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Chemistry Department

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CHEMISTRY DEPARTMENT G. W. COOKE

Much of the Department's programme is concerned with crop nutrition and the use of fertilisers. Recent changes in costs, and supplies, of crops and raw materials emphasise the importance of our work. Considerable increases in prices of foodstuffs, particularly of cereals and protein for animal feeding, make fertilisers more profitable and increase the need to grow as much as we can in Britain to save imports. Our present good yields of arable crops, and the expansion of output from grassland, are totally dependent on fertilisers, and particularly on nitrogen. Any shortage of fertilisers, or high prices that restrict their use will diminish production. The new mine opened in north Yorkshire will supply the potassium fertilisers British farmers need. Most of our nitrogen fertilisers are home produced too. However, the price of rock phosphate (all is imported) has recently increased three times and phosphate fertilisers must become much more expensive. All fertiliser manufacture needs power, nitrogen production also needs hydrogen that comes from refinery gases, natural gas, or by processing other fuels. Power and fuel are becoming scarcer and more expensive. There is little we can do to make manufacturing more efficient, but we are working to find how to use fertilisers more efficiently and we test products that are cheaper or require less processing. In particular we are seeking ways of lessening that fraction of the nitrogen in fertilisers that is leached or which volatilises, as this represents a serious loss to individual farmers and to the nation.

Potatoes. Yields are increased by all three components of NPK fertilisers and correct manuring is very important for a crop which is expensive to grow but which is rewarding to those farmers who obtain large yields of good quality tubers. We have found that applying more than our normal amount of compound fertiliser (1500 kg/ha of 13-13-20) can increase yield by 10 t/ha at Rothamsted and Woburn *provided* the large dressing is thoroughly mixed with the soil. The extra fertiliser not only increased total yield, but even more important, it increased the proportion of saleable tubers and did not impair their cooking quality. We think that farmers who grow potatoes on land like ours at Rothamsted and Wobum, but from which they obtain less yield than we do, should test extra fertiliser worked deeply into the soil on part of each of their fields. Some experiments have suggested that large dressings of nitrogen, particularly as nitrate, can delay tuber formation. Results this year show that a fertiliser which provided nitrate slowly (sulphur-coated urea) allowed tubers to form earlier than when ammonium nitrate was used.

Cereals. We have continued work to improve yields of wheat grown continuously at Saxmundham. In the five years (1966–70) of an earlier experiment average yields were only 4.0 t/ha. A new experiment on the same site over the three years 1971-73 gave an average of 5.5 t/ha with the best treatments yielding over 6 t/ha. This was even a little larger than the average yield $(4.8 \t{t/ha})$ of the same variety (Cappelle-Desprez) grown continuously on Broadbalk in the same three years. We will continue to experiment with continuous wheat at Saxmundham as the crop suits this difficult soil. We tested irrigation in 1972 and 1973 and found that extra water did not increase yields in these two years.

A three-year series of experiments on wheat and barley at Broom's Barn and Rothamsted was done to discover why wheat, in particular, often yields better at Rothamsted.

We have tested nitrogen fertilisers and extra water in experiments on both farms. Although wheat yielded well at Broom's Barn, Rothamsted wheat yielded more. Giving more nitrogen and water to the Broom's Barn wheat diminished, but did not eliminate this diference. Barley yields at Broom's Barn were large in l97l and 1972 but were larger still at Rothamsted; in 1973 with extra water and nitrogen, the Broom's Barn barley yielded as well as that at Rothamsted. Measurements on growth and chemical composition now being examined may show why Rothamsted wheat usually yields more.

Recent work gives some support for the idea that a good supply of nitrogen from the soil is one factor responsible for large cereal yields, and that a shortage of soil nitrogen cannot be completely compensated by using more fertiliser in spring. Our tissue tests, which measure nitrate concentrations in the growing crop, are valuable for showing whether soils are rich or poor in available nitrogen. The Rothamsted wheat has always contained more nitrate than Broom's Barn wheat. This extra nitrogen from the soil plus a larger capacity of our soil to hold water and, on average, a larger rainfall may explain why Rothamsted wheat has always yielded better. The barley grown at Broom's Bam in 1973 contained more nitrate than the Rothamsted crop and, when supplied with irrigation to make up for the drier summer at Broom's Barn, yielded as well as Rothamsted barley. Further indirect support comes from Saxmundham where, in the last three years, we have applied 75 kg N/ha when sowing in autumn and yields have been larger than previously. In relatively dry winters (such as we have had recendy) autumn-applied nitrogen may be retained in a heary subsoil and used by wheat.

We have also continued our efforts to explain the symptoms called 'scorch' which occur in wheat at Woburn during dry periods. In 1972 symptoms were similar to those of copper deficiency but leaves and soil appeared to contain sufficient copper. In 1973 scorch did not appear on this field and a test of copper oxychloride spray did not affect wheat yields. Other work in glasshouse and controlled environment cabinets gave no evidence that copper deficiency was associated with scorch symptoms at Woburn.

Liquid fertilisers offer savings in application costs to some farmers. We have tested a liquid which provided N, P and K against equivalent solid fertiliser for barley. When combine-drilled the liquid (which was rich in urea) damaged germination. It was safe when drilled away from the seed but gave a little less yield than solid fertiliser. Therefore there seems little purpose in designing expensive placement drills to avoid damage from the urea or potassium salts in liquid NPK fertilisers because then the phosphate needed by the young crops will be too far from the seed. Thus the best early growth and largest yield was from combine-drilling a liquid NPK starter containing little N.

Nitrogen in ammonia is cheaper to buy than nitrogen in solid fertilisers. Some of this advantage is lost because expensive equipment is needed to inject the anhydrous gas or aqueous solution below the soil surface, but there are considerable economies when large areas receive large amounts of N. Being the first product made in synthesising nitrogen fertilisers, ammonia needs least power in the factory. However, more power is needed in injecting it into soil than in broadcasting solid nitrogen fertiliser. We have found that large single dressings of aqueous ammonia applied in late winter or early spring promote the growth of grass throughout the summer. Laboratory work on soils from these experiments showed that high local concentrations of ammonia in an injected band delay nitrification so that much of the ammonia acts slowly. In fact aqueous ammonia injected in rows 60 cm apart to supply 250 kg N/ha was a better slow-acting fertiliser for grass than sulphur-coated urea. (fhe results we have obtained so far with this latter material suggest that the sulphur simply acts as a barrier to the urea dissolving, and has no effect on subsequent hydrolysis and nitrification.)

Grassland is still receiving too little nitrogen fertiliser; average dressings to leys are only one.third as much as can be justified; four or five times as much N could be applied to permanent grass as is now used. However, in our experiments grass recovers only 5G- 70% of the nitrogen applied; it is essential to try to improve the efficiency of nitrogen, partly to help farmers get the maximum return from fertiliser, and pardy to minimise the nitrate which leaches into streams and deep aquifers. Aqueous ammonia has considerable promise as a slow-acting fertiliser for grassland when a large dressing is injectcd in widely spaced rows in winter. These single dressings maintain growth of grass through the summer and save the cost of repeated application necessary with solid fertilisers if they are to equal the yield given by ammonia. We have yet to find whether the grass can recover more nitrogen from amnonia than from solid fertiliser.

Labour is saved when herbicides or plant protection chemicals, normally applied as sprays, are combined with liquid fertiliser. Adding herbicide to liquid nitrogen fertiliser was successful with permanent grass. The same practice was reasonably successful with winter wheat. But when we tested mildew fungicide plus herbicide mixed with a nitrogen solution the wheat was severely scorched and yield was diminished.

Phosphate. Over the last 14 seasons we have compared large single dressings of superphosphate against small annual dressings supplying the same total phosphate by the end of the rotation. The large single dressings increased soluble phosphate in soils and maintained yields of barley and swedes, grown in rotation, almost as effectively as equivalent phosphate split into annual dressings. For these crops, applying fertilisers every few years, rather than every year, saves labour and eases spring work. Potatoes, however, need fresh phosphate and benefited from superphosphate given in the seedbed even when the sodium bicarbonate-soluble P in Rothamsted soils exceeds 35 mg P/kg. These results and others from Woburn and Saxmundham will be used to estimate (i) increases in crop yields per unit of soluble phosphate in the soils and (ii) the amounts of bicarbonate-soluble P above which crops no longer benefit from fresh phosphate.

Boron in light soils. Deficiencies of both magnesium and boron have occurred in recent years on the light soils at Woburn. Most of the crops grown on sandy soil there have boron concentrations close to the lower limit of the range regarded as 'normal'. Only sugar beet has shown deficiency symptoms. A balance sheet shows more watersoluble boron has been lost from the soils than the crops removed. Applying much boron in organic manures hardly lessened these losses and we are now examining how this micronutrient is removed from topsoils.

Etrtrophication. Work on surface water receiving plant nutrients from fertilisers, farm efluents, or land drains shows how eutrophication leads to 'blooms' of micro-organisms. Work on a lake at Woburn which receives some of our land drainage showed phosphate concentration to be the factor limiting growth of algae. A moderate bloom developed in Spring 1973 and we found that of the total phosphorus in the water only one-eighth was soluble inorganic phosphate and so available for further growth; two-thirds of the total phosphate present was in the organisms themselves.

Crop composition. Potato haulm, usually destroyed before lifting, could be useful if it was recovered. The haulm contains 2–3 t/ha of fibre which is usually returned to the soil, but destruction wastes from 600 (end of July) to 300 (end of August) kg/ha of extractable protein—as much as in a medium crop of beans or hay. Surplus potatoes can be preserved for stock-feed if dried or otherwise protected from decay. It is more economical to

remove water mechanically than by evaporating it; we are trying to find ways of doing this.

More work on the efects of deficiencies of plaat nutrients on the organic composition of crops has shown large effects of magnesium deficiency. Chlorophyll concentrations in ryegrass were increased by 50% by applying magnesium to deficient plants; the fertiliser did not change concentrations of reducing sugars and sucrose but increased fructosan concentrations. Magnesium deficiency had very large effects on nitrogen metabolism of ryegrass. The deficient grass contained much larger concentrations of most amino acids present in the free state than did grass receiving magnesium.

Experiments on potatoes

Gains from large dressings of fertiliser used on potatoes. Experiments on small plots at Woburn (Rothamsted Report for 1970, Part 1, 44-45) showed that a large amount of fertiliser (500 kg N + 750 kg P₂O₅ and 750 kg K₂O/ha) worked deeply into the seedbed was safe, and gave almost l0 t/ha more total tubers than half as much fertiliser (an amount near to the recommended dressing). By contrast, when each was broadcast and worked in shallowly, the double amount gave no more yield than the single; the single amount of fertiliser plus farmyard manure (FYM) gave a larger yield than the double amount of fertiliser worked in shallowly, but not larger than from the double amount worked in deeply. These surprising results were verified in full scale field experiments at Rothamsted and Wobum.

In the first experiments four amounts $(1255-3137 \text{ kg/ha}, i.e. 10-25 \text{ cut/acre})$ of a standard potato fertiliser (containing 13% N, 13% P₂O₅, 20% K₂O, abbreviated to 13-13-20), were broadcast over the ploughing. The soil was rotavated twice to incorporate the fertiliser thoroughly. Then two varieties (King Edward and Pentland Crown at Rothamsted; Record and Pentland Crown at Woburn) were planted either 30 cm (12 in) or 45 cm (I8 in) apart in 71 cm (28 in) rows. Table I shows that both the total yield and the yield of saleable tubers (larger than 4.4 cm) increased with increasing amounts of fertiliser, though the increase from the final increment (251G-3137 kg/ha) was small. On soils like those at Rothamsted and Woburn 2510 kg/ha (20 cwt/acre) of 13–13–20 broadcast and thoroughly worked into the soil is worthwhile. Pentland Crown gave a larger yield of larger tubers than King Edward or Record did.

Joint experiments with the Farm and the Plant Pathology Department (Rothamsted Report for 1972, Part 1, 149-150) tested extra fertiliser as a factor in plant population

TABLE I

The effects of large amounts of an NPK fertiliser on the vield of two varieties of maincrop potatoes at Rothamsted and at Woburn, 1971-72

studies with 'healthier' King Edward potatoes. These produce a larger yield, but with more small tubers, than commercial seed does. The mean yields for the two years, given below, show that although total yield was smaller in the wider rows (from 20% fewer plants) the saleable vield (over 4.4 cm riddle) was not:

Mean yields of King Edward potatoes grown in 1971 and 1972

The extra fertiliser increased both total yield and the yield of tubers larger than 4'4 cm both years and similarly in normal (71 cm) and in wider (91 cm) rows, though it tendedto increase the yield of saleable tubers more in the normal rows (by 4'8 instead of 3.8 t/ha). This fertiliser was broadcast over the ploughing and then rotavated in once only; this may partly explain the response being smaller than when the fertiliser was worked in more thoroughly in the previous experiments.

New experiments begun in autumn 1971 examined alternative ways of applying large amounts of N, P and K. All or half of the three amounts of P and K being tested (as 0-2G-20) were either broadcast and ploughed down in autumn, or broadcast and rotavated-in in spring. Also, FYM was spread and ploughed-down in autumn to give the same amounts of N (but not of P and K), as the double amount of fertiliser. Table 2 shows that the P and K were less efective when applied in autumn than in spring. Early growth was inferior with autumn dressings, perhaps because the solubility of the phosphate diminished too much during the winter; there is no reason for K applied in autumn io be less effective. Yields were always larger with FYM than without, suggesting that it had some merit other than its content of N, P and K. However, if we assume that the N and K in the FYM were only half as effective as in fertilisers (Rothamsted Report for 1971, Part 2, 84), i.e. that the N in FYM was $=188$ kg N/ha, then yields from the single amount of fertiliser plus FYM were similar to those from the double amount of fertiliser. Again, the potential for extra yield (roughly 9 t/ha) from giving extra nutrients as FYM

TABLE 2

The effect of fertilisers and SYM upon yield (t/ha of total tubers) in four potato experiments made at Rothamsted and Woburn in 1972-73

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Amounts of fertiliser

and fertiliser was close to the 10 t/ha obtained in the first small-plot experiments at Woburn and relates closely to the extra yield from doubling fertiliser in Table 1. (Widdowson and Penny)

Delays in the formation of potato tubers caused by nitrate. Because large dressings of nitrogen can delay potato tuber formation, particularly when the N is applied as nitrate, we compared the slow-acting sulphur-coated urea with ammonium nitrate in an experiment in large pots; mixtures of the two fertilisers were also tested. When small amounts of N were applied, there was no difference in the time tubers formed. With larger amounts of total N, the larger the proportion supplied by sulphur-coated urea the sooner the tubers started to form. Restricting N severely greatly delayed tuber formation:

(Cox and Addiscott)

Experiments on cereals

Improving the yield of continuous winter wheat at Saxmundham, 1971-73. The site used by Slope, Etheridge and Williams from 1966-70 for their crop sequence experiment with Cappelle winter wheat (Rothamsted Report for 1972, Part 2, 160-165) was used to test four seed rates and two row-widths to see whether disappointing yields in 1966-70 had been due to a lack of ear-bearing stems. Their N test was continued (but with smaller amounts) and for continuity their sequence 5 plots (first wheat in 1970) were sown at the same seed rate as before and with the same Smythe drill (20 cm rows). To ensure that P and K were not limiting, 1260 kg of 0-20-20 were broadcast and ploughed in each autumn and 300 kg of 20-10-10 were broadcast at drilling to avoid early growth being limited by N-deficiency. The nitrogen (tested at 50, 100 or 150 kg/ha) was broadcast late in April (16-21) rather than in the second half of March, as it has been before. In 1971 and 1972 100 kg N/ha (plus the residue from the autumn dressing of 60 kg N/ha) was almost enough, and in 1973 too much for maximum yield. Giving 150 kg N/ha in spring increased yields little further in 1971 and 1972 and significantly decreased them in 1973 by inducing severe lodging.

TABLE 3

The effects of seed rate, row width and nitrogen on the yield of Cappelle-Desprez winter wheat at Saxmundham, 1971-73

Table 3 shows that the two largest mean yields were from sowing either 140 or 210 kg/ha of wheat seed $(1.12-1.67 \text{ cwt/acre})$ in rows 15 cm apart (6 in) with 300 kg/ha of 20-10-10 and then giving it a top-dressing of 100 kg N/ha (0.8 cwt/acre). Hence the conventional seed rate (180 kg/ha or 1.4 cwt/acre) appears sufficient on Saxmundham soil, providing that it is sown in narrow rows. With wider rows, or morc seed, yields were smaller. Thus the seed rate and sowing technique used in the preceding experiment were suitable, since the differences in yield from sowing conventional amounts of seed at the three row spacings were small and independent of the amount of N given. It appeared unwise to sow only 70 kg grain/ha in narrow rows (15 cm) for then yield was lost; surprisingly this did not happen with the wider rows (30 cm) for with this spacing yields were as large with 70 as with 140 kg seed/ha. When seed is scarce or expensive it seems best to sow in wide rather than narrow rows. (Widdowson and Johnston)

The growth and yield of winter wheat and spring barley at Rothamsted and Broom's Barn compared

The work begun in 1971 was concluded in 1973. Winter wheat (Cappelle-Desprez) followed spring beans, and spring barley (Julia) followed winter wheat, both at Rothamsted and at Broom's Bam. Six amounts of nitrogen (3G-180 kg N/ha) were applied to both crops and water was given (by overhead sprinklers) during June and early July whenever the soil moisture deficit exceeded 25 mm.

Nitrate concentrations in stems. The wheat was sampled periodically from December until harvest to measure growth (see Welbank and Taylor, Botany Department, p. 94) and its N, P and K contents. The nitrate concentrations in stem extracts were measurcd until the crop became too mature for further determinations (in mid-July). $NO₃-N$ concentrations increased from December to February at both farms (to a maximum of 450 ppm) and then decreased to near 50 ppm in mid-April, before the wheat was topdressed with N. By 5 May $NO₃$ -N had increased to a mean of 400 ppm at Rothamsted (range 70 ppm with least fertiliser N to 650 ppm with most N) and 330 ppm at Broom's Barn (range 30 ppm with least N to 550 ppm with most N). By early July mean values had decreased to 175 ppm at Rothamsted and 80 ppm at Broom's Bam. Hence the Rothamsted soil always provided more N for the wheat than the Broom's Barn soil did.

The barley was also sampled periodically, though is N was applied in the seedbed. Nitrate concentrations in the stems were measured from 14 May to 28 June. In mid-May Rothamsted barley stems contained a mean of only 230 ppm NO3-N (range 5 ppm with least to 420 ppm with most fertiliser N) whereas at Broom's Barn the barley stems contained 350 ppm of $NO₃-N$ (range 35 ppm with least, to 600 ppm with most fertiliser N). Thereafter the Broom's Barn barley always contained more nitrate, so that in late June mean values were 46 ppm there and 17 ppm at Rothamsted. Evidently the Broom's Barn soil was the richer in N of the two used for barley. (Williams)

A calculated moisture deficit of 17 mm at Rothamsted on 21 May was met by a severe thunderstorm later that day; it did not rain at Broom's Bam. Subsequently dry weather persisted at both Stations. Watering began at Broom's Barn on 8 June and at Rothamsted on 14 June. On 20 June severe storms at Rothamsted lodged both wheat and barley, but again little fell at Broom's Barn. Later in June more rain fell at Rothamsted and so no more water was giyen, but at Broom's Barn watering continued until 5 July, when rain fell there also. At Rothamsted watering consistently decreased wheat grain yields, while at first increasing (with little N) and then decreasing (with much N) straw yields. At Broom's Barn watering increased wheat grain yield little, though it always increased straw yields. At Rothamsted barley grain yields were at first increased (up to 60 kg N/ha)

and then decreased by watering, though straw yields were generally increased. At Broom's Bam watering consistently increased yields of grain and proportionately morc, of straw.

As in previous years, the largest yield of wheat grain at Rothamsted (7.47 t/ha) was larger than the best at Broom's Barn (6.03 t/ha) and was obtained with less N (30 kg/ha) and without irrigation water, whereas that at Broom's Barn needed more N (90 kg N/ha) and water too.

Though in 1971 and 1972 barley yields at Rothamsted and Broom's Barn were more alike than wheat yields were, Rothamsted's were the larger. In 1973, however, maxinum grain yields were similar at Rothamsted and at Broom's Barn, but the need for N was greater at Rothamsted (supporting our nitrate tests). Unusually, Broom's Barn produced the larger yield of straw, again suggesting that this was the richer soil (Table 4).

TABLE 4

The largest yields of grain and of straw (t/ha at 85% dry matter) and the amount of N required (kg/ha), with and without water, to give these yields at Rothamsted and Broom's Barn in 1973

The experiments showed that although wheat yielded well at Broon's Barn, identicallytreated wheat at Rothamsted yielded even more. Giving more N and water to the Broom's Barn wheat diminished, but did not eliminate this difference. Tissue tests showed that the Rothamsted wheat always contained more nitrate and this richness in soil N plus a larger soil water holding capacity and summer rainfall, may explain the larger yields. Again, the barley yields obtained each year at Broom's Barn were large, though they were larger still at Rothamsted in l97l and 1972. ln 1973 however the yield of grain from watered barley at Broom's Bam was similar to that from unwatered barley at Rothamsted. Hence water and nitrogen eliminated the difference between the Stations only in 1973. We conclude therefore from tbese results (Table 5) that the diflerence between grain yields at the two Stations is real, and know from our measurements that differences between the crops developed late, as the grain began to fill (see Welbank and Taylor, Botany Department, p. 94). Chemical analyses and other tests may help to explain why this happened. (Widdowson, with Welbank, Botany Department)

Growth of winter wheat on Broadbalk related to nitrate in soil and crop. Cappelle-Desprez winter wheat is now grown continuously on Section I of the Broadbalk Experiment. Crops on plots receiving FYM and two amounts of N fertiliser were sampled from emergence until harvest. Nitrate concentrations in leaves and stems were measured 50

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TABLE 5

Overall mean yields of grain and straw (t/ha at 85% dry matter) at Rothamsted and Broom's Barn each year, 1971-73

and records made of growth of the parts of the plants. Nitrate in the soil was also measured. We hoped to relate changes in nitrate concentrations to growth and yield and to explain why plots treated with FYM have recently yielded more than fertiliser-treated plots.

Spikelet numbers were counted from mid-April when the FYM-treated crops had 50% more than wheat on the other plots. By the beginning of May all treatments had a similar number of spikelets. Elongation of the inflorescence was most rapid with wheat having FYM or N fertiliser, being 50% greater at the end of May than in wheat receiving no N. The FYM-treated crop headed a few days before the N-treated crops; wheat receiving no N headed last. Although the FYM-treated crops developed more quickly and had more spikelets early in spring than plots receiving N fertiliser, there was no difference at later growth stages. Nevertheless the FYM-treated plots yielded more grain, and much more straw than plots treated with N fertiliser.

Attempts to relate differences in amount of N supplied and its source (fertiliser or FYM) to nitrate in the plants and to apical meristem development, and these to yield, were not successful. Larger yields from FYM than from fertilisers in both seasons on Broadbalk must be due to factors other than nitrogen supply. Greater yields from the larger N dressings and from FYM in 1972 are likely to be related to the lodging that occurred in 1973. (Williams and Rangeley)

Sulphur and micronutrients in Broadbalk wheat. The continuous wheat crops grown in 1972 on Section I were analysed for sulphur, copper and zinc. Sulphur in the grain dry matter was similar for all plots (0.13 to 0.16% S); there was 0.17 to 0.26% S in the straw; we believe these concentrations are sufficient for maximum yield. Removal of sulphur in the grain and straw ranged from 6.3 kg/ha for the unfertilised plot to 35.4 kg/ha for the FYM-plot given extra nitrogen. The grain contained 4 mg/kg copper and 27 mg/kg of zinc on average, with no consistent differences from the fertilisers or FYM.

Sulphur deficiency occurred in wheat in glasshouse and constant environment cabinet experiments. Sulphur fertilisers increased yields when the grain contained 0.07-0.12% S and the straw 0.02-0.05% S. Crops that did not respond to sulphate had 0.18% S in the grain and 0.19% S in the straw. (Bolton)

Placement of liquid fertilisers for barley. The experiments begun in 1972 (Rothamsted Report for 1972, Part 1, 45) were repeated; three were on arable farms and one on a dairy farm. All were sown in mid-March in good seedbeds. The liquid (rich in urea and containing 14% N, 6% P₂O₅, 8% K₂O) again checked the barley when combine-drilled,

especially with the double amount (126 kg N/ha) which killed some plants; yields were significantly decreased by it in three experiments. Placed mid-way between rows of barley (15 cm apart) this fertiliser was completely safe, though it gave slightly poorer early growth than when it was sprayed, or when granulated 20-10-10 fertiliser was broadcast. Early growth was most vigorous on plots given a combine-drilled 'starter dose' of a liquid with analysis 4-10-10 which supplied all of the P and K, but only one-fifth of the N. The same fertiliser placed between the rows again gave poor early growth.

We conclude that on soils deficient in N or P or both, a little of the N and all of the P should be combine-drilled with the barley seed (contact placement); this should encourage establishment and speed early growth without risk to germination. There seems to be little purpose in developing expensive placement drills simply to avoid damage from NPK fertilisers rich in urea (or potassium salts), because then the phosphate will be too far away from the young barley roots.

In 1973 grain yields were little larger with 126 than with 63 kg N/ha (because of lodging). Consequently there were only small differences between the yields from the different methods of manuring. The combine-drilled starter dose of 4-10-10 liquid fertiliser gave the largest yield with 63 kg N/ha; it had no advantage with 126 kg N/ha, because then the lodging and not the nutrients was limiting yield. Even so, the early damage to establishment and loss of plant from combine-drilling 126 kg N/ha as liquid fertiliser with 14-6-8 analysis was sufficient to decrease yields. (Widdowson, Penny and Flint)

Sulphur-coated urea

Sulphur-coated urea has been developed as a slow-release fertiliser with the hope that it may minimise losses of N by leaching or volatilisation. A British-made product was examined in laboratory and glasshouse experiments and is now being tested in field experiments on grass, barley and potatoes.

In laboratory experiments several nitrogen fertilisers were incubated with moist Barnfield soil. Ammonium N (added as ammonium sulphate) was completely nitrified after 28 days. Urea and a laboratory mixture of urea and sulphur behaved similarly; both were hydrolysed completely after 14 days and nitrified after 28 days. The percentages of N released from sulphur-coated urea after 1, 8, 14, 28 and 42 days were respectively 5, 27, 42, 50 and 61%. After 14 days concentrations of NH_4 ⁺ were small, indicating that nitrification proceeded as fast as the urea was released from the granules. The results so far obtained suggest that the sulphur acts as a physical barrier to the urea dissolving and has no effect on subsequent hydrolysis and nitrification.

In another 'incubation' experiment made in the glasshouse, analysing the soils during the first 21 weeks showed N had been lost to the atmosphere where urea had been added as sulphur-coated granules. As waterlogging in the jars was avoided, we presume this loss was of ammonia although the sulphur-coated urea was mixed with the soil in some treatments. (Cox)

Use of ammonia as fertiliser

Rates of nitrification. In soil containing ammonia injected in February (under permanent grass) nitrification became slower when local concentrations in the injected band were increased. When 250 kg N/ha was injected in rows 60, 40 or 20 cm apart (equivalent to 15, 10 or 5 g N/m), respectively 230, 120 and 90 kg N/ha remained as ammonium after 70 days. Nitrifying organisms did not occupy the ammonia band but multiplied around it. A rough measure of the increased numbers generated in summer by the fertiliser dressing was 30-40 millions per metre.

Nitrite N accumulated in the centre of the bands where pH was highest and Nitrobacter appeared not to be established. Nitrate was not formed uniformly around the ammonia band, but in a heart-shaped area. This effect was not found when only 5 g/m of NH₃-N was injected or with the largest rates when the pH in the injected band fell below 7, when the nitrite N also became negligible. Maximum concentrations of nitrite N and nitrate N were found in the field in July; they were, respectively 1 kg/ha and 55 kg/ha from 15 g N/m injected in February.

Cumulative dry matter yields of grass were similar from injected aqueous solutions of ammonia and ammonium sulphate. The third cut represented 27% of the total yield from plots supplied with 15 g $\overline{NH_3-N/m}$ whereas it contributed only 16% of the total when the amount applied was 5 g/m.

Harvests of the grass, and the nitrification studies, show that a single dressing of aqueous ammonia injected late in winter to give high local concentrations in the soil will behave as a slow-acting fertiliser and increase grass yields through the whole growing season. (Ashworth and Flint)

Comparisons of aqueous ammonia and solid fertilisers. In an experiment on permanent grass ammonium sulphate applied in a single broadcast dressing (250 kg N/ha) in spring and also in three equal split dressings (one for each cut) was compared with commercial sulphur-coated urea and with aqueous ammonia injected at 60 cm spacing to supply 15 g N/m. Largest yield was from the split ammonium sulphate and least was from the urea-sulphur granules. The single dressings of ammonium sulphate and aqueous ammonia gave similar intermediate yields. The sulphur-coated urea appeared not to function as a genuinely slow-acting fertiliser; yield at the third cut (in September) was a little greater from the single dressing of ammonium sulphate and appreciably greater from injected ammonia. Ammonia, injected at high local concentrations, seems a better slow-acting fertiliser than sulphur-coated urea. Residual effects will be measured next year to see if the urea-sulphur granules have a slow-acting value for grass that has not been revealed in this year's work. (Ashworth and Flint)

Adsorption of ammonia by dry soil. We have done more to try to discover how ammonia gas is sorbed by dry soils. After diffusion pumping at 22°C to constant weight, soils containing illitic and chloritic minerals sorbed similar amounts of NH₃ (approximately linearly related to the mass of water removed by pumping) and gave isotherms similar to those obtained previously with Rothamsted soil containing mainly inter-stratified montmorillonite (Rothamsted Report for 1971, Part 1, 57). Experiments with soils saturated with several mono- and di-valent cations suggest that exchangeable sodium and potassium do not react with ammonia gas, but that calcium, magnesium and lithium react to form ammines, or through hydrolysis form ammonium ions plus the metal hydroxide. By heating to 180°C more water of hydration was removed than by pumping at room temperature. Isotherms measured on these pre-heated soils suggested that ammination occurs on magnesium, but may not on other cations.

Experiments at very low relative pressure (p/p_0) showed that heats of adsorption were larger on Ca and Mg soils than with Na and K soils (intermediate with Li); at $p/p_0 > 0.01$ they were similar on all soils. This is consistent with the formation of up to three hydrogen bonds to the soil surface, from each molecule of NH₃ sorbed at the higher pressure.

The possibility that acidic hydroxyl groups in disordered alumino-silicates (allophanes) sorb ammonia was investigated using a Japanese soil containing roughly 40% allophane. This soil sorbed over three times as much ammonia as the other soils tested, but since these English soils probably have less than 2% of allophane, acidic hydroxyl groups on such materials can account for only a small proportion of the total ammonia sorbed.

S-shaped isotherms were obtained when homo-ionic montmorillonites were treated with $NH₃$ gas; their actual shape depended on the exchangeable cation present, and they were difficult to interpret. Sodium and potassium montmorillonites showed this effect after preliminary pumping at 22° C, Ca-montmorillonite after treatment at 95° C but Li- and Mg-montmorillonites needed pumping at 150° and 250° C. These results are consistent with published information on the contraction of montmorillonite lattices dehydrated by heating; above a critical pressure NH₃ can penetrate to sites that were previously inaccessible. Lithium, calcium and magnesium montmorillonites pumped at 22°C afterwards sorbed the most ammonia and gave one isotherm which was not S-shaped. This is consistent with ammine formation by these ions. (Ashworth)

Mixtures of liquid fertiliser with herbicide and mildew fungicide

Herbicide and liquid fertiliser combined. The experiment with permanent grass, begun on Ver Meadow in 1972, was continued with treatments applied cumulatively. The liquid fertiliser (26% N) made from urea and ammonium nitrate, was sprayed to supply 38, 75 and 113 kg N/ha per cut and compared with 'Nitro-Chalk' (21% N) broadcast to supply the same amounts of N. The herbicide, a mixture of dichlorprop and MCPA, was sprayed at 2.8, 5.6 (recommended dose) and 8.4 litres/ha per cut $(1.4, 2.8 \text{ and } 4.2 \text{ kg})$ acid-equivalent/ha per cut) either alone (on grass given 'Nitro-Chalk') or mixed with liquid N fertiliser. The nethods used to spray the liquid N and herbicide (and mildew fungicide) mixtures were described in the Rothamsted Report for 1970, Part 1, 59.

Treatments were applied on 10 April and 2 July and the grass cut on 6 June and 3 September. On 10 April it was sunny but cool (maximum air temperature, 10.4°C); it rained that night and drizzled during most of next day. Consequently none of the treatments scorched the grass, the first time this has happened in our experiments. By contrast, 2 July was less sunny, but much warmer (maximum air temperature 22.0° C); it was then warm, dry and sunny until 5 July when the plots were visually scored for scorch. Grass giyen 'Nitro-Chalk', without or with herbicide, was practically unscorched. Scorch was slight with liquid N alone, but increased as increasing amounts of liquid N and herbicide were sprayed together; thus it was very bad with 75 kg N/ha plus 8.4 litres/ha of herbicide and with 113 kg N/ha plus either 5.6 (recommended dose) or 8.4 litres/ha of herbicide.

The grass responded to the first increment of N (75-38 kg/ha), whether as 'Nitro-Chalk' or liquid N, but the response to the second increment (113–75 kg/ha) was irregular. 'Nitro-Chalk' gave larger yields in 11 of 12 comparisons (Table 6). More important, the repeated spraying of herbicide killed almost all the weeds. At the second cut, herbage from each plot given 75 kg N/ha was separated into grass and weeds; weeds accounted

TABLE 6

Comparisons of 'Nitro-Chalk' and a separate herbicide spray with a spray combining N fertiliser and herbicide used on permanent grass

	Herbicide litres/ha per cut	'Nitro-Chalk' (N kg/ha per cut)			Liquid N fertiliser (N kg/ha per cut)		
		38	75	113	38	75	113
		Yields of grass, t/ha of dry matter (total of two cuts)					
	None $2 - 8$ 5.6 8.4	9.93 9.85 9.94 8.88	$11 - 41$ $11 - 27$ $11 - 13$ $10 \cdot 00$	10.67 $11 - 60$ 10.85 $11 - 11$	8.43 8.11 8.58 9.26	$10 \cdot 14$ 10.61 10.27 9.98	$10 - 47$ 10.48 10.51 10.74
	Standard error $cv \frac{9}{6}$	\pm 0.503 8.5					

for 22% of the dry yield from plots given 'Nitro-Chalk' alone and 25% from plots given liquid N alone, but less than 1% from plots sprayed with herbicide.

Our work with permanent grass (1970–73) showed that liquid N fertiliser sprayed over the leaves scorched the grass little, but that adding herbicide to it increased the intensity of scorch; it was most severe with most N (113 kg N/ha) and most herbicide (1.5 times the recommended amount) in hot sunny weather. This scorch did not consistently affect yields, however, for although 'Nitro-Chalk' was superior to liquid N in 45 of 48 comparisons, spraying herbicide with the liquid N sometimes increased and sometimes decreased the difference between the two fertilisers. Weed control differed little between herbicide sprayed alone and in combination with the liquid N, but spraying for each cut gave almost weed-free herbage. We conclude that if liquid N fertiliser is used on permanent grass this type of herbicide may be added to it, provided that no more herbicide is used than recommended.

Herbicide and mildew fungicide combined with liquid fertiliser. One experiment with Joss Cambier winter wheat in 1972 and another with Cappelle-Desprez in 1973 tested all combinations of 'Nitro-Chalk' v. liquid N (urea/ammonium nitrate), 56 v. 112 kg N/ha, 0 v. 5.6 litres/ha of herbicide (dichlorprop plus MCPA) and 0 v. 0'7 litres/ha of mildew fungicide ('Calixin' (75% w/v of active ingredient tridemorph)). In both years treatments were applied in warm weather during early May at growth stage 4–5. On plots top-dressed with 'Nitro-Chalk', the herbicide and the mildew fungicide were sprayed either alone or together, but were added to the liquid N fertiliser where this was being tested.

In both years, wheat leaves sprayed with liquid N plus mildew fungicide showed symptoms of scorch within 2 hours, whether or not herbicide was also added. One week later wheat leaves sprayed with liquid N or with liquid N plus herbicide were slightly scorched, whereas those sprayed with liquid N plus mildew fungicide were badly scorched, and with liquid N plus herbicide and mildew fungicide severely scorched, especially with the larger amount of N. Scorch symptoms became less severe with time, but persisted for about three weeks. None of the wheat given 'Nitro-Chalk' was scorched by the sprays. Although the experimental sites were relatively free from weeds, control was a little better when the herbicide was sprayed with the liquid N than when sprayed alone.

In 1972 J. Jenkyn (Plant Pathology Department) measured mildew and yellow rust infection on $11-12$ July (growth stage 10.5.3 on the Feekes scale). The mean percentage of the area of the third leaf affected by mildew was more than doubled (from 6'8 to 14.2) by doubling the amount of N; it was less with herbicide than without $(9.5 \text{ and } 11.6)$, less with liquid N (9.1) than with 'Nitro-Chalk' (11.9), but only slightly less with than without mildew fungicide (10.2 and 10.9), perhaps because it was sprayed too early. Yellow rust infection (average of 6.3% of flag leaf area affected) also was doubled by doubling the amount of N, was decreased slightly by herbicide and yery slightly by mildew fungicide, but differed little with form of N.

Table 7 shows that, without mildew fungicide, yields in 1972 were similar with 'Nitro-Chalk' and with liquid N. With mildew fungicide, however, 'Nitro-Chalk' gave 0.32 t/ha (2.6 cut/acre) more grain, and with mildew fungicide and herbicide 0.39 t/ha $(3.1 \text{ cut/}$ acre) more grain than liquid N did, presumably because of leaf scorch. The 1973 experiment was spoiled by lodging. The larger crop grown with 'Nitro-Chalk' than with liquid N lodged more and yielded less grain, but the loss of straw from spraying liquid N and mildew fungicide together was similar to that in 1972.

The best time for applying N and herbicide to winter wheat is usually earlier than the best time for spraying mildew fungicide. Although the optimum times for applying N top-dressing, herbicide and mildew fungicide for spring barley may more closely coincide,

yield reduction from severe scorch may occur if all three are sprayed together, especially if much N is used. (Penny and Freeman)

TABLE 7 Comparison of 'Nitro-Chalk' with liquid N for winter wheat in the absence and presence of herbicide and mildew fungicide

Yields of grain and straw (t/ha) with 'Nitro-Chalk' minus yields with liquid N

Residual and cumulative value of superphosphate in a three-course rotation

The experiments on Sawyers I and Great Field IV at Rothamsted (Rothamsted Report for 1969, Part 1, 53) were re-designed in 1966 to compare the value of single dressings of superphosphate supplying 165, 330 and 495 kg P/ha (given at the beginning of a sixyear period) with cumulative annual dressings of superphosphate supplying one-sixth as much P each year in spring. Triennial dressings supplying 82.5 and 165 kg P/ha were compared with one-third as much P given as superphosphate each year in spring. Table 8

TABLE 8

Effects of superphosphate over 3 or 6 years in a rotation of potatoes, barley and swedes at Rothamsted

gives yields of potatoes, barley and swedes between 1970–72 and mean yields for two rotations of each crop between 1967-72.

Potatoes. Between 1967–69, potato yields were slightly smaller $(-1.4 \pm 0.75 \text{ t/ha})$ after single dressings of superphosphate than after annual dressings rotavated into the seedbed before planting. Between 1970-72, potato yields were always less from residues of superphosphate than from cumulative annual dressings (Table 8). During the two rotations (1967-72), single dressings of superphosphate gave yields that were less than those from cumulative dressings applied each year:

Swedes. Yields of swedes between 1969-72 were much smaller than earlier (1960-65) largely because summer rainfall was less than average. The crop failed on both fields in 1970 due to drought. For swedes, unlike potatoes, a single dressing of superphosphate (330–495 kg P/ha) maintained yields over two rotations (1967–72) equivalent to those from cumulative annual dressings of superphosphate when the two larger rates were applied. The small dressing was significantly better when split and applied annually:

Barley. Several of the crops on Great Field IV were damaged by birds; results below and in Table 8 are from Sawyers Field. Maris Badger was grown between 1967-69 and residues of superphosphate applied in 1959 and 1966 produced as much, or more, barley as the smaller cumulative dressings. However, results with Julia barley grown between 1970–72 were different. Yields increased with the amounts applied annually and 82.5 kg P/ha each year gave 0.49 \pm 0.119 t/ha more grain than 13.7 kg P/ha (0.25 cwt P₂O₅/acre) (Table 8).

Differences between yields from single dressings and yields from cumulative annual dressings varied with the total amounts of P applied. Between 1967-72, mean grain yields were significantly smaller, and straw yields slightly smaller, from residues of 165 kg P/ha applied in 1966 than from six annual dressings of 27.5 kg P/ha. Both grain and straw yields were slightly larger from residues of 330 kg P/ha applied in 1966 than from one-sixth as much broadcast each year. Mean grain yields were significantly less, and straw yields about the same, from residues of 495 kg P/ha applied in 1966 than from six annual dressings of 82.5 kg P/ha:

Mean yields of barley, grain and straw (at 85% dry matter),

The smaller mean grain yields between 1967-72 from residues of the largest amount of superphosphate applied in 1966 arise almost entirely from losses by lodging in 1967 and 1968. In both years barley grew very rapidly in the weeks after sowing. The amounts of N applied (75 kg N/ha in 1967, after a fallow in 1966 and 100 kg N/ha in 1968) were apparently too large for barley grown on soils enriched with much phosphate. (Grain yields in 1967 and 1968 were 0.61 and 1.04 t/ha respectively smaller on plots given 495 kg P/ha in 1966 than on plots given 330 kg P/ha.) On this evidence it seems unwise to use large dressings of superphosphate for barley without diminishing N dressings.

Changes in 0.5M NaHCO₃-soluble P. Bicarbonate-soluble P in soils from these experiments was only slightly less after single dressings of superphosphate than after equivalent amounts of P applied in cumulative annual dressings:

Soil research

Phosphate-adsorbing surfaces in limestones and calcareous soils. We showed (Rothamsted Report for 1972, Part 1, 50) that a two-surface Langmuir equation adequately describes P adsorption on a wide range of soils. This equation was used to study P adsorption by 24 soils containing from 0.8 to 24.2% CaCO₃ taken from field experiments on the Sherborne soil series in south-west England, and described by R. D. Russell (Journal of the Science of Food and Agriculture (1963), 14, 622). The high-energy P adsorption capacities (x_m') ranged from 140-346 mg P/kg soil and were mainly associated with dithionite-soluble Fe ($r^2 = 0.81$). Values of x_m ' were negatively-correlated with pH and decreased by 85 mg P/kg soil between pH 7.5-8.0. These results suggest that the highenergy adsorption sites in these calcareous soils were mainly on surfaces of amorphous and crystalline hydrous oxides. The mean areas of the hydrous oxide surfaces, assuming one PO₄ group occupies 66 Å², range from 34 to 53 m²/g FeO.OH.

The low-energy adsorption capacities (x_m) were larger and ranged from 400–633 mg P/kg soil. They were correlated, though not closely, with total organic matter contents $(r^2 = 0.53)$ and total surface areas of CaCO₃ in the soils $(r^2 = 0.46)$ but not with % CaCO₃, % dithionite-soluble Fe or pH. Total surface areas of CaCO₃ in these soils, measured by exchange with ⁴⁵Ca before and after decalcifying, ranged from 4.0-7.2 m²/g soil and low-energy adsorption capacities (x_m) agree closely with the value (100 μ g P/m²) 58

(Mattingly)

we obtained for chemisorption of phosphate on samples of Jurassic limestones obtained from quarries, Phosphate ions were, however, bonded much less strongly by the particles of calcium carbonate found in soils than by limestones.

The low-energy adsorption of phosphate on carbonate surfaces in soils can most reasonably be explained if some sites on the soil carbonate surfaces are occupied by organic anions (and probably also by silicate ions) which reduce the bonding energy of P adsorbed on the same sites. The proportion of high-enerry sites always decreased, in soils with similar total adsorption capacities $(x_m' + x_m'')$, as the % organic matter in them increased, which is consistent with this hypothesis. (Holford and Mattingly)

Potassium-calcium exchange in Hanslope soil. Potassium-calcium exchange isotherms were obtained on the $\langle 20 \mu M$ fraction of Hanslope series soil from the 'Reference Plots' experiment at Boxworth Experimental Husbandry Farm. The clay fraction is mainly montmorillonite with little kaolin or mica. Selective adsorption was not very pronounced in any of the soils. Potassium was preferentially adsorbed only by soil which had received no K fertiliser for 14 years. On plots treated annually with K the exchange complex contained more potassium. Percentage saturation with K was 5'2 in soil treated with K fertiliser, 4.2 in soil receiving FYM; soil receiving no K at all had only 1.4% K-saturation. In the K-treated soils, calcium was preferentially adsorbed. Preference for calcium increased with increasing temperature and soil organic matter. Except for the efrect of organic matter, these properties are unusual and suggest that much ofthe cation exchange capacity of the soil is contributed by a calcium-selective adsorbent. (Panther and Talibudeen)

Soil salinity and plant growth. Salinity damages crops in many arid regions and where sea-water floods occur. Tolerance to salt is defined by the electrical conductivity of a saturation extract of soil, but the ions which contribute are not defined. When much sodium is present, soil structure is damaged so that crops cannot grow. Because the efrects of sodium concentrations in soil solutions on plant growth are not well undentood, we made glasshouse experiments to study effects of increasing sodium concentrations on germination, growth, yield and chemical composition of broad beans, sugar beet and barley. (Broad beans are least and barley most tolerant of salinity.) Sodium chloride was added to Rothamsted (Geescroft) soil to give conductivities of 2-8 mmhos/cm (0-1600 mg/kg Na in the saturation extract). The soil was diluted with 20% of quartz grit, contained 2% of added calcium carbonate and was kept moist.

Germination of all three crops was delayed and seedlings were damaged to varying amounts by added salt; barley was only slightly affected but sugar beet was checked considerably. Early growth of broad beans was diminished and flowering was delayed by the higher salt concentrations. Sugar beet plants grew better throughout witb small concentrations of sodium; they were checked by larger concentrations in the early stages but later recovered and benefited appreciably from all the additions of salt. Sugar concentrations were 50% greater in plants receiving enough salt to give a conductivity of 6 mmhos/cm than in untreated plants. Smaller additions of salt increased growth of barley and, as with sugar beet, maximum yield (of grain and straw) was obtained at 6 mmhos/cm. Adding sodium chloride increased sodium and chloride concentrations in all the crops, increased potassium coocentratioos in beans, but had little effect on potassium in beet. In barley early uptake of K was diminished by salt, later it was increased. The largest increase of salt increased $\%$ P in the crop, but diminished $\%$ Ca and $\%$ Mg. (Hamid and Talibudeen)

Weathering and reactivity of calcareous soils

Surface properties of carbonates. There was an inverse and hyperbolic relationship between specific surface area and percentage of carbonate in soil. Exchange experiments with 45Ca showed nagnesium was specifically absorbed by soil carbonates, but sodium in saline soils was not. The method for determining the areas of soil carbonate surfaces was modified to allow for surface-active Mg2+.

Weathering in a catenary sequence. The distribution of carbonates in a catenary sequence of soils in Iran was examined. Carbonate concentrations in the soil increased down all the profiles; they also increased down the catena, being least in strongly-leached hill soils and most in slightly-leached lowland soils. In the highland soils residual carbonate was concentrated in the silt fraction, coaner fractions being broken down and the finest transported. The very large surface areas $(80 \text{ m}^2/\text{g})$ of silt-sized carbonates suggest that they have very small crystallites arranged in very porous and reactive granules. Low-lying soils in the alluvial plain had more uniformly distributed carbonates in silt and clay fractions and surface areas were small $(5 \text{ m}^2/\text{g})$. Free-draining soils in the lowlands lose calcium carbonate from the surface too. Soils in this area with impeded drainage, and affected by periodic but moderate alkalinity, have much more carbonate in the clay and silt fractions. This carbonate, with an intermediate surface area (20 m^2/g), appears to have been recrystallised as less porous particles.

Phosphate status. The distribution of labile phosphate on external and internal surfaces of the soils was examined. Silt-sized carbonates held most of the added P on external surfaces; clay-sized fractions held P mainly on internal surfaces. Recovery of added P in the labile fraction was related directly and positively to the initial soluble P in the soil and inversely to the total surface area of the soil carbonate. In the soils of this catena which were saline and alkaline, added P was uniformly distributed on both surfaces and a larger proportion remained labile. Solubility relationships suggest that octacalcium phosphate was mainly responsible in all the soils for governing the equilibrium concentration of P in the soil solution. (Abedi and Talibudeen)

Release of magnesium from soil. Earlier experiments in field and glasshouse with Woburn sandy loam failed to show that any non-exchangeable magnesium was released. A recent experiment on the same soil was cropped much morc intensively with ryegrass cut nine times in ten months. Deficiency symptoms had appeared by the fourth cut when leaves had less than 0.05% Mg in dry matter and Mg/Mg + Ca ratios in the soil solution had declined from the original 0'042 to 0.005. These low values were maintained to the end of the experiment. A balance sheet taking account of Mg removed in crops (ignoring roots), added as fertiliser, and changes in exchangeable Mg, showed that the grass had removed some non-exchangeable Mg from both limed and unlimed Woburn soils. (Bolton)

Boron contents of crops and soils at Woburn. In previous work (Rothamsted Report for 1970, Part 1, 56) sugar beet grown on Stackyard Field in 1969 in the Woburn Organic Manuring experiment (Rothamsted Report for 1973, Part 2, 98) showed symptoms of heart-rot on some plots. The hot-water soluble boron in soils when this experiment started in 1964 ranged from 0.4 to 0.7 mg B/kg and values had decreased by about 0.15 mg B/kg when the first phase of the experiment finished in 1971. Boron-deficiency might occur in some years in light soils containing these amounts of soluble B. All crops grown in the experiment between 1966-71 were analysed to measure boron in cereals, 60

beans and potatoes to see if organic manures, some of which (peat, FYM) contain boron, increased the B content of crops. Organic matter scarcely affected the B concentration in any of the crops, except sugar beet and beans. Peat and FYM slightly increased $\frac{9}{6}$ B in sugar beet leaves and crowns and peat increased $\frac{9}{6}$ B in grain and straw of beans.

None of the crops grown between 1966-71, except sugar beet, showed symptoms of boron deficiency. Few analyses are given in the literature for boron concentrations in barley, wheat, beans or rye and it is questionable whether the levels below which boron deficiency develops in these crops are known reliably. The B concentrations we measured appear adequate for all crops except sugar beet, but most are close to the lower limit of the range usually regarded as 'normal'.

Table 9 summarises the amounts of boron added in organic manures (l8G-124O g B/ha) and in a single dressing (4.8 t/ha) of lime (10 g B/ha), the total amounts removed by six arable crops and the changes, in g B/ha , in the hot water-soluble B in the surface soils (0-23 cm). This balance sheet shows that the water-soluble B in soils decreased more between 1964-71 than can be explained by the total amounts of boron (about 200 g/ha) removed in crops. Adding large amounts of boron in peat and FYM hardly lessened losses of water-soluble B from the surface soils and we are now following changes in boron in the subsoils. (Chater and Mattingly)

TABLE 9

Boron added to and removed from soils in the Woburn Organic Manuring experiment, 1964-71

* Excluding B in sugar beet tops which were ploughed in

Chemical composition of water related to algal growth

Plant nutrients added to water have the most noticeable effects on growth of algae and other micro-organisms when the water is stationary and shallow; solar radiation is then most eflective and gases exchange easily between air and water, providing enough carbon dioxide for the organisms. The results of eutrophication in running water are usually less obvious as surface 'blooms' of micro-organisms cannot develop, though rooted plants may grow vigorously. We investigated three examples of eutrophication of stationary water last year. One was a pool contaminated by fertiliser, the second water received silage effluent, the third example was of a lake at Woburn receiving field drainage. Concentrations of nutrients are in Table 10.

TARLE 10 Composition of surface waters affected by eutrophication in 1973

Diluted liquid fertiliser from washing of field equipment drained into a shallow pool exposed to sunshine and a very dense population of Chlamydomonas developed.

Silage effluent accidently entered a reservoir at Rothamsted Farm which is filled with good quality water from a deep bore into the Chalk. The large growth of Euglena which developed persisted for more than six months because much ammonium N was formed by the decomposition of organic matter in the effluent. (Euglena depends on NH₄-N for nitrogen.) The growth was so dense that it blocked the nozzles of irrigation spray lines.

Land drainage water which enters the lake at Woburn Experimental Station contains about 20 mg/litre of NO₃-N but so little PO₄-P (<0.1 mg/litre) that visible algal growth is rarely seen on the surface. A moderate 'bloom' of Chlamydomonas appeared in April 1973. Fractionating the total P in the lake water (0.08 mg/litre) showed that 63% of the total was in the organisms, 12% was as soluble inorganic P and 25% was soluble organic P. The 'bloom' never became serious as growth of the organisms was limited by the small amount of P in circulation in the system, and particularly by the very small concentration of inorganic phosphate. (Williams)

Adsorption of organic chemicals by soil

Organic matter is usually the most important adsorption site in soils for unionised organic compounds. Despite the complexity of soil organic matter, as an adsorbing medium it behaves much like a normal organic solvent and a relationship between Q, the organic matter/water partition coefficient for a chemical, and its partition coefficient between a suitable organic solvent and water (P) of the form $\log Q = a \log P + b$ can be expected $(a$ and b are constants). Octanol was chosen as the model solvent to test this because it is widely used in correlations of biological activity and chemical structure.

The adsorption on four Rothamsted clay loam soils (differing in clay and organic matter contents) of 30 organic chemicals (mainly pesticides) with a wide range of structures was found to be well correlated $(r^2 = 0.84)$ with their octanol/water partition coefficients and fitted the equation $\log Q = 0.524 \log P + 0.618$. This equation gave good prediction of Q for compounds widely different in structure from those in the original regression. For example, methiocarb 120 (calculated 138), captan 109 (calculated 87) and aldicarb 10 (calculated 11).

The wider validity of this relationship was tested using published R_F data from soil 62

thin layer chromatography. It can be shown that, if movement on a soil tlc plate is governed by adsorption on soil organic matter, then for a given soil

$$
\log(1/R_F-1)=\log Q+\text{constant}
$$

and hence that

$$
\mathcal{L} = \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} \mathcal{L} = \mathcal{L} \mathcal{L
$$

 $log(1/R_F - 1) = a log P + constant$

Helling's R_F values for 25 pesticides on a soil from Maryland, USA, gave a good fit $(r^2 = 0.96)$ to the equation

$$
\log{(1/R_F - 1)} = 0.517 \log{P} - 0.951
$$

and since the slopes of the two lines were similar $(0.524$ and $0.517)$ it indicates that octanol/water partition coefrcients can be used to predict soil adsorption and leaching behaviour.

Helling and Turner (Science (1968), 162, 562) divided pesticides into mobility classes based on R_F values on soil tlc plates. Broad ranges of R_F were chosen that gave good agreement with laboratory and field observations of leaching in a wide range of soils. The table below shows these classes and corresponding ranges of $log P$ and O calculated from the two regression lines:

Yirtually all the published work on adsorption and leaching of unionised pesticides and other chemicals in soil can be accommodated within this table which summarises the relationship between mobility in soil, adsorption by soil and octanol/water distribution. (Briggs)

Research on crop composition

Mechanical fractionation of the potato crop. When potato haulm is killed by an acid spray, or in other ways, the risk from blight is diminished and tuber-lifting is facilitated but the haulm is wasted and much of the fibre in it rcmains on the feld and may interfere with mechanised tuber lifting later. The haulm can be putped and fracionated by the methods described in past years in the Reports of the Biochemistry Department contained in the Rothamsted.Report. Yields of extractable protein diminished sharply as the crop matured-from 620 kg/ha at the end of July to 300 kg/ha at the end of August. The yield of fibre residue remained relatively constant at $2-3$ t/ha (dry matter) throughout the period in which haulm would normally be destroyed. The product contained $1.5-2\%$ N. If, as is probable, the two products are, or can be made, sufficiently free from solanine, haulm seems to be useful. Destruction is wasting as much protein concentrate and ruminant fodder as is present in a medium bean or hay crop.

Surplus or damaged potato tubers can be preserved for stock-feeding if completely dried, or if partly dried and treated with a fungicide. It is more economical to remove water by pulping and pressing than by freezing and pressing, or by evaporation. There is so little fibre in tubers that material, pulped sufficiently to allow a useful degree of juice expression, has to be pressed circumspectly. Pressure is applied too abruptly by the equipment used with leaf pulp. Various methods for applying pressure are being studied, and various types of grid to support the material being pressed. Large-scale cquipment is being modified in the light of these experiments. Starting with pulp

containing 20% dry matter it is already possible to make a cake containing 36% after pressing at 3-4 kg/cm² and 65% by pressing harder. (Carruthers and Pirie)

Effects of magnesium on the yield and composition of ryegrass. Italian ryegrass was grown in pots with or without added magnesium (20 or 40 mg/kg of soil) in a Woburn sandy loam containing only 13 mg/kg of exchangeable Mg. Nitrogen was given at two rates (40 and 160 mg/kg of soil) as ammonium nitrate or as ammonium sulphate plus a nitrification inhibitor ('N-Serve'). Each pot received basal P and K. Yields of the first two cuts of grass were hardly affected by the magnesium treatments. At the third cut magnesium increased the yield of grass given the higher rate of nitrogen and the increase was larger with ammonium sulphate than with ammonium nitrate (Table 11). At all cuts, yields of grass were larger from ammonium nitrate than from ammonium sulphate plus the inhibitor. Only the grass of the third cut given the higher rate of N fertiliser, was analysed for organic constituents.

TABLE 11

Effects of magnesium fertiliser and form of N fertiliser on the yield and composition of a third cut of ryegrass

Chlorophyll concentrations were increased by both rates of magnesium (Table 11).

Soluble carbohydrates. Magnesium treatments had little effect on concentrations of reducing sugars and sucrose but increased fructosan (Table 11).

Nitrogen fractions. Much more ammonium N was found in grass given ammonium sulphate (+inhibitor) than in grass supplied with ammonium nitrate (Table 12). With both N fertilisers giving magnesium decreased ammonium N. Much more nitrate N was found in the grass given ammonium nitrate but this accumulation was decreased by giving magnesium. Protein N, expressed as a percentage of total N, increased with increasing magnesium in grass given ammonium sulphate. With ammonium nitrate, however, both rates of magnesium increased protein N to the same extent. Irrespective of magnesium treatments, protein N was higher with ammonium nitrate than with ammonium sulphate.

Mg-deficient grass given ammonium sulphate contained much more free amino acids and amides than grass given ammonium nitrate (Table 12). With both N fertilisers magnesium greatly decreased the concentrations of individual amino acids. Dicarboxylic acids and their amides, proline, valine, isoleucine and basic amino acids, especially arginine, were most affected, γ -aminobutyric acid and ethanolamine the least. Free methionine was not found in Mg-deficient grass. (Nowakowski, Bolton and Lazarus) 64

TARLE 12

Effects of magnesium fertilisers and form of N fertiliser on free amino acids, ammonium and

$Tr = Trace$

Apparatus and techniques

A multi-channel atomic absorption flame photometer. A multi-channel atomic absorptiometer was designed and constructed using flexible u.v. fibre-optic ducts. These ducts convey light simultaneously from four hollow cathode sources to a solid quartz rod that integrates the light by multiple internal reflection. After collimation to an almost parallel beam, the light passes through the interconal absorption zone of a long-path flame to a quartz prism monochromator. A plate with six exit slits is substituted for the single exit slit of the monochromator. To this plate is attached a solid block with six flexible fibreoptic tails which conduct light from the exit slits to photomultiplier tubes. The circular cross-section of each is transformed within the block to a rectangular cross-section which matches the exit slits. The signal from each photomultiplier tube is integrated over 10 seconds, amplified and passed to a six-channel recorder. A 'narrow band-pass' filter over the photomultiplier tube window for Na prevents spectral interference from the neon 'filler gas' lines at 5852 Å and 5882 Å; argon gas cannot be used because its line spectrum interferes with that of K.

The instrument will be used to determine K, Na, Ca, Cu, Mg and Mn simultaneously in routine analysis. Other elements may be substituted for the six elements specified. (Rawson)

Genstat program for calculating cation exchange parameters. A Fortran program for calculating exchange selectivity coefficients ($\ln K_c$) of a cation exchange reaction, and \mathbf{C} 65

the fractional K saturation of soil cation exchange capacity (CEC), (N_K) , in soils in equilibrium with 0.02N Cl-solutions of various K^+ and Ca^{++} concentrations, was translated into Genstat Mark 2 version. It was also extended to generate plots of $\ln K_c$ against N_K from first and second degree regressions, so eliminating previous ambiguities incurred with freehand plots, and providing more accurate results in a more convenient form. These results are fed into a Fortran program (originally written to run on the IBM 360/50 at Edinbugh, via the Rothamsted link) for calculating the thermodynamic exchange constant ($\ln K$) of the cation exchange reaction and the activity coefficients of the adsorbed cations. The Genstat program is being altered to make it acceptable to the Mark 3 version. (Panther)

Staff and visiting workers

We greatly regret the sudden death of R. A. G. Rawson in December. He had worked in the Department since 1961 and had done much to develop new equipment for surface area measurements and for spectrophotometric analysis by atomic absorption techniques.

G. E. G. Mattingly was Acting Head of the Department until 31 March. S. C. R. Freeman retired after 24 years work in the Department. G. T. Elsmere, P. H. Le Mare and A. V. Watkins all left during the year. D. Cox was appointed to work on nitrogen fertilisers and M. B. Page to investigate nitrogen and potassium manuring of wheat.

The following visitors worked in the Department during the year: Dr. M. J. Abedi (Iran), Dr. A. Hamid (Pakistan) and Mr. I. C. R. Holford (Australia). J. R. Griffiths, W. D. Hudson and Anne Rangeley were sandwich course students.

G. W. Cooke visited the Rubber Research Institute of Malaysia at the invitation of the Institute, Malawi and Tanzania at the invitation of the Cotton Research Corporation and attended a Colloquium on Potassium in Tropical Crops and Soils in Abidjan, Ivory Coast, as a guest of the International Potash Institute. Cooke also visited Hunpry for two weeks under the arrangements for exchange visits of scientists between the Hungarian Academy of Sciences and the Royal Society. G. W. Cooke and O. Talibudecn were invited by the organisers to give papers at a Study Week on Soils and Fertilisers held in Gembloux, Belgium.

I. C. R. Holford and P. H. Le Mare were awarded the Ph.D. degree of London University. The Fellowship of the Royal Agriculturat Society was conferred on F. Y. Widdowson.

B. Benzian, S. C. R. Freeman and H. D. Patterson (now of the ARC Unit of Statistics at Edinburgh) were awarded the Silvicultural Prize in 1973 by the Institute of Foresters of Great Britain, for their paper on long-term experiments with Sitka spruce. G. W. Cooke was appointed Clive Behrens Memorial Lecturer in the University of Leeds for 1972-74 and also gave the George Scott Robertson Memorial Lecture in Belfast.