. Elsewhere at Rothamsted on fields with 2·5 to 3% organic matter, simazine used as recommended controlled weeds and did not harm the beans.



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Wheat, barley and grass are all liable to be 'scorched' by applying herbicide mixed with a solution of N fertiliser. Symptoms of scorch disappeared from cereals within three weeks and yields were not seriously depressed by the combined spray. Herbicide had little effect on wheat yields, though it controlled weeds satisfactorily when sprayed alone or with fertiliser; the form of N used gave larger and more consistent differences, with 'Nitro-Chalk' giving largest yields.

During the last 100 years, soils of the Broadbalk experiment have lost annually calcium equivalent to 630 to 880 kg/ha of limestone; by contrast exchangeable magnesium has changed little during the last 50 years. It seems that magnesium coming from the traces in dissolved limestone, rain, the seed and fertilisers, is usually enough to replace the magnesium leached and removed by crops. This applies of course to our Rothamsted clay-loam and silt-loam soils; we have reported previously that leaching removed much more magnesium at Woburn, where the sandy loam was rich in Mg in 1888 but by 1968 was so poor that crops responded to Mg fertilisers.

## Nitrogen fertilisers

**Aqueous ammonia for grazed grass.** In the experiment begun in 1969 a single dressing of aqueous ammonia was injected on 11 February (at 125, 250, 375 and 500 kg N/ha) and the yields (under cages) from it compared with those from repeated dressings of ammonium nitrate ('Nitro-Chalk 21') applied for each of six cuttings. Aqueous ammonia gave the larger yield at each of the first five cuttings (in contrast to 1969 and 1970 when it gave larger yields only at the first three), and neither fertiliser increased yields during dry weather at the final cutting. So this year, the value of a single spring injection of N for autumn grazing could not be fully assessed.

Table 1 shows that the two fertilisers gave almost the same mean yields over the three years, though in the first two, yields from aqueous ammonia were the smaller. In each year, yield was little or no more from 500 than from 375 kg N/ha as either fertiliser. Percentage N in the dry grass (in 1969 and 1970) was more with aqueous ammonia at the first three cuttings, but less later; the same amount of N was recovered from each fertiliser each year. Seemingly farmers who give large amounts of N to grazed grass can inject all of it as aqueous ammonia during spring and get the same yields as giving equal total N broadcast as ammonium nitrate in dressings given through the year. (Widdowson, Penny and Flint)

**Liquid fertilisers for barley.** Results described in 1970 (*Rothamsted Report for 1970*, Part 1, 38) showed that a liquid NPK fertiliser rich in urea often killed barley seedlings when combine-drilled and when sprayed over the seedbed was less effective than a comparable granular fertiliser. (The liquid contained 14% N, 6% $P_2O_5$, 8% $K_2O$ and was described as 14–6–8; other fertiliser analyses were similarly abbreviated.) However, urea dissolved in water and then injected in bands 30 cm apart, similarly to ammonia, was both safe and effective. Injecting NPK fertilisers containing urea between the rows of seed promised to prevent the urea from causing damage, but risked losing the benefits from combine-drilled P and K on poor soils. To test this technique, we either combine-drilled or injected two liquid fertilisers, one (14–6–8) supplying all the N, mostly as urea, and the other (4–10–10) one-fifth of the N, with little as urea (the other four-fifths was supplied by 'Nitro-Chalk' broadcast on the seedbed). Granular 20–10–10 compound, broadcast or combine-drilled was used as the standard. Of these experiments, one was sown early and rain followed. There, the combine-drilled liquid fertilisers did no damage and early growth was better than with broadcast granular fertiliser and much better than with the injected liquids. The two later sowings were followed by dry weather.



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TABLE 1

*Mean annual yields of grazed grass at Rothamsted from single spring injections of aqueous ammonia and from six broadcast dressings of 'Nitro-Chalk' from 1969 to 1971*

| Yields of dry grass (t/ha)* | | |
|---|---|---|
| With N applied kg/ha | Without nitrogen 12·0 Aqueous ammonia | 'Nitro-Chalk' |
| 125 | 15·5 | 15·2 |
| 250 | 17·4 | 17·8 |
| 375 | 18·6 | 18·3 |
| 500 | 18·3 | 18·0 |

* These yields (from under cages) are best used for comparative purposes only; they may over-estimate yields by as much as 20%.

TABLE 2

*The effect of applying nitrogen, either early (to seedbed) or late (in May) to two barley varieties grown at Saxmundham each year from 1967–1971 and comparative yields from barley grown on Rotation II experiment*

| Yields of grain (t/ha) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Annual experiments on Grove Plot | | | | | | | Rotation II Residual Phosphate Experiment | | | |
| | | | | Effect of | | | | | | | |
| Year | Previous* crop | Mean yield | Range | Variety† (DA–MB) | Nitrogen ($N_2$–$N_1$) | Time of N (E–L) | Other factors (F–O) | Previous* crop | Mean yield | Range | Variety† |
| 1967 | f | 4·93 | (3·8–5·8) | 0·36 | 0·35 | −0·75 | 0·21(1) | — | — | — | — |
| 1968 | b | 4·81 | (4·0–5·8) | 0·95 | 0·18 | 0·08 | 0·18(1) | sb | 3·89 | (3·0–4·3) | Z |
| 1969 | sb | 4·22 | (3·4–5·1) | 0·80 (M–S) | 0·14 | −0·39 | 0·14(2) | b | 3·70 | (1·1–4·5) | S |
| 1970 | b | 3·34 | (2·8–3·8) | 0·10 | 0·26 | 0·48 | 0·33(2) | sb and p | 4·22 | (2·5–5·0) | J |
| 1971 | sb | 2·52 | (2·3–2·8) | −0·14 | −0·14 | 0·28 | 0·20(3) | sb and p | 4·44 | (1·9–5·2) | J |

* b = Barley
f = Fallow
p = Potatoes
sb = Sugar beet

†DA = Deba Abed
MB = Maris Badger
J = Julia
M = Midas
S = Sultan
Z = Zephyr

Other factors
(1) = Soil drenched with formalin
(2) = Seed dressed with ethirimol
(3) = Seed dressed with phenyl phosphonic acid (PPA)
$N_1$ = 75 kg N/ha
$N_2$ = 150 kg N/ha

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There, combine-drilled 14–6–8 killed many plants, though when injected it was safe. Combine-drilled liquid 4–10–10 was safe and early growth was better than with combine-drilled solid 20–10–10. Yields harvested from combine-drilled 14–6–8 were smaller than from any other treatment in the two later-sown experiments (one significantly so), but not in the early-sown experiment. Yields from injecting fertiliser were similar to those from broadcasting granular 20–10–10, which in turn were not consistently larger or smaller than those from the other treatments. So, although injecting NPK fertilisers in bands 8–10 cm deep prevented the urea damaging seedlings, it also prevented the young barley shoots reaching the P and K soon enough. (Widdowson, Penny and Flint)

**Times and amounts of N for barley at Saxmundham.** In 1970 and 1971 we again compared yields from early (to seedbed) and late (May) N (as calcium nitrate 15·5% N), but on Sultan (tall) and Midas (short) barley varieties instead of the Maris Badger (tall) and Deba Abed (short) varieties used previously (*Rothamsted Report for 1969*, Part 1, 46). In 1970 we again tested seed dressed with a fungicide (ethirimol) to check mildew and in 1971 seed dressed with a growth regulator (phenyl phosphonic acid; other results are on p. 58). Table 2 shows that mean yields in both years were small, far smaller than in the three previous years and far smaller than from Julia barley on the adjacent Rotation II experiment. In June 1971 both varieties were attacked by brown rust, as they also were in 1970. This disease (to which both varieties are very susceptible) seems the probable main cause of the alarming loss of yield, for our results (Table 2) show that it was not from: (1) previous cropping; (2) shortage of N or P and K; (3) mildew; (4) the weather limiting growth.

The experiments made on barley at Saxmundham from 1967 to 1971 show: (1) the advantages of growing a short stiff strawed variety (Deba Abed); (2) the fact that during wet springs (two years in five) nitrate N was easily leached from this sandy clay soil; (3) there was little extra benefit from doubling the dressing of N (from 75 to 150 kg/ha); (4) that neither a soil sterilant (formalin), a systemic fungicide to control mildew (ethirimol), nor a growth regulator (phenyl phosphonic acid) greatly increased yields. (Widdowson, Penny and Flint)

**Reactions of ammonia with soil.** The adsorption of aqueous and anhydrous $NH_3$ by soils was further studied to assess the contribution to total $NH_3$ sorption made by mechanisms involving exchangeable cations. To avoid sorption of ammonia by organic matter, soils were treated with peroxide; the residues could not be saturated with Na and K, apparently because exchange sites were occupied by manganese released when $MnO_2$ decomposed.

**Sorption of anhydrous $NH_3$.** Dry $NH_3$ gas was added in successive increments to 1 g soil samples at 27°C in a non-adiabatic calorimeter and heats and amounts of adsorption measured. Soils were degassed by initial diffusion pumping, then kept under vacuum in a closed system containing $P_2O_5$ until they could be conveniently treated with ammonia.

Two hours or more initial pumping gave consistent 'heat' and 'amounts' by Geescroft soil; longer pumping had no further effect. This suggests that water bound physically to soil is desorbed by faster pumping than generally thought. Broadbalk soil (from Plot 3 without fertiliser or FYM, organic carbon content $<1\%$, CEC 12 meq/100 g) saturated with Na or K gave one isotherm with initial heat of adsorption 60 kJ $mol^{-1}$, but the Ca-saturated soil adsorbed *c.* 10 meq/100 g more $NH_3$ over the relative pressure range 0 to 0·01 (for definition of relative pressure see *Rothamsted Report for 1970*, Part 1, 39), with initial heat of adsorption 75 kJ $mol^{-1}$. The 10 meq difference was maintained but not increased at greater pressures, suggesting that sorption via protonation of one $NH_3$



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molecule at each cation-exchange site by strongly bound water of hydration is responsible. The K and Na soils probably sorb $NH_3$ only through protonation by weakly acidic hydroxyl groups. Other materials that are likely to adsorb $NH_3$ only in this way are silica gel, of which a sample gave an initial heat of sorption of 60 kJ $mol^{-1}$, and kaolin, which gave 45 kJ $mol^{-1}$.

**Sorption of aqueous ammonia.** Measurements of sorption of dilute aqueous $NH_3$ by aqueous suspensions of clay ($<2\ \mu$) separated from Broadbalk soil (Plot 3), saturated with different cations, showed that the Na-, Ca- and $NH_4$-soils adsorbed similar amounts of $NH_3$ (*c.* 10 meq/100 g from 0·01*M* $NH_3$), and more than the K-soil (5 meq/100 g). Sorption of $NH_3$ by protonation by water and displacement of the exchangeable ion into solution was significant (30% of the total) with Na-soil but not with K-soil. No net sorption can occur by this mechanism with $NH_4$-soil.

Heats of adsorption of aqueous ammonia were measured by microcalorimeter. K- and Ca-soils gave similar heat of adsorption curves (25 kJ $mol^{-1}$ at 10 meq $NH_3$ sorbed per 100 g soil) rising sharply to $>50$ kJ $mol^{-1}$ at small amounts of $NH_3$ sorbed, but the heat curve for Na-soil rose much less steeply, supporting the idea of a different sorption mechanism. The heat of adsorption at corresponding coverage on $NH_4$-soil was 35 kJ $mol^{-1}$, also rising sharply at small coverages. This larger value could come from sorption on proton-donor groups more acidic than those on the other soils, because of washing with $NH_4Cl$ solution (pH 4·6) and not with a neutral ammonium salt. (Ashworth)

### Effects of compounds of nitrogen and phosphorus on crops

**Phenylphosphonic acid.** Other workers (e.g. Williams, E. G. (1970) *Nature, London* **227**, 84–85) showed that phenylphosphonic acid (PPA) can increase crop yields; the reasons are not known.

Tests were made to find safe dressings. In germination tests in the laboratory, increasing concentrations decreased the numbers of barley seeds that germinated, delayed germination and shortened both roots and shoots. In tests with Rothamsted soil in pots, all dressings of PPA diminished germination and yield of barley, but 0·5% by weight of PPA on seed had only a small effect; with 1% yields were halved. Damage done by PPA was the same with or without an organo-mercury/BHC seed dressing ('Kotam'). In another test using soils taken from field experiments at Rothamsted and Saxmundham damage from PPA at the 1–2 leaf stage depended on the variety, and was more on Sultan than on Julia, and more with Rothamsted than with Saxmundham soil. Tests were also made with wheat and barley seed pelleted with clay containing PPA and grown in Rothamsted soil. The clay seed coating greatly diminished or eliminated damage by PPA to seedlings. Best yields of young plants were from 0·036% PPA on barley seed and 0·36% on wheat. (Gasser and Mitchell)

PPA could be sprayed (in concentrations up to 2% w/v) on leaves of wheat in the glasshouse without damaging them. When applied to the seed (0·25–2% by weight as 0·5–4*N* solutions) even the smallest amount prevented some seedlings from emerging and the larger concentrations retarded growth for a month. PPA applied to Geescroft (Rothamsted) soil at 100–400 mg/kg had only slight effect on germination, but checked growth for up to a month, depending on the amount used and the largest amount halved growth.

A larger experiment with Joss Cambier wheat in pots tested these three methods of applying PPA, with small and large amounts of N fertiliser and at small and moderate moisture stress. Seed treatment again lessened germination and checked early growth; PPA applied to the soil also depressed growth but less. Sprayed plants were not checked,



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though older leaves drooped and very young ones were distorted. Small amounts applied to the soil (150 mg/kg) or a spray (0·5% w/v solution) increased yields of tops harvested after seven weeks. Twice as much applied to the soil decreased yields, as did 1% or 2% PPA applied to the seed. Soil dressings and sprays increased the amount of N in the tops. Mineral-N in the soil was considerably increased by four of the six PPA treatments; possibly PPA alters nitrogen relationships in soil or plant, or in both. Nine weeks after planting there was no visible effect from PPA; tops were harvested from the remaining pots after 14 weeks. In none of the pots kept moderately dry, or in the moister ones given the smaller N dressing (1 g/pot), did PPA have any consistent or large effects, in pots kept moist and given 3 g N/pot, yields were slightly increased by small PPA dressings applied as spray or to the soil; PPA usually increased the amount of N in plants. (Waring and Mitchell)

Used at 1%, PPA applied to the seed sown at Rothamsted decreased the numbers of plants of both Julia and Sultan and at 0·5% the numbers of Julia. At 'stem extension' stage, 0·5% and 1% both decreased the dry matter of Julia, but only 1% did so for Sultan; both varieties were shortened by both dressings. These effects on growth were maintained to the 'heading' stage. Both varieties had mildew, Sultan the more. Sultan also lodged more with the larger dressing of N (112 kg N/ha), and at harvest yielded 1 t/ha less grain than Julia (averaging all treatments). With 112 kg N/ha as fertiliser, Julia yielded best with 0·5% PPA on the seed, Sultan without PPA. Averaging the two amounts of fertiliser, the gain in yield from using PPA on Julia barley was only 0·1 t/ha (an increase of 2·6%). (Gasser and Penny)

A seed dressing of a PPA derivative was one treatment in an experiment at Saxmundham with barley testing three amounts and two times of applying N with two varieties (Midas and Sultan). Brown rust (see p. 57) caused both varieties to yield badly—Midas 2·45 t/ha and Sultan 2·59 t/ha. Mean gains from the seed-dressing with PPA were 0·26 t/ha of Midas and 0·14 t/ha of Sultan. Averaging varieties, PPA increased yields most where the smaller amounts (50 and 100 kg/ha) of N were given. Straw yields were also increased by PPA, more with Sultan than with Midas; increases were largest with the largest amounts of N. (Widdowson, Penny and Flint)

**Amido phosphates.** Work reported last year (*Rothamsted Report for 1970*, Part 1, 42–44) continued, to measure effects of residues from 1970 and of fresh dressings. Basal dressings of N (112 kg N/ha for each of three cuts as ammonium nitrate) were given to plots in the grass experiment given NP fertilisers in 1970. The slight gain from diamido-phosphate over ammonium phosphate and other amido-phosphates, found in 1970, was maintained in 1971 but the difference in 1971 was not significant:

| | Total yields of dry grass (t/ha) | | | | |
|---|---|---|---|---|---|
| | Ammonium phosphate | Amido-phosphate | | | S.E. |
| | | Mono- | Di- | Tri- | |
| 1970 | 3·24 | 3·33 | 3·53 | 3·22 | ±0·087 |
| 1971 | 9·80 | 9·67 | 9·98 | 9·63 | ±0·176 |

New experiments on grass, potatoes and kale were of similar designs, testing two amounts of NP fertilisers (ammonium phosphate, sodium di-amido phosphate and urea phosphate) each with basal N and K fertilisers. (Ammonium phosphate (AP) was a mixture of monoammonium phosphate (MAP) with urea to balance the N : P ratio of the other compounds.) Kale and potatoes also had a smaller amount of AP in the seedbed and were sprayed with solutions of di-amido phosphate and phosphoryl triamide during growth.



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***Ryegrass.*** The site was initially sown with barley, but this was so damaged by birds that it was over-drilled with Westerwolds ryegrass during April; the harvests were of grass plus barley. At the first harvest, di-amido phosphate yielded most dry matter, but thereafter the forms did not differ in their effects on yields.

***Kale.*** Early growth was equally good with all three forms of NP fertiliser, but the best final yield was from urea phosphate. Spraying kale with di-amido phosphate or phosphoryl triamide did not give significantly more yield than ammonium phosphate.

***Potatoes*** received NP fertilisers supplying 22 kg P/ha or 45 kg P/ha applied to the seedbed and rotary cultivated into the surface soil; sprays supplying 11 kg P/ha as di-amido phosphate and phosphoryl triamide were tested when the crops were meeting in the rows. All NP fertilisers improved early growth, di-amido phosphate most. On average of the two amounts of NP fertiliser, all three forms increased dry matter yields of tubers slightly and similarly. Potatoes sprayed with amido phosphates yielded similarly to those without NP fertilisers. (Gasser, Penny and Flint)

***Pelleted seed.*** Sugar-beet and lettuce seeds pelleted with clay containing small amounts of di-amido phosphate and di-ammonium phosphate (DAP) were grown to seedlings in pots containing Rothamsted soil. Without a basal NP fertiliser, both amounts of di-amido phosphate (67% and 17% of the weight of the seed) improved early growth of beet, but 21% of DAP did not. With basal NP fertiliser, only 17% of di-amido phosphate improved growth of sugar beet. Without a basal NP fertiliser, both amounts (50 and 200% of weight of seed) of di-amido phosphate and the smaller amount of DAP increased early growth of lettuce. With basal NP fertiliser, the larger amount of di-amido phosphate and the smaller amount of DAP increased early growth. (Gasser and Mitchell)

These novel NP fertilisers cost much more than conventional water-soluble fertilisers; although they were roughly as effective as ordinary fertilisers, only di-amido phosphate was, on occasion, superior. Gains were too small to justify further work with the fertilisers applied to seedbeds. Because they are un-ionised, these compounds may be successful where conventional fertilisers would damage seeds or leaves. (Gasser, Penny and Flint)

### Experiments on growth and yield of wheat and barley at Rothamsted and Broom's Barn

Yields of winter wheat and sometimes barley too, are usually larger at Rothamsted than at Woburn (Beds) or at Broom's Barn (Suffolk). In 1971, therefore, the Botany and Chemistry Departments began to compare the growth, nutrient content and yields of winter wheat (Cappelle) and spring barley (Julia) grown in duplicated experiments at Rothamsted and Broom's Barn. We planned to measure and compare botanical and chemical values throughout the growing season and then to relate these measurements to yields at harvest. Because nitrogen and water seemed the factors most likely to increase growth and yield at Broom's Barn (summer rainfall is less and the soil there is shallower, lighter and less water retentive) both were tested on both crops and on both farms. In each experiment six equal increments of N (from 31 to 186 kg N/ha) were tested on each crop, both with and without irrigation water, given during May and June to bring the soils back to field capacity whenever the deficit reached 25 mm.

Analyses of soil samples taken during autumn showed three times more mineralisable N in the wheat soil at Rothamsted than at Broom's Barn and one and a half times more



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in the barley soil at Rothamsted than at Broom's Barn (Gasser). No soil was lacking in P or K. At Rothamsted wheat stems sampled on 29 March contained roughly 600 ppm of nitrate-N (Williams), whereas at the same time wheat at Broom's Barn contained hardly any. The Rothamsted wheat followed potatoes, that at Broom's Barn a one-year ley, so the nitrate concentrations in the wheat reflected not only inherent differences in soil N status, but also those from previous cropping. N top-dressings were applied during mid-April. With most N, maximum $NO_3$-N concentrations of 500 ppm were obtained on both soils from early May to late June, though except in early May at Rothamsted, there was never more than 10 ppm of nitrate-N in wheat given only 31 kg N/ha. Similar tests on barley showed maximum amounts of 700 ppm $NO_3$-N (with 186 kg N/ha) in stems at mid-May, which diminished to 70 ppm late in June on both soils (each experiment followed a cereal in 1970). There was little nitrate-N in barley given only 31 kg N/ha during May and June at either farm.

With 31 kg N/ha, wheat at Rothamsted yielded 7·40 t/ha grain, but at Broom's Barn only 4·61. The largest grain yields were 7·54 t/ha (with 93 kg N/ha and without irrigation) at Rothamsted and 6·88 t/ha (with 155 kg N/ha and with irrigation) at Broom's Barn. Thus, giving enough nitrogen decreased the yield difference between the sites to only 0·66 tonnes of wheat, suggesting that the abilities of the soils to supply N was the main factor that altered yields. Comparable values for barley given 31 kg N/ha were 5·65 t/ha grain at Rothamsted and 4·07 at Broom's Barn and largest yields (in t/ha) were 6·85 and 6·11 at Rothamsted and Broom's Barn respectively, both crops receiving 155 kg N/ha and irrigation water. Irrigation increased both grain and straw yields of both wheat and barley at Broom's Barn, but only of straw at Rothamsted. (Widdowson, with P. J. Welbank, Botany Department, see p. 106)

### Comparisons of crop rotations, and of fertilisers with compost, in 15-year experiments with Sitka spruce

In 1945, composts and green manuring were used in Forestry Commission nurseries to maintain their fertility. As a result of experiments between 1945 and 1950, safe methods of using soluble fertilisers were developed for all seedlings and most transplants of common conifers. To test whether continued cropping with conifers and repeated dressings of fertilisers had any ill-effects, experiments with Sitka spruce (*Picea sitchensis*) were begun at Kennington and Wareham in 1951 and continued to 1965. Kennington was an acid sandy loam (pH 4·5 in $CaCl_2$-solution) used for farming until 1950, Wareham a very acid sand on heathland. Growing conifer seedlings continuously was compared with rotations of crops, including one year in three of fallow or green crops (rye, ryegrass or yellow lupins), and of one or two years in three of conifer transplants. Composts made from young green bracken (*Pteridium aquilinum*) and hopwaste were compared with fertilisers ('Nitro-Chalk', superphosphate, potassium chloride and magnesium sulphate). The nutrients supplied to seedbeds are given below; fertilisers supplied more inorganic N, P and Ca, the composts more K:

| | Average amounts per year (1954–65) in g element per m² | | | | | |
|---|---|---|---|---|---|---|
| | Total N | Inorg. N | P | K | Mg | Ca |
| Fertiliser | | | | | | |
| Kennington and Wareham | — | 14 | 10 | 11 | 4 | 36 |
| Compost* | | | | | | |
| Kennington | 43·7 | 3·3 | 8·1 | 24·9 | 3·8 | 19·1 |
| Wareham | 50·0 | 3·5 | 5·8 | 22·4 | 3·7 | 13·1 |

* *Fresh produce* (*per year*). Kennington 5·4 kg; Wareham 1954–57: 5·4, 1958–61: 6·7, 1962–65: 8·2.



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No benefit was derived from interrupting the growing of conifers. At both sites, seedlings were often smaller and fewer after green crops than with continuous conifers. There was often a small benefit from growing transplants before seedlings, but not the converse.

Responses to manuring were much larger than any effects from cropping treatments. *Kennington*: seedlings were consistently taller with fertilisers than with compost, especially in the wetter seasons:

| | Average height (cm) | |
|---|---|---|
| | Dry years | Wet years |
| Fertiliser | 4·9 | 6·5 |
| Compost | 4·0 | 4·3 |

Giving compost (about 50 t/ha annually) to fertilised plots did not increase seedling height. The lack of response of seedlings to good compost at Kennington remains unexplained, though in 1959 damage from fungal attack was suspected. *Wareham*: during the earlier years seedlings with fertiliser were as superior to those with compost as at Kennington, but in the last years of the experiment fertilisers gave seedlings that were only a little larger, if at all. Compost and fertilisers used together were better than either alone, especially towards the end.

Fertilisers and composts are compared in the table below which shows the usable seedlings (exceeding 3·8 cm high), large enough to transplant:

| | Number of usable seedlings/m² | | | | | |
|---|---|---|---|---|---|---|
| | Kennington | | | Wareham* | | |
| | 1954 –57 | 1958 –61 | 1962 –65 | 1954 –57 | 1958 –61 | 1962 –65 |
| Unmanured | 348 | 370 | 108 | 0 | 16 | 7 |
| Fertiliser | 566 | 961 | 1085 | 887 | 622 | 588 |
| Compost | 357 | 578 | 729 | 520 | 462 | 583 |
| Both | 440 | 858 | 1028 | 953 | 864 | 1022 |

* Limed plots only.

Without fertiliser or compost, usable seedlings became fewer during the experiment at Kennington; at Wareham there were none or few fit to use at any time.

Nutrient concentrations in seedlings (Table 3) at Kennington were similar with compost or fertiliser. At Wareham the only considerable difference was in % K (nearly

**TABLE 3**

*Dry matter (DM) and nutrient concentrations of seedlings (tops + roots)*

| | Means of 12 years | | | | | | |
|---|---|---|---|---|---|---|---|
| | DM mg/plant | % in DM N | P | K | Ca | Mg | ppm Mn |
| Kennington | | | | | | | |
| Unmanured | 137 | 1·79 | 0·28 | 0·78 | 0·68 | 0·15 | 599 |
| Fertiliser | 315 | 1·94 | 0·30 | 1·24 | 0·61 | 0·13 | 878 |
| Compost | 281 | 2·14 | 0·30 | 1·55 | 0·57 | 0·13 | 1065 |
| Both | 337 | 2·09 | 0·31 | 1·51 | 0·66 | 0·14 | 1243 |
| Wareham* | | | | | | | |
| Fertiliser | 240 | 1·58 | 0·24 | 0·68 | 0·60 | 0·13 | 65 |
| Compost | 234 | 1·71 | 0·29 | 1·29 | 0·51 | 0·13 | 346 |
| Both | 338 | 1·70 | 0·26 | 0·96 | 0·57 | 0·14 | 317 |

* Unmanured plots not sampled.



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doubled by compost) and % Mn; % K in seedlings with fertiliser also declined during the experiment from 0·8–0·6; in wet years, the fertilised plants showed severe signs of K-deficiency (similar deficiencies were cured elsewhere in the nursery by top-dressing with $KNO_3$).

Transplants responded well to manuring (Table 4); at Kennington they were 20–60% taller, at Wareham 200–300%. At both nurseries differences with composts and fertilisers were relatively small, but fertiliser was usually better in early years, composts later; the two together were a little better than either alone. Quality in seedlings is measured by their ability to grow after transplanting; the lower part of Table 4 shows that, at Kennington, seedlings grown with fertiliser grew slightly better as transplants in the early periods; at Wareham, the compost-grown seedlings were slightly better later.

**TABLE 4**

*Height (cm) of transplants*

| | Kennington | | | Wareham | | |
|---|---|---|---|---|---|---|
| | 1954 –57 | 1958 –61 | 1962 –65 | 1954 –57 | 1958 –61 | 1962 –65 |
| (a) Unmanured | 21·7 | 22·0 | 20·5 | 8·9 | 10·2 | 9·9 |
| Fertiliser | 27·6 | 31·5 | 27·1 | 23·0 | 22·6 | 19·1 |
| Compost | 26·8 | 33·8 | 28·4 | 20·9 | 24·1 | 20·6 |
| Both | 27·9 | 36·1 | 29·7 | 25·3 | 24·1 | 21·6 |
| S.E. ± | 0·25 | 0·45 | 0·31 | 0·33 | 0·35 | 0·25 |
| (b) Ex fertiliser | 27·0 | 31·3 | 26·6 | 19·5 | 19·3 | 17·6 |
| Ex compost | 25·1 | 30·4 | 26·3 | 19·6 | 21·2 | 18·0 |
| S.E. ± | 0·18 | 0·32 | 0·22 | 0·33 | 0·35 | 0·25 |
| c.v.% | 2·7 | 4·1 | 3·3 | 4·9 | 5·0 | 4·1 |

**Changes in soil organic matter and nutrients.** The analyses of the two soils before cropping were:

| | pH in 0·01 *M* $CaCl_2$ | % org. C | Total elements % N | Total elements ppm P | K | Ca | Mg | Mn | Exchangeable ppm K | Ca | Mg | CEC me/100 g |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Kennington | 5·1 | 1·2 | 0·118 | 350 | 4800 | 1450 | 1030 | 208 | 74 | 1400 | 51 | 7·7 |
| Wareham | 3·4 | 2·4 | 0·082 | 58 | 700 | 200 | 152 | 26 | 19 | 140 | 33 | 3·0 |

Tables 5 and 6 show analyses of the soils after cropping. Although all the produce of green crops was dug in (except that some ryegrass cuts were removed), differences in soil composition from the contrasted cropping were small. Compost-treated soils had twice as much organic carbon as fertiliser-treated at Kennington and 70% more at Wareham (without allowing for a possible decrease in bulk density). Except for P at Kennington and Ca at both places, compost-treated soils contained more nutrients.

These experiments are important because, although the Forestry Commission stopped using compost in most nurseries by about 1955, they were the only long-continued test of the fertiliser regime now commonly used. Compost made *Kennington* soil richer in organic matter and total nutrients than did fertilisers, but these apparent 'improvements' did not produce better seedlings; indeed, seedlings with fertiliser were larger throughout. Neither fertiliser nor compost alone released enough nutrients at *Wareham* for Sitka to grow well during the 15 years, but tests associated with these long-term experiments showed that the decline in growth on fertilised plots could have been stopped by using slow-release fertilisers or by additional top-dressings of N and K. We have no evidence



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**TABLE 5**

*Organic carbon in soils of Rotation experiments after cropping, 1965*

| | % C in air-dry soil (to 15 cm) Kennington | Wareham |
|---|---|---|
| Averaging manuring treatments | | |
| Fallow | 1·23 | 2·69 |
| Lupins | 1·24 | 3·06 |
| Rye | 1·24 | 3·02 |
| Ryegrass | 1·28 | 3·16 |
| Sitka spruce | | |
| Seedlings | 1·18 | 2·84 |
| Transplants | 1·26 | 3·17 |
| Averaging cropping treatments | | |
| Fertiliser | 0·87 | 2·23 |
| Compost | 1·60 | 3·76 |

**TABLE 6**

*Nutrients in soils of Rotation experiments after cropping, 1965*

| | In air-dry soil (to 15 cm) | | | | |
|---|---|---|---|---|---|
| | Total (%) | Total (ppm) | Exchangeable (ppm) | | |
| | N | P | K | Mg | Ca |
| Kennington | | | | | |
| Fertiliser | 0·092 | 814 | 135 | 86 | 1017 |
| Compost | 0·166 | 738 | 258 | 96 | 829 |
| Wareham | | | | | |
| Fertiliser | 0·076 | 108 | 12 | 14 | 492 |
| Compost | 0·220 | 140 | 39 | 64 | 482 |

that any factor other than shortage of nutrients interfered with growth at Wareham. (Benzian and Freeman, with Patterson, Statistics Department)

## Soil phosphate

**Adsorption.** Sorption processes directly control the intensity, capacity and diffusion factors governing the availability of phosphate to plants. Adsorption also determines how much phosphate needs to be given to get maximum yields on deficient soils. Previous work showed that amounts of P desorbed from soil, and taken up by ryegrass in pots, were linearly related to changes in monocalcium phosphate potential ($\frac{1}{2}$pCa + $pH_2PO_4$) of the soils. These desorption processes are well described by a Temkin isotherm. We have now used one or more Langmuir-type isotherms to investigate P adsorption in the range 3–800 $\times 10^{-6}M$ and assess the relative importance of the bonding energy term ($k$) and the total phosphorus adsorption maximum ($b$). For the range of calcareous soils and the concentrations tested, the linear form of the Langmuir isotherms gave correlation coefficients $>0{\cdot}99$. Slight curvature in the relationship suggested the isotherms were in two regions with P concentrations above and below $10^{-4}M$.

Because soil type and equilibration conditions alter the Langmuir constants, a standard equilibration in 0·02$M$ KCl for 24 hours was used. Adsorption maxima ($b$) were measured accurately in all soils, but bonding energies ($k$) were less reproducible, particularly in soils with $<20\%$ clay ($<2\ \mu$m). The Langmuir equations, calculated over the whole concentration range, underestimated adsorption maxima; using concentrations $>10^{-4}M$ increased P adsorption maxima and the reproducibility of the bonding energy.



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Twenty-four soils from eight sites on the Sherborne series (described by R. D. Russell (1963) *Journal of the Science of Food and Agriculture* **14**, 622–628) had a four-fold variation in bonding energies but less than two-fold variation in adsorption maxima. Applying superphosphate for several years to the field soils had no significant effect on Langmuir constants. Both Langmuir constants were highly correlated with surface areas of the soils (measured by glycol adsorption) and with $CaCO_3$ contents. Adsorption maxima also correlated well with organic-matter contents. The coefficients in the multiple regression equations showed that % $CaCO_3$ had the largest (negative) effects on the bonding energy and % organic matter the largest (positive) effects on the P adsorption maxima. Surface area, % $CaCO_3$ and % organic matter together accounted for 65% of the total variance in bonding energy and 80% of variance in P adsorption maxima. (Holford and Mattingly)

**Response curves in tropical soils.** Work continued on soils from Namulonge (Uganda) where anomalously large concentrations of superphosphate are needed to increase yields of cotton and beans. Results last year suggested that the acid triple point solution leaving monocalcium phosphate (MCP) hydrolysing in soil, increases manganese concentration in solution in soil and hence in plants. This year, soil enriched by triple point solution from hydrolysed MCP was compared with the residue of dicalcium phosphate (DCP) left after hydrolysis at the site where the MCP was placed. The two sources of phosphorus similarly increased yields of ryegrass grown in pots. Two Namulonge soils were used; with one, phosphate dressings had no effect on the Mn concentrations in any of the ryegrass harvests; with the other, soil phosphate did not increase % Mn in dry matter of the first four cuts, but did in the fifth, sixth and seventh cuts. Because the soil containing triple point solution and soil containing residues of DCP behaved similarly, the effects of superphosphate on manganese uptake cannot be from manganese dissolved by the acid solution that diffuses from the fertiliser granules. (Le Mare)

## Cations in soils

**Broadbalk.** Some plots of the wheat experiment have received Mg fertilisers annually since 1843. As few analyses have been made, we did not know whether exchangeable-Mg was increasing in plots given Mg or decreasing in untreated plots. In a similar experiment at Woburn, exchangeable-Mg declined from 129 mg/kg soil in 1888 to 15 mg/kg in 1968 when the crops had Mg deficiency symptoms and responded to Mg fertilisers. Top-soil samples taken from Broadbalk in 1865, 1893, 1914, 1944 and 1966, were reanalysed to follow the changes in Mg, Ca, K and Na exchangeable with *N* ammonium acetate.

Most Broadbalk soils contain free limestone and ammonium acetate dissolved much more Ca from all the samples than necessary to saturate the soil CEC. There was only a slight decrease until 1944 when ammonium acetate soluble Ca decreased much faster in soils given 95 kg N/ha as ammonium salts than in those without N or with FYM. These apparent losses of 'exchangeable' Ca were less than Ca losses calculated from decreases in free limestone.

Carbonate analyses made at various times show a linear decline from about 4·7% limestone in 1843 to about 1·5% in plots untreated and 0·5% in plots treated with N-fertilisers. These figures correspond to annual losses of 630 and 880 kg/ha of limestone respectively.

Ammonium acetate dissolved about 10 mg/kg of magnesium from free limestone in the soils. When corrections were made for this (using soil CEC values to calculate excess Ca dissolved from limestone), residual 'exchangeable' Mg values were the same for all



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years in all soils not given Mg-fertilisers; that is, 'exchangeable' Mg had not decreased, as it had at Woburn. There was a slight increase in exchangeable Mg up to 1914, then a slight decline in plots given 11 kg Mg/ha annually and a larger increase up to 1914 in plots given 26 kg Mg/ha or FYM. Since 1914 exchangeable Mg has decreased in soil of the FYM plot, we cannot interpret this as we have insufficient FYM analyses. Apart from this treatment, exchangeable Mg in soils of the differently treated plots has changed little during the past 50 years.

Previous work suggested that minerals in Rothamsted soil do not release Mg easily, even when exchangeable Mg becomes very small, so it should be possible to balance annual additions and losses of Mg for each plot. Mg lost by leaching was determined from annual Ca losses and Mg/(Ca + Mg) ratios ($AR^{Mg}$ values) in solutions in equilibrium with the soils—interpolated from linear Mg exchange isotherms. Annual Ca losses were found from the rate limestone has disappeared since 1865, plus Ca added in the fertilisers. Additions of Mg from dissolved limestone, rain, seed and fertilisers were similar to the estimated losses by leaching and removed in the grain and straw (Table 7) except that on $N_2$ and $N_2PK$ plots the losses were larger than known additions. This deficit could come from soil minerals or the subsoil. These calculations show that it is feasible for exchangeable Mg to remain constant for 50 years in Rothamsted soil. (Bolton)

**TABLE 7**

*Estimated annual additions and losses of magnesium from the topsoil (0–23 cm) of some Broadbalk plots*

| | kg/ha of Mg | | | | | | |
|---|---|---|---|---|---|---|---|
| Plot | 3 | 5 | 10 | 13 | 7 | 14 | 2B |
| Treatment | None | PKNaMg | $N_2$ | $N_2PK$ | $N_2PKNaMg$ | $N_2PMg$ | FYM |
| Added from: | | | | | | | |
| Fertilisers[1] | 0 | 9·7 | 0 | 0·7 | 9·7 | 25·8 | 20·9 |
| Rain[2] and seed | 2·5 | 2·5 | 2·5 | 2·5 | 2·5 | 2·5 | 2·5 |
| Limestone[3] | 0·8 | 1·0 | 1·3 | 1·3 | 1·2 | 1·3 | 1·0 |
| Total | 3·2 | 13·2 | 3·8 | 4·5 | 13·4 | 29·6 | 24·4 |
| Losses from: | | | | | | | |
| Crop uptake[4] | 1·7 | 1·8 | 2·4 | 4·0 | 4·5 | 4·6 | 5·0 |
| Leaching | 3·3 | 11·2 | 4·0 | 5·5 | 9·9 | 24·1 | 25·0 |
| Total | 5·0 | 13·0 | 6·4 | 9·5 | 14·4 | 28·7 | 30·0 |
| $AR^{Mg}$ (1944) | 0·020 | 0·046 | 0·016 | 0·019 | 0·036 | 0·078 | 0·093 |

1. Allowing for fallow years.
2. 762 mm/annum containing 0·3 mg/l of Mg.
3. Limestone contained 39·0% Ca and 0·124% Mg.
4. Johnston, A. E. (*Rothamsted Report for 1968*, Part 2, 61).

**Magnesium exchange isotherms.** Last year we reported discrepancies between exchangeable Mg in soils measured by extrapolating $Q/I$ curves to zero Mg concentrations in solution and Mg soluble in $N$ ammonium acetate. These differences were mostly caused by the presence of soluble salts, but a small additional error was caused by re-adsorption of Mg by the soil in exchange for K desorbed by the $CaCl_2$ solutions when making the isotherm measurements. With the calcareous Broadbalk soils, there was a large discrepancy from Mg in limestone particles dissolved by $N$ ammonium acetate. With these soils, equilibrium Mg/(Ca + Mg) ratios found by interpolation from the linear isotherms were closely correlated with $N$ ammonium acetate-soluble Mg values ($r = 0{\cdot}96$). (Bolton)



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**Residual effects of potassium, magnesium and sodium fertilisers at Woburn.** In a long-term experiment, K and Mg sulphates were applied annually from 1960 to 1967 and NaCl in 1966 and 1967, when ryegrass was grown with N and P fertilisers only, to see how long the fertiliser residues lasted. Top-soils (0–23 cm) and sub-soils (23–46 cm) from each plot were sampled and analysed in 1967 and after the last cut of grass in 1970.

K and Mg, but not Na, residues still increased yields of dry matter in 1970, and all the pre-1967 fertilisers affected the composition of the grass. Residual sodium increased Na in grass dry matter from 0·19% to 0·31% (±0·007), and residual Mg increased Mg concentrations from 0·12% to 0·22% (±0·004). However, yields of dry matter were small (mean 6·68 t/ha per year), probably because K deficiency limited yields on all plots. All three cuts of grass contained less than 0·9% K in dry matter. Mg and Na percentages in grass are important in animal nutrition, and that sodium fertilisers applied in 1966 and 1967 almost doubled % Na in grass grown in 1970 may be important.

The soil analyses showed that the fertilisers left small residues of K and Na but large residues of Mg in both top-soils (0–23 cm) and sub-soils (23–46 cm). During the ten years of the experiment, apparent recoveries were: fertiliser K, 71% in crops and 1% remained in surface soil in 1970; fertiliser Mg, about 20% in crops and 65% remained in soil in 1970; fertiliser Na, 52% was recovered in crops and 2% remained in the soil. (Untreated plots were used to estimate the amounts of nutrients in the crops and soil from sources other than fertilisers.) The chloride balance was discussed in *Journal of the Science of Food and Agriculture* (1971) **22**, 292–294.

Potassium fertilisers were applied to all plots in autumn 1970 and ryegrass again sown. Residues from the Na and Mg fertilisers still affected the composition, but not yields, of two cuts of grass taken during 1971. (Bolton and Penny)

**Ca–Rb exchange isotherms.** $^{86}$Rb is used as a tracer for K in soils and plants. Ca–Rb exchange isotherms were measured on Hanslope series soils from the Reference Plots at Boxworth Experimental Husbandry Farm. The soils had received: (i) no fertiliser (nil); (ii) 50 kg/ha of K (K) and 20 t/ha of FYM annually for 14 years, and contained 0·33, 1·12 and 1·00 me/100 g respectively of exchangeable K. The calculated standard free energies of exchange showed that, over the complete isotherm, from 0% to 100% Rb saturation, soils with larger exchangeable K derived from fertiliser had greater affinity for Rb (nil: −644 and K: −797 cal/mol); because organic matter has a greater affinity for calcium ions, FYM reversed this trend (−542 cal/mol). However, when the soil was nearly saturated with calcium ions, the activity coefficient of adsorbed Rb (the most direct measure of the soil's affinity for Rb), decreased with increasing activity of soil K (nil: 0·58, K: 0·53 and FYM: 0·36). This confirms earlier results that, when using $^{86}$Rb as a tracer for K in soil, specific Rb adsorption sites must be allowed for. Increases in potassium reserves in the soil, by fertilisers or manures, increase the specific adsorption sites for Rb. (Panther and Talibudeen)

### Ion interactions in potato nutrition

Potato tubers are a 'sink' for assimilates and their growth is closely related to senescence of the plants and interactions between potassium and other ions. In an experiment with potatoes grown in buckets under glass, K and Mg fertilisers were tested separately and together; tubers were removed as they formed from half of the plants, and the other half remained untouched. Where tubers were removed axillary buds made abnormal growths, the stem bases were thick and the plants used less water (the water saved was ten times greater than the tubers formed on intact plants contained). Removing tubers prolonged the life of the plants by 50 days and supplying them with K by 27 days; the



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two effects were additive. Both treatments lessened or prevented the increases in % Ca and % Mg that occurred in leaves of other plants. Giving Mg fertiliser had little effect on plant duration or composition of the leaves.

Last year (p. 55) we showed that adding K to the soil increased both % Mg and % K in tuber dry matter. Other 'sinks' may have similar effects; for example, the growing points of the shoots, which are sinks before tubers form. In fact, leaves taken close to active growing points showed that added K increased both % Mg and % K, the ratio meq K/meq Mg varying little. Relationships between K and Mg in such leaves changed as the plants developed. When tubers started to form, supplying K had, at first, no effect on % Mg; as the tubers grew, supplying K increasingly lessened % Mg in the leaves—which is the interaction between K and Mg usually found in studies of leaf composition. K fertiliser again increased both % K and % Mg in tubers. The change in the effect of K fertiliser on % Mg in leaves is gradual, and removing the tubers had only a small effect on rate of change; this suggests that the process is part of the development and senescence of the plants and not specifically associated with tuber formation. (Addiscott)

### Effects of N, K and Na fertilisers on the yield and composition of ryegrass

Work on replacing K by Na for ryegrass (*Rothamsted Report for 1969*, Part 1, 55–56) was continued with soil containing 88 ppm of exchangeable K. Three amounts of N, K, Na were tested in a factorial arrangement replicated three times; the ryegrass grown in pots was cut three times. With 160 mg of N/kg of soil, dry matter was twice as much as with 40 mg/kg. 120 mg of K/kg and 70 mg of Na/kg both increased yields by 11%, but the percentage response to Na alone was larger than when given with K. Table 8 shows that increasing nitrogen four times slightly lessened total soluble carbohydrates in the grass; a large decrease in fructosan was compensated by increases in reducing sugars and sucrose. The carbohydrate fractions were affected much less by sodium and potassium than by nitrogen. Free amino acids in the grass were usually decreased by either Na or K, and more by both. Asparagine, glutamine, serine and valine were most affected, alanine and $\gamma$-aminobutyric acid least. The effects of Na and K fertilisers on carbohydrate and nitrogenous fractions of the ryegrass were less than in 1969, when the experiment was made with a soil containing only half as much exchangeable K. (Nowakowski, Bolton and Lazarus)

**TABLE 8**

*Effects of N, K and Na fertilisers on carbohydrate fractions in ryegrass*

| Fertiliser supplying (as mg/kg of soil) | | Per cent in dry matter | | | |
|---|---|---|---|---|---|
| | | Reducing sugars | Sucrose | Fructosan | Total soluble carbohydrates |
| N | 40 | 1·9 | 3·9 | 18·2 | 24·0 |
| | 80 | 3·7 | 5·1 | 15·7 | 24·6 |
| | 160 | 7·7 | 5·9 | 6·8 | 20·4 |
| K | 0 | 4·6 | 5·0 | 12·4 | 22·0 |
| | 120 | 4·2 | 5·1 | 15·2 | 24·5 |
| Na | 0 | 4·8 | 5·0 | 12·6 | 22·4 |
| | 70 | 4·0 | 4·9 | 14·1 | 23·0 |

### Acid-soluble trace constituents of limestones

Most published analyses of major- and micro-nutrients in limestones are of total concentrations; less is known of the amounts that are soluble in acids and may therefore



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become soluble when limestones weather in acid soils. Eighty-six limestones from fresh exposures at quarries in many parts of Britain, three shell sands, Cretaceous Chalk fragments from Rothamsted and Saxmundham soils, and Jurassic limestone from a Lincolnshire soil were all extracted with cold 5*N* HCl (which did not dissolve clay minerals and oxidised iron minerals). Cu, Cd, Ni and Zn were determined polarographically; Co, Fe, Mn, Mo and P spectrophotometrically, Mg by atomic adsorption and the $NO_3$-N soluble in water by 'Technicon AutoAnalyser'.

Shell sand and Cambrian limestone had on average about 25% of material insoluble in water, the other limestones about 10% or less. Most samples were of Chalk and Carboniferous Limestones (23 samples of each); on average about 3% of their total weight was insoluble in 5*N* HCl. Table 9 gives concentrations of micronutrients and other constituents. The largest dressing of limestone likely to be recommended is about 10 t/ha.

**TABLE 9**

*Minimum, maximum and mean concentrations of trace constituents and of magnesium in limestones*

| | Amounts soluble in cold 5*N* HCl (mg/kg) | | | |
|---|---|---|---|---|
| | Min | Mean | Max | In three shell sands mean |
| Cadmium | 0·03 | 0·30 | 5·1 | 0·12 |
| Cobalt | nil | 0·52 | 4·0 | 0·55 |
| Copper | 0·19 | 1·63 | 18·5 | 7·3 |
| Iron | 36·0 | 1019·0 | 6590·0 | 596·0 |
| Manganese | 22·0 | 335·0 | 1600·0 | 121·0 |
| Molybdenum | nil | 0·04 | 0·4 | 0·03 |
| Nickel | 0·1 | 1·10 | 10·0 | 0·5 |
| Zinc | 1·4 | 11·9 | 196·0 | 38·0 |
| Phosphorus | 3·8 | 184·0 | 2210·0 | 193·0 |
| Nitrate* | nil | 1·07 | 9·2 | 0·4 |
| Magnesium | | (per cent) | | |
| Calcitic limestones | 0·03 | 0·27 | 1·58 | 0·43 |
| Dolomitic limestones | 9·2 | 12·1 | 13·5 | — |

* Soluble in water.

The mean concentrations of elements in Table 9 show that this dressing will supply less than 20 g/ha of cadmium, cobalt, copper, molybdenum and nickel and a little more than 100 g/ha of zinc. The only trace element supplied in quantities that may be important is manganese (over 3 kg/ha); the small quantity of phosphorus supplied (about 2 kg/ha) is much less than one crop removes. The magnesium supplied, averaging 27 kg in 10 t/ha of calcitic limestone and 1210 kg/ha in the same weight of dolomitic limestone, is very much more important in crop nutrition than any of the trace elements investigated. It is sometimes stated that liming materials derived from marine organisms and taken from the sea-shore are richer in trace elements than other limes, and so may benefit crops more. Average results for three 'shell sands' included in the survey are shown separately in Table 9. The mean concentrations of most elements were similar to mean values for the whole group of limestones. The shell sands were notably richer in copper, zinc and magnesium and poorer in manganese and iron, but the differences were too small to alter the above conclusions on the value of limestones as sources of trace elements. (Chater and Williams)



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## Experiments with herbicides

### Simazine and beans

***On Barnfield,*** simazine remaining in the soil from previous years again decreased yields of field beans; again, newly applied simazine had only small effects on FYM-treated plots, but on plots given only inorganic fertilisers yield losses were larger than previously.

| Annual manuring 1876–1971 | Yields of beans (t/ha) in 1971 | | |
|---|---|---|---|
| | Without simazine | With fresh simazine | With simazine residues |
| None | 1·34 | 0·34 | 0·86 |
| PK fertilisers | 1·62 | 0·46 | 1·36 |
| 35 t/ha of FYM | 1·33 | 1·16 | 1·20 |

***At Woburn*** winter wheat followed two years of beans given various amounts of simazine on plots containing different amounts of organic matter. Shallow cultivations (<5 cm) did not disturb residues from simazine applied in 1969 (buried in autumn 1969) or applied in 1970 and leached below the surface (*Rothamsted Report for 1970*, Part 1, 58). Bio-assays with ryegrass, made on soil profiles taken by slotted tubes removed during December 1970, detected simazine in a band 10–15 cm below the surface in soil from the plot with least organic matter and most simazine (1·7 kg/ha); wheat germinated well, but on this plot became pale yellow. Yellowing disappeared after giving N fertiliser in April. Where simazine was not applied in 1969 or 1970, wheat yields *decreased* with increasing organic matter in the soil. We cannot explain this. Where simazine was applied, wheat yielded least on plots with least organic matter; as organic matter in soil increased so did yields, except that the plot with most organic matter yielded less than some others.

On fields of heavier soil at Woburn, recommended amounts of simazine did not control weeds in beans. These soils had from 1·9 to 2·7% organic carbon (compared with 0·7 to 1·2% C in the light soils where simazine diminished yields). Barnfield soils given fertilisers only, where simazine damages beans, have 0·7% C; the FYM plots (where simazine has little effect on bean yields) have 2·4% C. Even on the soils rich in organic matter, weeds have been controlled well by simazine on Barnfield, perhaps because root crops have been regularly hand-hoed for 100 years and there are few weed seeds to germinate. On other Rothamsted fields, simazine has controlled weeds well and has not harmed bean yields on soils with 1·4–1·5% C. Clearly, simazine used as recommended is liable to damage beans on either light or heavy soils that contain little organic matter, though it controls weeds well. Damage has not occurred where beans were grown on soils rich in organic matter but weeds have sometimes not been controlled. Whether these differences reflect differences in weather or the compositions of the soils is unknown. (Johnston and Briggs)

**Herbicides and liquid fertilisers combined.** One experiment with winter wheat and one with spring barley repeated those described last year; the one with permanent grass begun in 1970 was continued with treatments applied cumulatively; S24 ryegrass sown in September 1970 was used for a fourth experiment. All were at Rothamsted and all compared liquid with granular N fertiliser, without and with a herbicide.

***The liquid fertiliser,*** made from urea and ammonium nitrate (26% N), was sprayed over the leaves to supply 38, 75 and 113 kg N/ha and compared with the same amounts of N as 'Nitro-Chalk' top-dressings.



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***The herbicide***, a mixture of dichlorprop and MCPA, was applied at 2·8, 5·6 and 8·4 litres/ha (1·4, 2·8 and 4·2 kg a.e.) either in a combined spray with the liquid fertiliser, or by itself (on 'Nitro-Chalk' plots). The treatments were applied for each cut of grass. The methods used were described last year (*Rothamsted Report for 1970*, Part 1, 59).

***Winter wheat (Cappelle Desprez).*** The fertilisers and herbicides were applied on 21 April; next day none of the leaves of wheat given 'Nitro-Chalk' (without or with herbicide) was scorched. Wheat given liquid N alone was either not or only slightly scorched, but all wheat sprayed with liquid N and herbicide together showed scorch, which increased with increasing amounts of both, so that it was severe with the most liquid N and herbicide combined. By 30 April, the symptoms had diminished, but were still visible on 4 May.

By early June herbicide combined with liquid N had controlled the weeds (mostly chickweed (*Stellaria media*)) slightly better than when applied alone (on 'Nitro-Chalk' plots), and this was confirmed by estimating the weed population in the stubble after harvest.

Yields of grain increased with each increment of both 'Nitro-Chalk' and liquid N, but the effects of herbicide on yield were irregular (Table 10). However, herbicide did

**TABLE 10**

*Comparisons of 'Nitro-Chalk' and a separate herbicide spray with a spray combining N fertiliser and herbicide*

| | 'Nitro-Chalk' | | | Liquid N fertiliser | | |
|---|---|---|---|---|---|---|
| N kg/ha | 38 | 75 | 113 | 38 | 75 | 113 |
| Herbicide litres/ha | | | | | | |
| Winter wheat, t/ha of grain (with 15% moisture) | | | | | | |
| None | 5·80 | 6·45 | 6·63 | 5·51 | 6·24 | 6·34 |
| 2·8 | 5·51 | 6·38 | 7·14 | 5·33 | 6·37 | 6·63 |
| 5·6 | 5·70 | 6·54 | 6·90 | 5·53 | 5·98 | 6·40 |
| 8·4 | 5·88 | 6·72 | 6·65 | 5·37 | 6·23 | 6·53 |
| Standard error | | | ±0·193 | | | |
| Spring barley, t/ha of grain (with 15% moisture) | | | | | | |
| None | 5·24 | 5·63 | 5·62 | 4·86 | 5·79 | 5·92 |
| 2·8 | 4·89 | 5·61 | 5·75 | 5·16 | 5·41 | 5·88 |
| 5·6 | 4·84 | 5·68 | 5·65 | 4·62 | 5·23 | 5·69 |
| 8·4 | 5·07 | 5·65 | 6·03 | 4·49 | 5·36 | 5·53 |
| Standard error | | | ±0·186 | | | |
| Permanent grass, t/ha of dry matter (total of three cuts) | | | | | | |
| None | 7·51 | 10·28 | 11·02 | 6·26 | 8·25 | 10·41 |
| 2·8 | 7·76 | 9·95 | 10·96 | 5·80 | 8·25 | 10·19 |
| 5·6 | 7·29 | 9·73 | 11·27 | 5·48 | 7·74 | 9·83 |
| 8·4 | 7·13 | 9·73 | 10·95 | 5·69 | 7·85 | 9·04 |
| Standard error | | | ±0·330 | | | |
| S24 perennial ryegrass, t/ha of dry matter (total of three cuts) | | | | | | |
| None | 13·16 | 15·22 | 16·49 | 10·67 | 12·64 | 14·16 |
| 2·8 | 13·03 | 14·70 | 15·65 | 10·17 | 13·25 | 14·69 |
| 5·6 | 12·31 | 14·65 | 15·35 | 9·54 | 12·10 | 14·86 |
| 8·4 | 12·01 | 14·28 | 15·95 | 9·14 | 13·12 | 13·32 |
| Standard error | | | ±0·459 | | | |

The treatments were applied for each cut of permanent grass and of perennial ryegrass.



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not affect the difference between the two forms of N, and 'Nitro-Chalk' was superior to liquid N in all comparisons. Largest yields with both 'Nitro-Chalk' and liquid N came from applying the largest amount of either together with the smallest amount of herbicide (half the recommended amount).

***Spring barley (Julia).*** The fertilisers and herbicides were applied on 11 May. Next day none of the barley given 'Nitro-Chalk' (without or with herbicide spray) was scorched, but all sprayed with liquid N was. Without herbicide, scorch was negligible with the smallest amount of liquid N and slight with the two larger amounts. With herbicide and liquid N combined, scorch was worse and was increased by increasing amounts of both. It was increased more by herbicide than by liquid N and was very bad with a combination of the largest amount of herbicide with either the medium or large amount of liquid N. On 14 May the barley still showed scorch but not on 1 June.

The whole site had few weeds, so no information was obtained on the relative effectiveness of herbicide applied by itself or in combination with the liquid N.

The effects of the treatments on yields of barley were much less consistent than on yields of wheat (Table 10). Yields of grain increased with each increment of liquid N, but not with more than 75 kg N/ha as 'Nitro-Chalk' in two of four comparisons. Without herbicide, yields were usually larger with liquid N than with 'Nitro-Chalk', but with herbicide, 'Nitro-Chalk' was superior to liquid N in six of nine comparisons, presumably because scorch from spraying the herbicide and liquid N together checked the crop seriously. Herbicide inconsistently affected yields of barley given 'Nitro-Chalk', but when applied with the liquid N it decreased yield eight times out of nine.

In late July Mr. D. R. Tottman of the Weed Research Organisation examined the ears of both wheat and barley for deformities, but found only a few in both crops sprayed with the largest amounts of liquid N and herbicide combined.

***Permanent grass.*** Treatments were applied on 27 April, 16 June and again on 5 August and the grass cut on 26 May, 22 July and 14 October. Observations one day after the treatments in April and June and four days after the one in August, all showed the same pattern for leaf scorch, none on grass given 'Nitro-Chalk' (either with or without herbicide) and a negligible or slight amount on grass given liquid N without herbicide. With a combined spray of liquid N and herbicide, however, scorch increased with increasing amounts of both. It was never serious after the April treatments, but was very bad in June with the largest amount of liquid N combined with either the medium or larger amount of herbicide. Rain interrupted spraying on 5 August and fell again 3 hours afterwards, so scorch was diminished, but it was still bad where most liquid N and herbicide were applied together.

Without herbicide, the sward in May contained many weeds, but with the least amount of herbicide there were only half as many in plots given 'Nitro-Chalk' and a quarter in plots given liquid N. With the larger amounts of herbicide the grass was almost weed-free, except for some hogweed (*Heracleum sphondylium*).

Yields (Table 10) were smaller with liquid N than with 'Nitro-Chalk', partly because liquid N and herbicide sprayed together caused scorch; when the liquid N was sprayed first and the herbicide 4 hours afterwards (on additional plots), scorch was less and yields larger, but again smaller than with 'Nitro-Chalk'. The larger amounts of herbicide often decreased yield, but rarely affected the difference between yields from the two forms of N.

***S24 perennial ryegrass ley.*** Treatments applied on 29 April, 9 June and 2 August for grass cut on 28 May, 21 July and 21 October, produced a scorch pattern resembling that on the permanent grass (none with 'Nitro-Chalk' and most where most liquid N and



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most herbicide were applied together). This happened after each spraying, even though the next day was dry in April, but wet in June and in August, so the damage done was immediate. The few weeds were well controlled by the two larger amounts of herbicide—but not with less.

'Nitro-Chalk' again produced more grass than liquid N at all three cuttings (Table 10) and its superiority was greater at the second and third cuts than at the first, even though yields from these were much smaller. Herbicide generally decreased yields even though it did not scorch grass given 'Nitro-Chalk', but amounts of herbicide did not alter consistently the difference between the two forms of N. (Freeman and Penny)

### Breakdown of $^{14}C$-labelled compounds in soil

Soils from long-term experiments made by the Weed Research Organisation (W.R.O.) in which several annual dressings of three times the recommended amount of linuron have been given, were incubated with ring-labelled metobromuron. These soils evolved about five times as much labelled $CO_2$ as was evolved from soils not treated with linuron, although metobromuron itself disappeared only slightly faster. This suggested that the soils were enriched with organisms able to decompose halogenated anilines, following exposure to 3,4-dichloroaniline derived from linuron. Labelled *p*-bromoaniline, the parent amine of metobromuron decomposed very quickly in linuron-treated soils, and about 10% of the carbon was evolved in 24 hours. However, the amine quickly became unavailable; even in linuron-treated soils only 20% of the carbon was metabolised, in untreated soils less than 5% during several weeks. Presumably the amine combines with organic matter by radical coupling, as suggested last year. The $C^{14}O_2$ evolved from metobromuron and *p*-bromoaniline in 14 soils was measured. There was good agreement between metobromuron decomposition determined by solvent extraction and calculated values from $C^{14}O_2$ evolved, assuming that all metobromuron degrades to *p*-bromoaniline before ring cleavage.

The W.R.O. soil used was able to degrade *p*-bromoaniline rapidly more than three years after the last dressing of linuron. In the Rothamsted Cultivation–Weedkiller experiment linuron is used for the potatoes, grown every fourth year, but this does not seem to have increased micro-organisms adapted to decomposing metobromuron and *p*-bromoaniline. The differences in the rates $CO_2$ was evolved from labelled metobromuron were not related to the herbicide history of the plots, or to recent spraying with linuron, but varied with previous cropping. (Briggs)

### Methods and apparatus

**Potassium removed from soil by ryegrass in different environments.** Three experiments with S23 ryegrass tested all combinations of five amounts each of $NO_3$-N and K in the glasshouse in summer 1970 and in constant environment (C.E.) cabinets in winter 1970 and summer 1971. Hanslope series soils from the 'Reference Plots' at Boxworth Experimental Husbandry Farm were used. Three cuts were taken in 13 weeks—long enough for all the exchangeable K to be used. Yields and K uptakes were:

| | | Yield of dry matter g/kg soil | K uptake mg/kg soil |
|---|---|---|---|
| Glasshouse (summer 1970) | | 5·55 | 100 |
| C.E. cabinets | summer 1971 | 5·95 | 110 |
| | winter 1970 | 7·95 | 115 |



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Dry-matter yields and K uptakes were largest in the winter 1970 C.E. experiment, because of optimum light, temperature and humidity. In both C.E. experiments, the ryegrass became chlorotic, and sulphur deficiency was suspected. Symptoms were most severe in the summer experiment when records at Luton show the air contains only half as much $SO_2$ as in winter.

***Sulphur deficiency.*** To test this suspicion, half of the summer C.E. experiment was continued for seven weeks more and given ammonium sulphate; the other half had calcium nitrate. Chlorosis disappeared from the ryegrass given ammonium sulphate and results were:

| | Yield of dry matter g/kg soil | K uptake mg/kg soil |
|---|---|---|
| With ammonium sulphate | 2·38 | 100 |
| With calcium nitrate | 0·95 | 35 |

The air used in the C.E. chambers is not scrubbed but is recirculated from the adjoining rooms, and seems deficient in sulphur during summer. The air in the glasshouse changes much more frequently and supplies enough $SO_2$ even during summer. (Mitchell and Talibudeen)

**Controlling soil pH in pot experiments with ryegrass.** Perennial ryegrass is much used in pot experiments because it grows well in different soils and withstands frequent cutting. However, soil pH often changes during cropping as the amount and type of fertilisers used alter relative uptakes of cations and anions. With ammonium nitrate, soil pH may decline one or more pH units during cropping. Growth of ryegrass given ammonium nitrate or calcium nitrate was compared using Rothamsted soil over the pH range 4·4–7·5 (in 0·01*M* $CaCl_2$). Yields and N uptakes of four cuts of grass were the same in all pots, but concentrations of other elements depended on both pH and type of N fertiliser. Soil pH in the middle range, measured after each cut of grass, increased with calcium nitrate and decreased with ammonium nitrate; changes above pH 7·2 and below pH 4·5 were small. A mixture of equal amounts of N as ammonium nitrate and calcium nitrate should maintain soil pH constant. (Bolton and Mitchell)

**Buffer systems for measuring cation-exchange capacity.** To measure its cation exchange capacity (CEC), soil is usually saturated with a cation at one pH or a series of pH values. pH is conveniently controlled by buffer systems and several mixtures recommended by others were investigated; barium was the saturating cation. Triethanolamine/acetate buffers were not satisfactory between pH 5·2 and 7·2. In addition triethanolamine is protonated at the pH values used and competes slightly with the saturating cation. Recommended buffer systems based on barium acetate, barium chloride, *p*-nitrophenol and monochloracetic acid were improved by omitting monochloracetic acid from the basic buffer, but this acid was used where necessary to lessen the pH and to buffer at small pH values. Phenol was added as a non-protonated buffer without side-effects. The buffer finally selected contained 0·1*N* barium acetate, 0·056*N* *p*-nitrophenol, 0·4*N* barium chloride, and 0·2*N* phenol. The unadjusted pH of 5·7 was adjusted to less than pH 3 by monochloracetic acid, or to more than pH 9 with saturated barium hydroxide solution. Buffering was satisfactory through this range. (Addiscott)

**Amino acid analysis**

***Buffer systems.*** Analyses made on the Technicon Amino Acid AutoAnalyzer (Model NC-1) have become more accurate with more experience in running the apparatus.



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Difficulties were experienced in separating $\gamma$-aminobutyric acid and ammonia, and phenylalanine, and ethanolamine; earlier these substances had been separated satisfactorily. New elution buffers and cleaning the ion exchange resin with acid and alkali did not improve results and we concluded that the properties of the resin had changed with use, possibly because some contaminant had been absorbed from the plant extracts used. The standard Technicon buffer system was slightly modified by increasing pH values of the buffers in autograd chambers 5 and 6. Separations are now satisfactory.

***Purification of plant extracts.*** When extracting amino acids for ion exchange chromatography, interfering peptides and proteins are largely eliminated by choosing suitable solvents. However, mucilaginous substances or other interfering materials may also be extracted, which could affect the operation of the column or alter the properties of the resin. We therefore developed methods of purifying the extracts. The ion exchange procedure of Harris *et al. Canadian Journal of Biochemistry and Physiology* (1961), **39**, 439–451) with minor modifications was adopted. The resin used (Dowex 50Wx4) was eluted with 0·2*N* NaOH instead of 2*N* triethylamine. Colour in the extracts was retained at the top of the column. Amino acids were measured in purified and unpurified extracts. No difference in the results was found attributable to the pretreatment. Solutions of standard amino acid mixtures were also subjected to the pretreatment process; recovery of most of the acids was good. Pretreatment did not improve the chromatographic analyses of the plant extracts, but it did improve their appearance and may benefit performance of the column and life of the resin; it may also eliminate time-consuming extraction with chloroform to remove pigments and lipids. (Lazarus and Nowakowski)

**Analysis of radioactive samples.** Since the Beckman liquid scintillation spectrometer was installed in September 1970, more than 20 000 samples have been analysed for five radioisotopes, singly or in two-isotope mixtures. Most analyses were for tritium and $^{14}C$. About 3000 solid samples were analysed on the solid automatic G.M. assembly. With both instruments about half of the total were for other Departments. (Elsmere)

***Effects of leaf extracts and organic solvents on scintillation counting.*** The effects of leaf extracts and of organic solvents on the 'quench' characteristics of scintillation phosphors and the efficiency of $^{14}C$ assay were investigated on the Beckman scintillation spectrometer. Toluene quenched the scintillation process least, hexane more, and hexane + isopropanol mixtures most. Potassium permanganate, used to oxidise colouring matter in leaf extracts, quenched less than sodium hypochorite. Green leaves quenched more than chlorotic leaves. Fluorescence from chlorotic leaves contributed more to count rates than green leaves, after allowing for the difference in their abilities to quench the scintillation process. (Elsmere and Talibudeen with Kavadia, Insecticides Department)

**Analyses of crops and soils.** Nitrogen was estimated in 8000 crop and 500 soil samples. Twenty-four thousand analyses were made on the Technicon AutoAnalyzer for $NH_4$-N, $NO_3$-N, $NO_2$-N and P, K, S, Al and Cl. Eight thousand five hundred analyses for K were made by 'EEL' flame photometer. About 80 fertilisers and organic manures were analysed for all nutrients.

*The Technicon Dual Channel Flame Photometer* (*Rothamsted Report for 1970*, Part 1, 62) was developed further by substituting an EEL nebuliser-burner assembly and using an air–town gas mixture instead of oxygen and propane. In dual-channel working this was satisfactory for K, but not for Ca.

*The SP900 flame photometer* was used for Ca, Mg, Na, K, Rb, Ba and Mn analyses



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until it was superseded by the *SP90 atomic absorption flame photometer*. This instrument was coupled to a Technicon sampler and peristaltic pump for fully automated analyses of cations. (Avery, Cosimini, Messer, Rawson, Smith and Talibudeen)

## Staff and visiting workers

K. W. Petts left and W. Lazarus was appointed. J. K. R. Gasser was seconded to act as a Scientific Advisor to the Agricultural Research Council.

Visiting workers included Mrs. Anne Fenerty (U.S.A.), G. Johansen (Denmark), Mr. I. C. R. Holford (Australia), Dr. P. K. R. Nair (India), Professor L. E. Nelson (U.S.A.), Dr. S. J. Kalembasa (Poland), Professor E. Takahashi (Japan) and Dr. S. A. Waring (Australia).

T. Z. Nowakowski visited Sweden for the 8th Colloquium of the International Potash Institute (on 'Potassium in Biochemistry and Physiology'); he was a guest of the Institute. He also attended a symposium in Warsaw on 'Nitrogen and Fertilisation of Vegetables' as a guest of the Polish Academy of Sciences. O. Talibudeen attended a Symposium on Soil Fertility Evaluation arranged by the International Society of Soil Science in Delhi in March; he was sponsored by the British Council and the Indian Council of Agricultural Research. He was also invited by UNESCO to visit Universities and Research Institutes in India. Talibudeen also visited the Rubber Research Institute of Malaya as a guest of the Institute, and attended a FAO/IAEA symposium in Vienna by invitation of IAEA.



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