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# **Chemistry Department**

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#### G. W. COOKE

#### Practical implications of the 1969 work

Anhydrous ammonia is the cheapest form of fertiliser nitrogen, but is difficult to inject into grassland, and was less efficient than ammonium nitrate in tests using farm-scale equipment. When injected without loss, it was as efficient as solid fertiliser, and further research on injecting ammonia efficiently into grassland is justified. Strong solutions of ammonia in water, which are nearly as cheap as anhydrous ammonia, are easier to inject efficiently. Solutions of either ammonia or urea injected 4 in. deep into soil were as efficient as broadcast ammonium nitrate for barley. Either solid or liquid NPK fertilisers (especially liquids containing urea) need to be applied correctly to give maximum yields; nitrogen is easily lost from urea, and large dressings of either when combine-drilled damaged young seedlings; the liquid killed many plants. As previously, yields from combine-drilled PK fertilisers were larger than from broadcasting them, but the large amount of nitrogen needed was better applied separately.

Much nitrogen was lost by leaching during the wet and cold spring of 1969, which is always possible when heavy rain falls before crops have taken up much of the N usually given at sowing. Insoluble nitrogen fertilisers may prevent losses but they act too slowly to give maximum yields of barley. Such losses can be prevented only by withholding spring dressings of nitrogen until crops need them, and leaf analysis is being developed to show when top-dressings should be given.

An experiment in which wheat and potatoes followed a long grass ley suggested how to avoid on one hand 'luxury' uptake of K by the grass and, on the other hand, yield losses in succeeding arable crops from K-deficiency. K manuring of permanent grass is difficult to plan by customary analysis of either soil or leaf. However, agmatine accumulates in grass very deficient in K, and measuring this in herbage may help to diagnose severe K-deficiencies.

On the Clay-with-flints soil at Rothamsted neither magnesium fertilisers nor trace-element sprays have consistently affected crop yield after many years of supplying. Sulphur slightly increased yields in two-thirds of the comparisons made; it also increased yields of radish on sandy soil at Wareham in Dorset (as in 1968). However, on the sandy soil at Woburn, where farmyard manure gives yields of potatoes and sugar beet not yet equalled with inorganic fertilisers, magnesium deficiency has appeared in the last five years and is now common where no magnesium has been applied. In this soil, too, K-deficiency becomes important within three years.

Large triennial dressings of phosphate fertiliser had large residual effects and produced as much yield as smaller dressings applied each year. This means labour can be saved, and spring work eased, by giving P and K fertilisers in autumn rather than before sowing every year in spring, or by giving phosphate only once in two or three years.

In some crops sodium can substitute for potassium; sodium diminished the amounts of free amino acids, ammonia and nitrate that accumulated in potassium-deficient ryegrass grown in pots. That sodium can replace some of the functions of potassium in grass is important scientifically, and may be important in animal nutrition.

Simazine, used as recommended by the manufacturers to control weeds in bean crops, lessened yields seriously, especially on soils poor in organic matter. Yields were unaffected only on soils dressed each year with farmyard manure or given much peat. Such effects must interfere with the results of experiments on organic manures and farming systems where beans are a test crop, and indicate the risks of yield losses where simazine is used for beans grown on soils long in arable cultivation.

#### Anhydrous and aqueous ammonia as fertilisers

#### Experiments on grass in large plots at Rothamsted

Cut grass. Both sorts of ammonia were injected during November and March and yields from them were compared with those from equivalent dressings of 'Nitro-Chalk' (21% N) applied either all at once during March or divided equally between March, June and August for each of three cuts. The applicator for anhydrous ammonia was unsatisfactory; the time between entering and leaving the applicator was too long, probably because the meter was too far from the tines. Therefore the plots injected during autumn received less ammonia than intended, and their yields are excluded from Table 1; the amounts given to those injected during spring are suspect too. Aqueous ammonia injected either in November or in March gave yields as large or larger than from equivalent single dressings of 'Nitro-Chalk' broadcast in March. This year slightly larger yields were obtained by injecting this ammonia in March rather than in November, perhaps because some was lost by leaching during the mild, and unusually wet winter.

#### TABLE 1

#### Comparisons of aqueous and anhydrous ammonia with ammonium nitrate ('Nitro-Chalk 21') for grass

Yields of dry grass (cwt/acre)

	Ammonia in autumn	Ammonia in spring					itro-Chalk' dressing	
N/cwt/acre	Aqueous	Anhydrous	Aqueous	Single	Divided			
1	58.2	57.4	60.3	57.4	65.6			
2	65.8	60.3	69.8	71.3	81.0			
3	77.2	64.8	77.1	74.8	83.1			
4	77.9	73.3	79.8	77.6	77.5			

Table 1 also shows that divided dressings of 'Nitro-Chalk' produced the largest yield (83.1 cwt dry grass/acre), which was produced by only 3.0 cwt N/acre. Equivalent single doses of aqueous ammonia produced 42

6 cwt/acre less. However, with 4.0 cwt N/acre, yields from 'Nitro-Chalk' and aqueous ammonia were similar.

TA	DI	F	2	
14	DI		4	

# Mean yields from three experiments comparing anhydrous and aqueous ammonia for grass

	Yield	Ammonia in autumn			onia in ing		'Nitro-Chalk' dressing		
Year	without	An- hydrous	Aqueous	An- hydrous	Aqueous	Single	Divided	S.E.	
1967 1968 1969	45·8 62·8 32·2	70·4 82·3	84·0 86·4 69·8	77·0 83·4 63·9	$78 \cdot 5$ 84 · 2 71 · 8	77 · 7 80 · 9 70 · 3	88·3 79·2 76·8	${{\pm 1\cdot 70}\atop{{\pm 1\cdot 44}\atop{{\pm 0\cdot 97}}}}$	

Table 2 summarises 3 years' work; in each year yields were larger with aqueous than with anhydrous ammonia; the problems of injecting anhydrous ammonia (as a liquified gas) under grass, accurately and without loss, were not resolved in these experiments. Injecting aqueous ammonia, however, involved few mechanical problems, and the table shows that it gave yields as large or larger than from single dressings of 'Nitro-Chalk'; in two of the three years it was better to inject it during November than March, so that losses of N from it during winter were minimal. Divided dressings of 'Nitro-Chalk' gave the largest yield in 1967 and in 1969, as expected, but in 1968 it gave the smallest, because in the dull wet autumn it decreased yields most.

**Grazed grass.** In another experiment aqueous ammonia was injected in March 1969 at 1.0, 2.0, 3.0 or 4.0 cwt N/acre. Equivalent N as 'Nitro-Chalk' was broadcast in six equal doses for cuts of grass taken (from under cages) early each month from May to September and in late October. Yields from the single dressing of aqueous ammonia were as large as from divided ones of 'Nitro-Chalk' at the first four cuttings, but smaller at the last two, so 'Nitro-Chalk' produced the larger total yield. Each fertiliser increased yields by approximately a half; with 'Nitro-Chalk', 3.0 cwt N/acre gave maximum yield, but with aqueous ammonia 4.0 cwt N/acre was needed. (Widdowson, Penny and Flint)

#### Microplot experiments with grass

**Saxmundham.** Ammonia injected by a hand machine to avoid loss to the air was compared with equivalent N in single and split amounts of 'Nitro-Chalk' broadcast on the surface. 'Nitro-Chalk' and ammonia applied all in March gave similar yield at the first cutting in May; the total grass from 4 cuts was much less at 2.5 cwt N with 'Nitro-Chalk' than with ammonia, but at 5 cwt N/acre was the same with the two. 'Nitro-Chalk' given as three dressings (March, May and July) was no more effective than the single March dressing of ammonia at 2.5 cwt N but was significantly better at 5 cwt N/acre; it made no difference whether the first of the three dressings was 'Nitro-Chalk' or anhydrous ammonia. Adding a nitrification inhibitor ('N-Serve') to the anhydrous ammonia

gave slightly less grass at the first cut and slightly more at late cuts but the small gain from 'N-Serve' for the year as a whole was not significant. Whereas the grass recovered only 42% of 2.5 cwt N/acre from 'Nitro-Chalk', it recovered 71% from anhydrous ammonia; 'N-Serve' diminished losses from ammonia and 81% of the dressing was recovered. Only 50% of the double dressing of ammonia (5 cwt N/acre) was recovered—the same as from 'Nitro-Chalk'; 60% of this was recovered when half was applied as ammonia in March and the rest as split dressings of 'Nitro-Chalk'. (Williams and Cooke)

Spacings between injections. Last year, (Rothamsted Report for 1968, Part 1, 39–40) yield of grass and N uptake depended on how injections of anhydrous ammonia were spaced. This year we tested three row widths, 6, 9 and 12 in., with distances within the row to give areas per injection of 18, 36, 72 and 144 in.<sup>2</sup>, but keeping the distance within the row equal or less than the row width. Ammonia was injected (early April) 4 in. deep to supply 200 and 400 lb N/acre to a long-ley in Appletree field. Injections spaced most widely gave slowest growth during spring, but the differences diminished later. Totalling the three cuts and averaging amounts of ammonia applied, dry matter yields did not differ significantly with the pattern of injection; N uptake was least from ammonia injected 6 in.  $\times$  3 in. and 9 in.  $\times$  8 in. and most from 9 in.  $\times$  2 in. and 12 in.  $\times$  3 in. spacings. (Gasser, Penny and Flint)

An experiment with ryegrass in pots compared anhydrous ammonia injected all near the centre of the pot, or in three equal portions in the mid-plane of the pot, with solid ammonium nitrate similarly placed. Equal volumes of a sandy loam from Woburn (Cottenham Series) and a Batcombe Series clay loam from Rothamsted were used. The total ryegrass (dry matter) did not differ with form or method of applying N; the largest amount of N, which retarded germination and early growth of the ryegrass, gave the smallest yields at the first cut. The clay-loam produced more grass, containing more fertiliser-N, than the sandy-loam; the grass recovered slightly more N from anhydrous ammonia (72%) than from ammonium nitrate (70%) in the clay loam soil but less in the sandy-loam (64% from ammonia, 68% from NH<sub>4</sub>NO<sub>3</sub>). (Gasser and Mitchell)

**Reactions between ammonia and soil.** Since anhydrous ammonia was introduced as a fertiliser 20 years ago, many papers have described how differing conditions affect its movement, fixation and nitrification in soils, and uptake by plants, but how ammonia reacts with soils has been little studied, and the reactions involved have been largely inferred from the properties of soil constituents. There is good evidence that ammonia molecules can displace water molecules involved in cation co-ordination and that protonation followed by retention as ammonium ion can occur in montmorillonite. Ammonia may become weakly fixed to clay minerals by various forms of hydrogen bond; soil organic matter also will probably react with ammonia because it has suitable hydroxylic groups. To obtain more information on the reactions, equipment is being built to measure the heats of interaction of soils and clay minerals with ammonia gas.

Fartilizers applied to give

Preliminary measurements of adsorption isotherms over the pressure range 0-1 atmosphere, using a range of soils containing different amounts of organic matter, showed that reaction with the initial 0.2 atmosphere of ammonia is rapid but then slows, with equilibrium established only after several hours. On desorption, all the isotherms exhibited hysteresis. At 1 atmosphere, all the soils adsorbed about five times as much ammonia from the gas as from 0.05 *M* aqueous ammonia (which contains an approximately equal number of ammonia molecules per unit volume as ammonia gas at 1 atmosphere). With aqueous ammonia, equilibrium was not reached even after ten days. The organic matter in soils can fix ammonia; one sample of Barnfield soil containing 1% organic matter adsorbed 58 meq per 100 g at 1 atmosphere, whereas a second sample containing 2.6% organic matter, adsorbed 77 meq per 100 g; greater hysteresis in the isotherm of the second sample also indicated stronger adsorption. (Ashworth)

#### Liquid fertilisers for barley

Five experiments compared yields from aqueous ammonia (25% N) and from a solution of urea (18% N) injected in bands 12 in. apart and 4 in. deep with those from broadcast 'Nitro-Chalk'. Also, a granular NPK (20-10-10) was combine-drilled and broadcast and a liquid NPK (14-6-8) fertiliser combine-drilled and sprayed. Three experiments were on light loams overlying Chalk, one on Clay-with-Flints and one on a sandy-loam overlying Lower Greensand. P and K significantly increased yields in three experiments and nitrogen greatly in all.

#### TABLE 3

#### Mean yields of spring barley from five experiments with N and NPK fertilisers

#### Yields of grain at 15% moisture content: cwt/acre Without fertiliser 19.2

	Fertilisers applied to give		
Fertilisers tested	0.5 cwt N/acre	1.0 cwt N/acre	
Broadcast 'Nitro-Chalk'	31.0	34.3	
Broadcast 'Nitro-Chalk' + drilled 0-20-20	34.1	38.5	
Injected aqueous ammonia + drilled 0-20-20	35.6	40.2	
Injected aqueous ammonia + drilled 6-15-15	35.7	39.8	
Injected solution of urea + drilled 0-20-20	35.5	39.5	
Broadcast granular 20-10-10	31.3	38.0	
Drilled granular 20-10-10	35.2	37.4	
Sprayed liquid 14-6-8	30.4	36.6	
Drilled liquid 14-6-8	32.1	35.5	

Table 3 shows that aqueous ammonia and urea, injected into the seedbed, each gave similar yields, which were a little larger than from equivalent 'Nitro-Chalk' broadcast after sowing. This confirms that losses from the aqueous ammonia were negligible and that yields were not diminished by concentrating the nitrogen in bands 12 in. apart. Combine-drilling the single amount of the NPK fertilisers checked early growth a little, but combine-drilling the double amount (1.0 cwt N/acre)

checked growth greatly, more with the liquid than the solid, and killed many plants. The liquid fertiliser was made from urea and di-ammonium phosphate; presumably the urea caused the damage. The smaller yields from spraying the liquid than from broadcasting the granular NPK fertiliser may have been caused: (1) by losses of ammonia from the urea; (2) by phosphate in the granular fertiliser remaining accessible longer than that dispersed through the soil in the liquid fertiliser. (Four of the soils used were phosphate-deficient.) The largest yields were from combinedrilling the P and K and giving the large amounts of N needed in some other way. (Widdowson, Penny and Flint)

#### Experiments with solid nitrogen fertilisers

Times and amounts of N, and ethirimol for barley. An experiment at Saxmundham compared yields from 0.6 and from 1.2 cwt N/acre given either in early April or in mid-May to a short (Deba Abed) and to a tall (Maris Badger) variety. Seed dressed with ethirimol (5n butyl-2-ethylamino-4-hydroxy-6-methyl-pyrimidine) was sown on half of each plot and undressed seed on the other. The barley followed two successive crops of sugar beet.

#### TABLE 4

#### The effects of nitrogen and ethirimol (PP149) on two barley varieties Yields of grain at 15% moisture content: cwt/acre

Without nitrogen {Deba Abed 19.3 Maris Badger 16.7

	N cwt/acre					
	(	0.6	1	1.2		
Variety	April	May	April	May		
Deba Abed Maris Badger	28.6 30.5	39·7 34·2	38·7 31·2	41·0 26·6		
Mean lodging %	3	31	6	44		
Fungicide	Deba Abed	Maris Badger	Deba Abed	Maris Badger		
None Ethirimol	32·1 36·3	31·1 33·6	39·2 40·4	30·7 27·1		
Mean lodging %	0	8	3	72		

Table 4 shows that Deba Abed yielded more when either amount of N was given in May than in April, but Maris Badger, which lodged, did not, and yielded less when the double amount of N was given in May. The fungicide (ethirimol) increased yields of the shorter variety with both N dressings, but of the taller only with 0.6 cwt N/acre; with 1.2 cwt N, it decreased yield, presumably because the larger crop lodged more severely. It increased yields of straw of both varieties with both amounts of N. (Widdowson, Penny and Flint)

**IBDU** as a fertiliser for barley. Two experiments have compared IBDU (isobutylidene di-urea) with 'Nitro-Chalk' for spring barley. The first, in 46

1968, was on sandy soil at Herringswell (West Suffolk) adjoining the rotation experiment described in *Rothamsted Report for 1966*, (pp. 283–284), the second on sandy clay-loam at Saxmundham in 1969. Yields at both sites were small (largest 26 cwt/acre at Herringswell and 28 cwt/acre at Saxmundham). Inorganic N was lost by leaching at both sites during spring, and these losses were not prevented by using the slow-acting fertiliser. At Herringswell IBDU applied as powder ultimately released more N than 'Nitro-Chalk'—but too late even to increase straw yields. Granules of IBDU acted much more slowly and by the end of the growing period had supplied less N than the 'Nitro-Chalk'. Slow-acting sources of N such as IBDU may be more useful for root crops which grow actively during late July, August and September, but seem to offer no prospect of increasing the efficiency of nitrogen used for cereals. (Gasser with Draycott, Broom's Barn)

#### The residual effects of nitrogen and potassium fertilisers

**Residues of N in roots in a pot experiment.** Six crops (barley, ryegrass, spinach, kale, turnips and tomatoes) grown in pots under glass tested two amounts of N fertiliser (125 and 250 ppm in the weight of soil used). After six weeks the crops were harvested at soil surface. The larger roots were removed from half the pots and their N content measured. Ryegrass was then sown in all the pots without any further fertiliser. Yields of the ryegrass and its N content were not related to fertiliser-N used for the first crop, to weights of root removed, or to amount of N remaining in the soil. They were positively correlated with %N in the roots and negatively with the C/N ratio of the roots. The proportion of the 250 ppm N applied to the first crops that was removed in their tops differed; of the N remaining in the roots of these crops and soil 5% was recovered in the second crop after grass and 19% after kale. (Gasser and Hamlyn)

**Residues of N and K used for grass in a field experiment.** From 1958–67 grass was grown without N or K, or with three amounts of N (0·3, 0·6 or 0·9 cwt/acre) and three amounts of K (0·0, 0·3 or 0·6 cwt K<sub>2</sub>O/acre) for each cut. The grass was cut three or four times in a year and carted away. Yields, and the amounts of K in the grass and in the soil in 1963, were given in *Rothamsted Report for 1963* (p. 49). Table 5 shows total yields of grass and of K from 1964–67 and amounts of K in grass and in soil in 1967. Whereas K increased yields of grass given 0·3 cwt N/acre/cut by only 7·9 cwt/acre in four years, it increased yields of grass given 0·9 cwt N/acre/cut by 47·4 cwt/acre. 0·3 cwt K<sub>2</sub>O/acre/cut was enough for the grass to contain at least 2% K (mean of four cuts) during the tenth and final year, but was not enough to maintain CaCl<sub>2</sub>-soluble K in the surface soil. This decreased with time except on plots given two parts of K<sub>2</sub>O to one of N (0·6 cwt K<sub>2</sub>O plus 0·3 cwt N/acre/cut).

In November 1967 the grass was ploughed, and in 1968 spring wheat (Kloka), given 1.0 cwt N/acre uniformly, measured residues. In 1969 potatoes (Pentland Dell) were given 1.0 cwt N/acre uniformly and 1.0 cwt K<sub>2</sub>O/acre on half of each plot. Although K had little effect on yields of

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# The effects of applying different amounts of and on the wheat

			(
	Grass,		
Fertiliser treatment to grass 1958–67 cwt/acre/cut	Total yield of dry grass (11 cuts)	Total K taken up cwt/acre	
Without N or K fertilisers	72.0	1.7	2.1
0.3 N plus			
0.0 K	173.4	3.4	1.8
0·25 K*	185.7	4.6	2.3
0·50 K*	181.3	4.9	2.5
0.6 N plus			
0.0 K	231.2	4.2	1.6
0.25 K	252.7	5.7	2.1
0.20 K	253.8	7.0	2.6
0.9 N plus			
0.0 K	233.7	4.0	1.4
0·25 K	268.2	5.7	2.0
0.20 K	281.1	7.6	2.5
	27.2.7 ST 27.0		

\* Equivalent to 0.30 or 0.60 cwt K<sub>2</sub>O/acre. † NaHCO<sub>3</sub>-sol. P 43 ppm (meaned over all plots).

grass, the residues greatly increased both %K in the green wheat and the yield of grain. These residues also greatly increased %K in the leaves of the potatoes in 1969 and they almost doubled the yield of tubers. The N applied for the grass consistently decreased yields of wheat and of potatoes, unless the grass had been given enough K. Applying K in 1969 for the potatoes consistently increased yields (by a mean amount of 4 tons/acre) but most (6.9 tons/acre) where the grass had been given 0.9 cwt N/acre/cut without K, and least (1.7 tons/acre) where the grass had been given 0.6 cwt K<sub>2</sub>O with 0.3 cwt N/acre/cut.

The K given in 1969 greatly and consistently increased %K in the potato leaves, but almost independently of the N and K fertilisers applied for the grass. With K in 1969, mean amounts in the potato leaves ranged from 1.6 to 3.4% K, and without it, from 0.6 to 2.2%. By contrast, the absolute amounts of K in the leaves were well correlated with the amounts of K removed by the grass. The potato leaves that contained the most K (3.4%) were from plots given 1.0 cwt K<sub>2</sub>O/acre in 1969 following grass given 0.3 cwt N and 0.6 cwt K<sub>2</sub>O/acre/cut for ten years; they also produced the largest yield of tubers (16.46 tons/acre).

The leaves of the potatoes growing on the Rothamsted Reference Plots (*Rothamsted Report for 1965*, 45) were sampled on the same day. These plots test all combinations of N, P and K fertilisers, and of FYM with and without NPK fertilisers, in a five course rotation of arable crops. The mean amounts of K in these leaves were: (1) 0.8% where K had not been given; (2) 3.4% with 2.0 cwt K<sub>2</sub>O applied each year; (3) 4.0% where FYM had been given. Yields on these plots also increased with increasing K in the leaves. Thus, it seems that on soils like those of the Rothamsted farm, potato yields may be limited by shortage of K, unless their upper leaves contain 3.5% K during early July. (Widdowson, Penny and Flint)

#### Effects of N and K fertilisers on the composition of crops

Non-protein nitrogen in grass. We reported last year (p. 52) that large amounts of free amino acids accumulate in K-deficient plants, which also contain much unidentified nitrogenous material. As Richards and Coleman (*Nature, Lond.* (1952), **170**, 460) and Smith and Richards (*Biochem. J.* (1962), **84**, 292) found putrescine and its precursor agmatine in K-deficient barley, we looked for these in the unidentified nitrogenous fraction of the grass. Table 6 shows the agmatine content, determined by Smith's procedure (*Phytochemistry* (1963), **2**, 241) in grass from the 1967 experiment. (Putrescine was determined only in the samples given the most N and the three amounts of K, only these gave enough plant material.) Increasing fertiliser K decreased both agmatine and putrescine concentrations, and the concentrations of the substances indicated potassium deficiency more sensitively than did the potassium concentration. As agmatine is much easier to measure than putrescine, % agmatine in herbage is proposed to indicate potassium status of soils under grass. (Nowakowski)

N in nursery conifers and subsequent growth in the forest. To see whether increasing N concentrations of trees in the nursery benefits them after

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Fe (as	ppm o	supplying f weight of used)	DM yield	%K	μg amine/g mate	
	N	K	g/pot	in DM	Agmatine	Putrescine
4	40	0	3.45	0.51	18.4	n.d.
4	40	60	5.04	0.91	4.5	n.d.
	40	120	5.73	1.52	6.2	n.d.
4	40	240	6.03	2.79	5.4	n.d.
8	80	0	4.34	0.45	88.0	n.d.
5	80	60	7.18	0.53	28.8	n.d.
8	80	120	9.14	0.76	19.5	n.d.
8	80	240	10.48	1.68	19.6	n.d.
12	20	0	4.72	0.47	94.2	n.d.
12	20	60	9.27	0.43	82.2	1246.0
12	20	120	11.01	0.60	53.2	332.0
12	20	240	14.67	1.08	16.2	63.2

#### TABLE 6

#### Agmatine and putrescine concentrations in the second cut of Italian ryegrass (Experiment 1967)

planting in the forest, green healthy transplants of Sitka spruce (*Picea sitchensis*) were grown at Wareham and Kennington Extension nurseries in 1968 with uniform inorganic fertilisers supplying N, P, K and Mg. During early September, when growth had nearly ceased, half the plots were top-dressed with extra 'Nitro-Chalk'; the large dressings increased %N in the trees by about 40% at Wareham and 85% at Kennington. The trees were kept in a cold store during the winter and then planted during spring 1969 in Aberhirnant Forest (North Wales), an exposed site at 1700 feet and in Rheidol Forest (Central Wales), a sheltered site in a frost hollow at 800 feet. In both forests the nitrogen speeded bud development and greatly increased growth of the trees. Biggest effects were with trees from Kennington Extension; those with the largest %N produced shoots 70% longer at Aberhirnant and 85% longer at Rheidol than trees without the extra nursery top-dressing.

		sery	Length	of 1-season	orest n shoot growt 9 with trees f	h (cm) rom
N giuan	%N in dry matter* of trees, Nov. 1968		Wareham		Kennington	
N given Sept. 1968 g/m <sup>2</sup>	Wareham	Kenning- ton	at Aber- hirnant	at Rheidol	at Aber- hirnant	at Rheidol
0 7 14	1 · 14 1 · 46 1 · 60	0.81 1.23 1.50	6·9 8·5 8·4	8·0 11·5 13·2	5·9 8·8 10·1	$7 \cdot 1$ 11 · 2 13 · 1
	* tops + ro	S.E.	$\pm 0.55$	$\pm 0.51$	$\pm 0.47$	$\pm 0.38$

These results have important practical implications, by disproving a widely accepted opinion that a large N content is a disadvantage for plantings on exposed sites. (Benzian and Freeman with Mr. R. M. Brown, Forest Research Station, Alice Holt)

#### Nitrate in crops related to rainfall, leaching and fertiliser dressings

The nitrate concentrations in several crops from the Saxmundham experiments were measured to try to assess the effects of rain and leaching on uptake of N fertilisers and the need for mid-season top-dressings. The sampling and analytical methods have been described (*Chemy Ind.* (1969), 1735–1736).

Winter wheat. Plants from Rotation I experiment contained little or no nitrate after mid-May unless given more than 0.5 cwt N/acre. Nitrate in crops given 1 cwt N/acre fell from 300 to 3 ppm between 22 and 29 May; a top-dressing of 0.5 cwt N/acre (applied on 29 May) increased NO<sub>3</sub>-N concentration in stems until mid-June and increased grain yield by 2.4 cwt/acre. Plants from the Intensive Wheat Experiment (Rothamsted Report for 1966, 251-252) were also sampled. With 1.2 cwt N/acre given in March, plants had no nitrate in stems by 12 June; those given 1.8 cwt N/acre in March, still contained nitrate at the beginning of July, and the extra 0.6 cwt N increased grain yield by 2.4 cwt N/acre. Nitrate concentrations in wheat grown after beans was the same as after wheat; in Rotation I experiment annual dressings of FYM did not increase nitrate in wheat stems. These sources of nitrate probably had no effect because the more than average rain from autumn 1968 to summer 1969 leached much nitrate from the soil and mineralisation was less than usual during the cold weather of spring and early summer.

**Barley.** One cwt N/acre applied to Sultan barley in Rotation I maintained large concentrations of nitrate in the stems (300 ppm or more) only until 22 May, and by 29 May nitrate had diminished to <1 ppm. The test top-dressing of 0.5 cwt N/acre was applied on 3 June. Unfortunately this coincided with a long dry period, rain did not fall until 24 June, so the fertiliser remained on the surface and nitrate in tissues did not increase until July.

The greater leaching in spring 1969 than in 1968 is shown by comparisons with last year's figures (*Rothamsted Report for 1968*, Part 1, 50). In 1968 1 cwt N/acre in the seedbed maintained large nitrate concentrations in stems until mid-June and a late top-dressing of 0.5 cwt N/acre maintained much nitrate until July; the top-dressing did not increase yields. In 1969 nitrate in stems diminished nearly a month earlier and, although the effect of the top-dressing was delayed by dry weather, it increased yields from 21 to 30 cwt/acre. In the adjacent experiment testing seedbed dressings against later N fertiliser for barley, top-dressings were applied on 14 May. Two inches of rain fell before the end of May, top-dressing maintained nitrate in the stems when crops with seedbed N contained none and gave 7 cwt/acre more grain of Deba Abed than was obtained from seedbed dressings.

Sugar beet. The nitrate in petioles of leaves of beet receiving 1 cwt N/acre at sowing in early April had diminished to 300 ppm by 3 July when a first test of top-dressing with 0.5 cwt N/acre was made. This dressing main-

tained NO<sub>3</sub>-N concentration above 100 ppm until early August; a second top-dressing on 20 August maintained some nitrate in the petioles until harvest in October. The July top-dressing with 0.5 cwt N/acre was fully justified (it was additional to the usual recommendation for sugar beet of 1 cwt/N/acre to the seedbed), for it gave extra root and top dry matter and 10 cwt/acre more sugar. The *additional* August top-dressing, (bringing the total N applied to 2 cwt/acre) diminished root and sugar yields slightly and had little effect on tops. By contrast, in 1968 (*Rothamsted Report for 1968*, 50) 1 cwt N/acre applied to the seedbed maintained NO<sub>3</sub>-N in leaf petioles until the end of July and was enough for maximum yields of roots and sugar; the July top-dressing maintained nitrate in the petioles until harvest in 1968 and increased yield of tops but not roots.

Nitrate lost in drainage. In each of the last three years, there was a peak concentration of nitrate in drainage water during the first week of May. In 1967 43-50 ppm was measured, in 1968 45-91 ppm, and in 1969 57-91 ppm. Such losses must diminish the value of dressings of nitrogen given at sowing, but total losses depend on both concentration and volume of drainage. In 1967 the drains at Saxmundham ran from mid-April to the end of May and then stopped until September. In 1968 less rain fell in spring and an irregular flow lasted only three weeks in late April and early May but, in contrast to 1967, heavy summer rain caused further drainage containing much nitrate. In 1969 the drains ran on every day of the year until 20 June whereas in both 1967 and 1968 there were long dry periods with no drainage during March and April. The much greater volume of drainage in 1969 undoubtedly leached more nitrate in winter and spring than in the two previous years and caused Saxmundham soil to have a smaller than average reserve of nitrate. Serious losses of N from seedbed dressings seem to be associated with large spring rains that fall in a short time (say 1 in. or more in 24 hours); these conditions occurred in 1967 and 1969 but not in 1968; in 1967 and 1969 late top-dressings (given in addition to annual seedbed dressings) increased yields of both barley and sugar beet; (top-dressings were not tested on wheat in 1967, they increased yield in 1969). In 1968 extra top-dressings had no effect on any crop. Much rainfall in late June, July and August in 1969 caused more leaching and was responsible for the rapidly diminishing concentrations of nitrate in cereal stems and beet leaves even where top-dressings had been applied. The losses, however, did not justify the very late (August) top-dressing tested this year on the beet. (Williams)

#### **Residual effects of phosphate fertilisers**

Only part of a fresh dressing of phosphate fertiliser is taken up by a first-year crop, the rest accumulates in soil and can benefit later crops. Most arable and some grassland in Britain has received phosphate regularly for many years and many soils have accumulated considerable reserves so that it is now rare for any but sensitive crops (potatoes are the best example) to respond to fresh P in experiments on ordinary land. Estimating the values of phosphate residues by field experiments, measuring them by

soil analyses, and relating the two kinds of information, are therefore important for planning to use P fertilisers efficiently in Britain and countries with a similar history of using fertilisers. We are using suitable long-term and classical experiments at Rothamsted, Woburn and Saxmundham on sites where known manuring and cropping has allowed residues to accumulate; we are also increasing residues in some experiments more quickly than in the past by giving larger dressings. From 1970 onwards we will have the same manuring and cropping systems in experiments on the three kinds of soil to measure responses to fresh P fertiliser on soils containing various amounts of soluble P.

Residual and cumulative value of superphosphate in a three-course rotation. The results from the first six years of two experiments on residual and cumulative effects of different phosphate fertilisers were summarised in the *Rothamsted Report for 1966*, (p. 45) and *for 1967* (p. 46). In 1966, both sites (Sawyers I and Great Field IV) were fallowed and the experiments were modified to compare single dressings of 147, 293 and 440 lb P/acre in 1966 with cumulative annual dressings of superphosphate supplying 49 and 73.5 lb/acre; tests on potatoes, barley and swedes will continue for six years. Seven of the original 12 treatments were continued and five new treatments randomised on plots which, in 1959, had single dressings of 147 lb P/acre in different forms. Table 7 summarises results for the first three years.

#### TABLE 7

	Tatal D		Mean yields/acre, 1967-69			
	Total P applied (lb/acre)		Potatoes		Barley, straw*	
	1959-65	1966-69	(tons)	(cwt)	(cwt)	(tons)
Yield without P	0.0	0.0	12.40	28.6	25.8	5.06
			]	Increases	in yield	
(a) Annual dressing	73·5 147 147 147	36·8 73·5 147 220	$0.92 \\ 1.45 \\ 2.15 \\ 2.60$	7.6 7.6 6.7 6.7	6·9 9·0 10·3 7·4	$6 \cdot 94 \\ 9 \cdot 65 \\ 11 \cdot 04 \\ 10 \cdot 32$
(b) P in 1962, 1965, 1969	73·5 147	36·8 73·5	$\begin{array}{c} 0\cdot 11 \\ 1\cdot 43 \end{array}$	5·1 8·1	4·1 5·6	5·56 8·42
(c) P in 1959, 1966	147 147 147	147 193 440	$1.59 \\ 2.66 \\ 3.36$	5·8 8·6 7·1	$   \begin{array}{r}     10.5 \\     12.2 \\     12.9   \end{array} $	$10.00 \\ 11.69 \\ 11.85$
(d) P in 1959 (as superphosphate) (as Gafsa rock phosphate)	147 147	0·0 0·0	0·58 -0·12	5·5 5·6	3·1 3·1	3·60 4·39
S.E. of increase	-		$\pm 0.300$	$\pm 1.60$	$\pm 1.99$	$\pm 0.575$
* Crain and strow at 150						

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

\* Grain and straw at 15% moisture content.

**Potatoes.** Potato yields increased almost linearly with the amounts of P given either as three annual dressings (1967–69) or one dressing in 1966. 440 lb P/acre, given in 1966, gave largest yields,  $\frac{3}{4}$  ton/acre more than from annual dressings supplying altogether 220 lb P/acre. Mean yields from residues of single dressings supplying the same total amounts of P gave about  $\frac{1}{2}$  ton/acre less than cumulative dressings.

Total P	Mean yields (tubers) tons/acre					
applied 1966–69 (lb/acre)	From a single dressing	From cumulative dressings	Difference			
147	14.0	14.6	-0.6			
220	14.5	15.0	-0.5			
Standa	ard error $\pm 0$ .	21	±0·30			

**Barley.** Annual dressings of 12.3 lb P/acre gave grain yields as large as from residues from much larger dressings (Table 7). Residues increased straw yields and more than half the crop lodged severely in 1968 on Sawyers (but not on Great Field) where large dressings of superphosphate were given in 1966.

*Swedes.* Annual dressings of superphosphate (up to 49 lb P/acre/year) significantly increased yields, but larger ones (73.5 lb P/acre/year) produced slightly less (Table 7). The largest yields (as of potatoes) were from 440 lb P/acre given in 1966, but differences between cumulative and single dressings were less consistent than with potatoes.

Total P applied 1966–69 (lb P/acre)	Mean yields (total roots), tons/acre					
	From a single dressing	From cumulative dressings	Difference			
147 220	147 15.1		-1.0 + 0.5			
Standard	error $\pm 0.41$		$\pm 0.58$			

**Conclusions.** Applying fertilisers only every two or three years saves labour and giving P (and K) in autumn eases work during spring. These results show this can be done without risk at Rothamsted; single dressings of superphosphate (147–220 lb P/acre) maintained yields of potatoes within  $\frac{1}{2}$  ton/acre, and swedes within 1 ton/acre, of those obtained with the same total P given in each of three years at sowing. Single dressings of superphosphate gave as much or more barley than annual dressings. Residues from the largest dressings tested (293 and 440 lb P/acre), however, increased growth and weight of straw, particularly in wet years and these crops lodged severely. These results and others on West Barnfield, with continuous barley, suggest that single dressings of superphosphate in autumn should not supply more than 147 lb P/acre. (Mattingly)

#### Potassium, magnesium and sodium fertilisers

**Residual effects.** Ryegrass used to measure residual effects of K, Na and Mg fertilisers applied between 1960 and 1967 at Woburn gave an 54

unexpected result. Na residues increased yields up to the end of 1969 more than two years after it was last applied and after two winters with more than average rain. Chloride residues from NaCl significantly increased Cl uptake and % Cl in the dry matter during 1968 but not 1969. Potassium fertilisers had the largest residual effects but they were nearly exhausted by the end of 1969. Potassium concentrations in the dry matter have declined steadily since 1967 and did not increase between the last autumn and first spring crops, as would be expected if non-exchangeable reserves were released when the soil was frozen. Magnesium residues increased the Mg concentration in grass but not the yield of dry matter. (Bolton and Penny)

Effects of sodium and potassium fertilisers on the composition of ryegrass. Sodium can partly replace potassium for some plants but the effects of this on organic constituents have been little investigated. Italian ryegrass was grown in pots containing a potassium-deficient soil, with and without potassium and sodium sulphates (given on an equivalent basis) and two amounts of nitrogen. Table 8 shows yields and inorganic compositions

#### TABLE 8

Effects of nitrogen, potassium and sodium fertilisers on yields and the composition of the second cut of ryegrass

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(as ppm of weight of soil used)			DM yield	In g	grass dry ma	atter
N	K	Na	g/pot	%N	%K	%Na
40	0	0	3.94	1.76	1.94	0.04
40	120	0	4.37	1.65	2.21	0.04
40	0	70	3.85	1.80	2.20	0.42
40	120	70	4.23	1.73	3.05	0.23
160	0	0	6.19	4.53	0.73	0.05
160	120	0	9.92	2.77	1.19	0.04
160	0	70	8.80	3.12	0.82	0.33
160	120	70	10.84	2.64	1.20	0.57

of the second cut. (The two cuts showed similar effects, but yields of the second were larger.) Both sodium and potassium increased yields (especially with the larger dressings of nitrogen) but potassium more than sodium. Table 9 shows that grass given the larger amount of N contained less free amino acids, ammonia, and nitrate when also given either K or Na than when not; the two cations had generally similar effects but these were greater with potassium. Dicarboxylic acids and their amides and serine were most affected, alanine and 4-amino-*n*-butyric acid the least. Free methionine occurred only in grass given potassium, but except for this, it seems that whatever physiological processes are disturbed by K-deficiency, these can be at least partially corrected by Na.

**Protein** N in the grass of the second cut was increased by either potassium or sodium and more by both (Table 9). (Nowakowski and Bolton with Byers, Biochemistry Department)

Fertiliser supplying (as ppm of weight of soil used)				
Na	0	0	70	70
K	0	120	0	120
	µg ar	nino acid p	er 1.0 g dry	leaf
Aspartic acid	549	293	375	396
Asparagine	4050	283	1131	189
Threonine	903	280	360	211
Serine	1304	471	574	334
Glutamic acid	592	225	252	327
Glutamine	6362	730	1252	834
Proline	369	119	134	90
Glycine	129	53	61	44
Alanine	881	732	756	612
Valine	783	237	298	172
Methionine		25		8
iso-Leucine	369	132	164	99
Leucine	337	183	212	146
Tyrosine	242	119	148	99
Phenylalanine	485	208	258	178
β-Alanine	48	21	tr.	tr.
4-amino-n-butyric acid	1265	1024	1119	923
Ethanolamine	336	248	253	182
Lysine	548	169	205	118
Histidine	158	61	29	37
Arginine	318	108	133	78
Ammonia (as NH <sub>4</sub> )	990	244	270	103
Nitrate (as $NO_3$ )	6330	400	885	355
Tillate (as 1103)	0550	400	005	555
Protein N as % of total N	78	88	88	91

#### TABLE 9

#### Effects of potassium and sodium on free amino acids, ammonia and nitrate concentrations in Italian ryegrass

#### Reference Experiments at Rothamsted and Woburn

In the experiment begun at Rothamsted in 1960 to see whether calcium, sulphur, magnesium and a mixture of trace elements would affect yields of crops given ample N, P and K fertilisers (Rothamsted Report for 1964, 64), basal lime was applied in autumn 1965 because the pH on the plots then ranged only from 5.0-5.5. Since then the plots receiving calcium have had 5 cwt CaO/acre annually. The mean effects of applying NPK fertilisers without the other elements were large. They increased yields of wheat grain and of the ley by a half, they more than doubled yields of barley and of kale and more than quadrupled potato yields. Applying Ca, Mg or S or mixtures of trace elements with the NPK fertilisers had little extra effect. Magnesium decreased yields as often as it increased them. Calcium increased yields of the ley and of wheat and barley straw, but otherwise decreased yields. Sulphur slightly increased yields of all the crops except kale (which it decreased) but, in contrast to the other two elements, gave positive benefit in two-thirds of the comparisons. The trace elements usually scorched the leaves, but had no consistent effect on yield. Mean effects averaged over crops and as cwt dry matter/acre were: (1) -0.3for Mg, (2) +0.1 for Ca, (3) +1.3 for S and (4) -0.4 for the trace elements.

The experiment, started at Woburn in 1960 (Rothamsted Report for 1964, 63), completed its second five year cycle in 1969. As at Rothamsted, large yields of roots (sugar beet and potatoes) were obtained only where FYM and NPK fertilisers were applied together, so that the largest amount of fertiliser given (1.5 cwt N, 0.5 cwt P2O5, 2.0 cwt K2O/acre) was evidently too little. Mean yields of King Edward potatoes from 1960-69 with this amount of fertiliser alone were 12.4 tons/acre, but were 20.4 tons/acre when given together with 20 tons/acre of FYM. Sugar beet (Klein E) showed similar benefits; comparable yields were 15.6 tons/acre of washed roots with the most fertiliser and 20.4 tons/acre with FYM and fertilisers together; these roots gave 51.0 and 67.5 cwt sugar/acre respectively. The mean effects of N, P and K fertilisers from 1965-69 averaged over the five crops and in cwt dry matter/acre were: (1) 18.5 for N, (2) 0.2 for P and (3) 13.8 for K. N was important for barley, oats and sugar beet, but not for the grass-clover ley or the potatoes that followed it. P slightly increased yields of potatoes, but otherwise had negligible effects. K greatly increased yields of potatoes, sugar beet roots (but not tops) and the grass-clover ley; it increased yields of barley more than of oats. FYM greatly increased yields of potatoes and sugar beet, with or without NPK fertilisers, though the increase was a third less with the fertilisers. In 1965 Mg deficiency was confirmed in the sugar beet (Rothamsted Report for 1965, 46), so from 1966 Mg was tested on the sugar beet and from 1968 on the potatoes. Mg increased yields of sugar beet roots most on plots given K. Giving 0.75 cwt N/acre with the K did not change this result, but when 1.5 cwt N/acre was given the Mg increased yields little. FYM almost eliminated the response to Mg. The response varied greatly with treatment and with year, but was largest (2.2 tons/acre) with 0.75 cwt N, 0.5 cwt P2O5 and 2.0 cwt K2O. Mg similarly increased the yields of the sugar beet tops. In contrast to sugar beet, the potatoes responded consistently to Mg, although it gave the greatest increase where K or N and K fertilisers were also given. FYM diminished, but did not eliminate the response of potatoes to Mg. (Widdowson, Penny and Flint)

#### Experiments with organic manures

The experiment started on sandy loam soil on Stackyard Field, Woburn, in 1965 was described in *Rothamsted Report for 1967*, (pp. 37–38); it uses crop yields and soil analyses to compare the cumulative effects of different forms of organic manures. Plots given only fertilisers serve as controls, and the total nutrients applied are balanced each spring to allow for the different amounts removed by cropping. The net amounts of P, K and Mg applied by spring 1969, in organic or inorganic manures, or both, were:

	Р	K	Mg	
		(lb/acre)		
Green manure, peat, straw or equivalent fertilisers FYM or equivalent fertilisers	147 392	430 1090	54 203	

**Direct effects of organic manuring on wheat in 1968.** Winter wheat (Cappelle) was the third arable crop, following potatoes in 1967; the green manure was red clover undersown in the wheat. Table 10 gives yields of grain and shows the interactions between four amounts of N, applied as

#### TABLE 10

#### Yields of wheat on Stackyard Field, Woburn, with or without organic manures

## Yields of grain at 15% moisture content: cwt/acre

	1	N applied, lb/acre				Cton doud
(a) Inorganic manuring (PKMg) equivalent to straw + superphosphate	22	67	112	157	Mean	Standard error
Without organics Straw (3 tons/acre/year) Peat (3 tons/acre/year) Green manures	$21 \cdot 0$ $20 \cdot 5$ $21 \cdot 1$ $25 \cdot 5$	31.6 31.2 30.4 37.7	37·0 36·4 36·5 36·0	38·4 38·2 37·5 35·5	32.031.631.433.7	±1·09
(b) Inorganic manuring (PKMg) equivalent to farmyard manure						
Without organics Farmyard manure	20.6	33.4	37.5	36.8	32.1	±1.09
(20 tons/acre/year)	30.3	39.8	39.0	35.6	36.2∫	T
Standard error	$\pm 1.39$ (for horizontal comparisons) $\pm 1.63$ (for vertical comparisons)				ons)	

'Nitro-Chalk' in spring, and the organic manures or the fertilisers. Without organic manures, yields were the same at both amounts of PKMg fertilisers. Yields with straw and peat (a total of 9 tons dry matter/acre since 1965) were the same as with fertilisers supplying the same total amounts of P, K and Mg. Wheat benefited from neither the small increase in soil organic matter (discussed more fully below), nor from the larger amounts of PKMg applied as fertilisers equivalent to farmyard manure.

Green manures gave 4.5 and 6.1 cwt/acre more grain than equivalent inorganic PKMg with 22 and 67 lb N/acre, but almost the same yields (Table 10) with 112 or 157 lb N/acre. FYM gave 9.7 and 6.4 cwt/acre more grain than equivalent fertilisers with 22 and 67 lb N/acre but nearly the same yields with 112 and 157 lb N/acre. Wheat yielded more with green manures and with FYM than with equivalent dressings of inorganic fertilisers only when it was given too little N-fertiliser.

**Residual effects on wheat of N applied to potatoes.** The amount of N in the wheat grown in 1968 depended on the amount given to potatoes in 1967. The table below shows the mean amounts in wheat following potatoes given 22 lb N/acre, averaging all amounts applied in 1968, and the recoveries of N from 67, 112 and 157 lb N/acre given in 1967. (Recoveries from both fertiliser treatments, and from peat and straw plots did not differ significantly.)

N removed* by wheat in 1968 (lb/acre)				
Fertilisers	Green manures	FYM		
63.2	62.1	81.7		
Increases in +4.0 +6.9 +9.0	n N removed +7.9 +15.2 +19.6	by wheat +10.0 +9.4 +7.0		
$\pm 1.78$	±4	·26		
	Fertilisers only $63 \cdot 2$ Increases in $+4 \cdot 0$ $+6 \cdot 9$ $+9 \cdot 0$	(lb/acre) Fertilisers Green only manures $63 \cdot 2$ $62 \cdot 1$ Increases in N removed $+4 \cdot 0$ $+7 \cdot 9$ $+6 \cdot 9$ $+15 \cdot 2$ $+9 \cdot 0$ $+19 \cdot 6$		

\* Average of all rates applied in 1968.

The percentage of N applied in 1967 and 1968 (means of 67, 112 and 157 lb N/acre minus 22 lb N/acre) recovered by the wheat in 1968 were:

....

	%N recovered from					
Year applied	Fertilisers	Green manures	FYM			
1967	7	17	10			
1968	48	41	37			

The extra N coming from 'Nitro-Chalk' given to potatoes increased yields of wheat on green manure plots by  $4.6 \pm 1.79$  cwt/acre; the smaller amounts recovered on fertiliser and FYM plots had negligible effects on yield.

**Grass leys, 1965–68.** Leys containing timothy, meadow fescue and smooth-stalked meadow grass, with and without white clover, were established in 1965. 56 lb N/acre was given to the grass ley each spring and after each cut. Total yields and the nutrients removed in four years were:

Totals, 1965-68	Grass-clover ley (Lc)	Grass ley (Ln)
Dry matter (cwt/acre)	161	198
N	455	316
P	58	57
K > lb/acre	478	506
K   lb/acre Ca	199	107
Mg	31	29

The grass-clover ley produced about 2 tons dry matter/acre/year and the ley, with inorganic nitrogen, about  $2\frac{1}{2}$  tons. Similar amounts of P, K and Mg were removed by the two leys, probably because differential removals were adjusted by balancing dressings each spring. The clover ley removed more N and Ca than the grass ley.

Over four years, the nitrogen content of the soil (Table 11) under the grass-clover ley increased by 0.006 and by 0.004% N under the all-grass leys. The total N given to the grass ley was 504 lb/acre. Assuming one acre of soil (0–9 in.) weighs  $3 \times 10^6$  lb, the amounts of N removed or accumulated in the soils were:

	ley lb N/acre	Grass ley lb N/acre	
Removed in herbage Accumulated in soil	455 180	316 120	
Total	635	436	(Mattingly)

**Changes in C, N, organic P and soluble P.** Table 11 gives some analyses on soil samples in 1964 before sowing the first crops and in October 1968 before ploughing, and shows changes for the main treatments (averaging all amounts of N) between 1964 and 1968. Total C, which decreased slightly where organic manures were not given, increased most on plots given peat (+0.27%) and least (+0.04%) on plots given straw. Changes in carbon and N contents were highly correlated (r = 0.927\*\*) for the seven treatments excluding peat. Much more C than N accumulated in plots given peat.

#### TABLE 11

#### Total carbon, nitrogen, organic P (by ignition) and 0.5M NaHCO<sub>3</sub>-soluble P in 1964 and increases between 1964 and 1968 (averaging over all N treatments)

	%C*	%N	Organic P, ppm (by ignition)	0.5 M NaHCO <sub>3</sub> - soluble P (ppm)
Mean value in 1964	0.77	0.085	227†	28
<ul> <li>(a) Inorganic manuring (PKMg) equivalent to straw + super- phosphate</li> </ul>		Increases	1964 to 196	8
Without organics Straw (3 tons/acre/year) Peat (3 tons/acre/year) Green manures Ley, clover Ley, inorganic N	$- \begin{array}{c} - 0 \cdot 03 \\ 0 \cdot 04 \\ 0 \cdot 27 \\ 0 \cdot 07 \\ 0 \cdot 15 \\ 0 \cdot 09 \end{array}$	$\begin{array}{c} -0.003 \\ 0.003 \\ 0.002 \\ 0.002 \\ 0.006 \\ 0.004 \end{array}$	8 18 13 20 33 6	13 12 15 12 7 11
(b) Inorganic manuring (PKMg) equivalent to farmyard manure				
Without organics Farmyard manure (20 tons/acre/	0.00	-0.006	7	33
year)	0.15	0.010	25	28
Standard error of increase * Walkley-Black, ×1·3. †135 ppm	12 10 10 10 10 10	$\pm 0.0018$ tion.	±4·9	$\pm 1.6$

The mean organic P in the soils in 1964, estimated by W. M. H. Saunders and E. G. Williams' ignition method (J. Soil Sci. (1955), 6, 254–267), was 227 ppm P. Without organic manures it had increased slightly  $(7-8 \pm 4.9 \text{ ppm})$  by 1968 and significantly  $(13-33 \pm 4.9 \text{ ppm})$  with all organic manures, except the ley dressed with 'Nitro-Chalk'. Changes in soil carbon (excluding the peat treatment) were positive correlated  $(r = 0.758^*)$  with changes in organic P by ignition.

Sodium bicarbonate-soluble P increased significantly on all plots between 1964 and 1968, least in the clover ley plots where the most organic P had accumulated. Increases on the plots without organic manures (+13 and +33 ppm P) were 25–27% of the net gains in total P (147 and 392 lb P/acre) since 1964. In the Rotation II experiment at Saxmundham, NaHCO<sub>3</sub>-soluble P also increased, between 1965 and 1968, by about one-quarter of the total P gained by the soil (*Rothamsted Report for 1969*, Part 2, 109). (Mattingly)

 $\mathbf{NII} + \mathbf{I} \mathbf{NO} = \mathbf{N}(\mathbf{nnm})$ 

**Mineralisable nitrogen.** Soils taken in 1968 under wheat stubble were incubated at 25°C for 3 and 8 weeks. Table 12 gives the total mineralisable N (NH<sub>4</sub><sup>+</sup> + NO<sub>3</sub><sup>-</sup>) in the soils with inorganic fertilisers and the increases with organic manures. The amounts mineralised varied much more after 3 than after 8 weeks.

#### TABLE 12

#### Mineralisable N in soils after wheat in 1968 (averaging over all N treatments)

$NH_4^+ + NO_3^ N$ (ppr	
After 3 weeks	After 8 weeks
18.6	21.5
8.9 1.5 2.6 11.6 0.2	8·1 0·3 7·9 12·8 5·3
10.2	21.7
18.2	21.7
3.4	6.4
±3·87	$\pm 1.14$
	After 3 weeks 18.6 8.9 1.5 2.6 11.6 0.2 18.2 3.4

These tests confirmed that soils with residues of green manures and farmyard manure, even at the end of the growing season, release significantly more N than soils without them. Nitrogen residues from peat were inert. Although yields of wheat (Table 10) were the same without as with straw or peat, straw residues released some nitrogen on incubation. Nitrogen, immobilised when straw is ploughed under during autumn, probably mineralised too slowly to affect the growth of wheat. (Chater and Mattingly)

#### Organic phosphorus in soils

How manuring and cultivations affect the amounts of organic phosphorus in Rothamsted soils has not been measured for 30 years. Jenkinson (*Rothamsted Report for 1965*, 77–78) found extraction and ignition methods gave different results and emphasised that results by currently accepted methods must be interpreted cautiously. Organic P was estimated in a range of Rothamsted surface soils (Table 13) by Saunders and Williams' ignition method and by the extraction method of N. C. Mehta *et al.* (*Proc. Soil Sci. Soc. Am.* (1954), **18**, 443–449). Ignition gave, on average, 108 ppm P more than extraction, as Jenkinson found with soils from Broadbalk Wilderness. Organic P (by extraction) ranged from 34% of the total soil P under unmanured old grass (Park Grass, Plot 2 + 3 L) to 7% in Barnfield soil (Plot 4-N), continuously cultivated since 1843.

Inositol penta- and hexa-phosphates (IPP and IHP) were extracted from the soils and estimated by ion-exchange chromatography on Dowex-1 (formate) by Anderson's method (*Trans. 8th int. Congr. Soil Sci.*, Bucarest (1964), **IV**, 563–572). The two esters, which were not estimated separately, ranged from 38 ppm in the arable soil (Barnfield Plot 8-N), not given phosphate since 1843, to 90 ppm in the mineral fraction of unlimed Park Grass soils (Plot 16U), given superphosphate for more than a century (Table 13). Inositol phosphates were 29–45% of the total organic P, about the same range as Anderson found for Scottish soils. Liming Park Grass soils lessened the proportion of inositol phosphates slightly.

#### TABLE 13

#### Total and organic P (by extraction and ignition) and total inositol pentaphosphates (IPP) and hexaphosphates (IHP) in Park Grass and Barnfield soils

			pH		Organic	P (ppm)	IPP +	(IPP + IHP) as %
Soil	Plot No.	Treatment*	0.01M CaCl <sub>2</sub>	Total P (ppm)	Extrac-	Igni- tion	IHP (ppm)	organic P (extraction)
Park Grass (mineral soil) approx. 3-9 in.	$\begin{cases} 2+3U\\ 2+3L\\ 16U\\ 16L \end{cases}$	Unmanured Unmanured NPKNaMg NPKNaMg	4.5 6.4 4.6 6.2	510 640 1032 1238	152 218 245 280	257 324 320 370	48 64 90 80	32 29 37 29
Barnfield 0-9 in.	$\begin{cases} 1-N\\ 2-N\\ 4-N\\ 8-N \end{cases}$	FYM + N FYM + NPK NPKNaMg N	7·1 7·1 7·4 7·4	1276 1748 1234 688	130 132 88 112	256 377 153 168	42 42 40 38	32 32 45 34

\* Nitrogen as sodium nitrate.

Repeated dressings of superphosphate and FYM scarcely changed either the total organic P or inositol P in the arable soils. About 18% of the total P remaining from superphosphate was converted to organic P at pH 4.6 and about 10% at pH 6.2–6.4 in soils from the permanent Park Grass Experiment.

Similar measurements were made on very acid soils from the Tea Research Institutes of Georgia (USSR) and Ceylon. Repeated applications of superphosphate have increased total organic P (+ 47 ppm) and inositol phosphates (+ 17 ppm) in the Georgian soils but not in the Ceylon soils, which contain only 2–3 ppm of inositol phosphates.

		pH in		ppm in soi	1
		0.01 M CaCl <sub>2</sub>	Total P	Organic P (extraction)	Inositol
Georgia (USSR)	$\begin{cases} no P \\ P \end{cases}$	3·4 3·2	510 1926	115 162	37 54
Ceylon	{no P P	3.6 3.7	736 1944	288 270	23
			(Onian	i, Chater and	d Mattingly)

#### Potassium in soils

Applications of the potassium quantity/potential relationship. The quantity/ potential relationship for potassium relates change in exchangeable K to potassium potential, defined as the change in free energy associated with 62

replacing one equivalent of K by one equivalent of Ca + Mg (treated together),  $\Delta \overline{G} = \operatorname{RT} \ln \frac{a_{\mathrm{K}}}{\sqrt{a_{\mathrm{Ca+Mg}}}}$ . Alternatively change in exchangeable K

may be related to the activity ratio  $\frac{a_{\rm K}}{\sqrt{a_{\rm Ca} + Mg}}$ .

Quantity/activity ratio (Q/I) curves of soils given different K manuring. Q/I curves were measured for soils from different treatments in the Broadbalk, Hoosfield and Barnfield experiments at Rothamsted and the Market Garden, Ley-Arable and Classical Barley experiments at Woburn. Within each experiment, the Q/I curves were super-imposable, both mutually and on the curve obtained by plotting ammonium-exchangeable K against the equilibrium activity ratio for the state when K is neither gained nor lost by the soil. Curves for Broadbalk and Hoosfield (both have grown cereals continuously for more than 100 years on the same phase of the Batcombe Series) were super-imposable, but differed from curves for the Barnfield soils, which are on a different phase of Batcombe soil and have grown mangolds during most of the last century. At Woburn, the ley-arable and classical barley experiments are at opposite ends of Stackyard field, their Q/I curves differed slightly and both differed from curves for the Market Garden experiment (which is a mile away). The K buffer capacities of the soils (measured as the slope of the tangent to the Q/I curve where the soil neither gains nor loses K) was, within each experiment, related to the %K saturation of the cation exchange capacity.

**Comparisons of extractants for removing soil K.** The quantity/potential relationship shows how the K-potential in a soil falls as K is extracted and can be used to compare both electrolyte solutions and species of plants as extractants. Mean values of 'soil extraction potentials' were obtained for 27 Rothamsted and Woburn soils using three extractants that differ in pH and exchanging cation:

Neutral N ammonium acetate	$-4995 \pm 97$ cal/eq
H-resin (1 hour extraction)	$-6081 \pm 88$ cal/eq
0.5 M sodium bicarbonate (pH 8.5)	$-4336 \pm 117$ cal/eq

In mixtures of ammonium acetate and acetic acid, normal in acetate ions, changing the normality of ammonium ions from 0.1 N to 1 N affected the ability to extract K very little. A mixture of ammonium acetate and ammonium hydroxide (0.5 N : 0.5 N) removed a similar amount of K. Repeated extractions with neutral N ammonium acetate were significantly more effective than one extraction.

*Measuring 'uptake potentials'.* The potential that limits uptake of soil potassium by a crop ('the uptake potential') was derived for ryegrass, potatoes and lettuce from K taken up by these crops and the K quantity/ potential relationships of the Rothamsted soils in which they were grown. Because there is no way of knowing when a crop stops taking up initially available K, a measurement analogous to the 'soil extraction potential'

is not possible. However, the amount of K that can be removed from a soil to bring its K potential to a specified value was again used to measure K availability, and the uptake potential was found by determining what K potentials gave values of available K best correlated with K uptakes.

With Rothamsted soils growing perennial ryegrass, the uptake potential remained unchanged at -5600 cal/eq during the first three cuts. Even after 608 days, when about twice as much K had been taken up as was initially available, the grass still grew and the mean potentials in Rothamsted and Woburn soils had fallen to only  $-5189 \pm 76$  and  $-5336 \pm 86$  cal/eq respectively. With Pentland Dell potato plants, harvested before tubers were set, the uptake potential inferred was -4150 cal/eq. When tubers were set, and all the initially available K used, uptake potential was -4900 cal/eq; K potential measured directly in the exhausted soils was -4710 cal/eq. Two crops of lettuce were grown in succession in the same soils; for the first crop the uptake potential was -5100 cal/eq and for the second crop -4900 cal/eq.

The results suggest that the uptake potential for lettuce and ryegrass does not alter as soil K is used. Change in uptake potential for potatoes may be because of increased demand for K when tubers are set. This method of measuring uptake potential could not be used for ryegrass grown in Woburn soils because K was released faster than in Rothamsted soils. Neither potatoes nor lettuce took up initially non-available K; ryegrass did. (Addiscott)

**Release from soils at different pH values.** In some laboratory work, increasing soil acidity increased the release of non-exchangeable K, but this has not been confirmed by other work using solutions or plants to remove K. Ryegrass grown in pots and repeatedly cut was used to remove non-exchangeable K from two acid K-deficient soils limed to several pH values from 4.5 to 7.5. The release of K that was not exchangeable with NH<sub>4</sub><sup>+</sup> was decreased by liming either soil (Woburn (Stackyard) and Rothamsted (Sawyers)) up to about pH 5.5. Potassium intensities (activity ratios in solutions in equilibrium with the soils) were lessened by liming. The first crops of ryegrass considerably decreased intensities and further crops still more; there was no recovery towards the initial intensities during cropping as was reported by Talibudeen and Dey (*J. agric. Sci. Camb.* (1968), **71**, 95–104). Intensities increased considerably when cropped soils were air-dried but did not reach their initial values. (Islam and Bolton)

#### Sulphur deficiency

Last year we reported that elemental sulphur increased yields of a first crop of spring-sown radishes on a sandy podsol at Wareham (Dorset), but decreased yields of second and third crops, probably because the soil became acid. In 1969 three successive radish crops were grown with and without sulphur on a different site at Wareham limed to pH 7. Sulphur increased the dry matter of the first crop, but had no effect on the second and third crops, (Table 14); nor did it affect soil pH. The amount of 64

sulphur in radishes in untreated soil again increased during the season, but the reason is not known. (Bolton)

#### TABLE 14 Effects of sulphur on dry matter of radishes at Wareham in 1969 Third crop Second crop First crop %S in DM %S in DM Yield Yield Yield %S S applied g/m<sup>2</sup> g/m<sup>2</sup> in DM g/m<sup>2</sup> g/m<sup>2</sup> 0.50 0.22 185 0.37 136 227 0 19 0.82 192 0.81 132 0.84275 ±5.6 ±0.016 +8.9 $\pm 0.014$ $\pm 2.4$ $\pm 0.027$ Standard errors

#### Copper deficiency in conifer seedlings

'Needle tip-burn' of Sitka spruce (*Picea sitchensis*) was identified as a sign of copper deficiency in 1955 and shown to be preventable by spraying seedlings with solutions of copper salts. The symptoms commonly appear during hot dry spells and were much more in evidence at Wareham this year than for some years. However, they occurred only on plots not previously sprayed, and seedlings on plots treated as long ago as 1965 were free from the symptoms. Seedlings are small when they are sprayed, so that much of the solution reaches the soil and residues remain. Seedlings with symptoms had  $2\cdot4$  ppm Cu in dry matter of tops (similar to the amount found in 1955). Where sprays were applied in 1960–65 (with none since) the plants had  $4\cdot0$  ppm, and where sprayed in 1967 and 1968,  $5\cdot8$  to  $6\cdot4$  ppm of Cu. (Benzian and Freeman, with Hill, Biochemistry Department)

# The effect of aluminium in Ceylon soils on growth and composition of tea seedlings

Tea in Ceylon is given much N and some P and K; the N gives profitable increases in tea leaf but the K seldom has large effects on yield. Ammonium sulphate, the traditional N fertiliser, has made the soils so very acid (often pH 3.2) that they contain much exchangeable and non-exchangeable aluminium and tea leaves may contain as much as 2.5% Al in dry matter. There is little known about how soil Al affects growth and composition of tea, how much Al may be taken up without damaging the crop, or how uptake can be prevented. Also lowland and upland soils contain different amounts and kinds of organic matter, which could affect the behaviour of aluminium. Soils from long-term manurial trials in Ceylon were used to study some of these points.

**Exchangeable and non-exchangeable aluminium** were separated by leaching with M NH<sub>4</sub>Cl at the soil pH; exchangeable Al was extracted in about 15 hours, when the non-exchangeable Al leached out at a constant rate, roughly equivalent to the solubility of gibbsite at the soil pH. Although the *total* exchangeable Al changed from 2.9 to 4.8 me/100 g with increasing elevation of the sites from where the soils came, the exchangeable Al

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per g of  $<2 \mu$  clay was remarkably constant (0.119  $\pm$  0.012 me). M ammonium acetate (at pH 4.8) extracted more Al than M ammonium chloride from all soils, and the amount extra was closely associated with soil organic matter.

**K**: Al exchange isotherms of the Ceylon soils showed that when the exchange capacity was <10-15% saturated with K, Al was taken up preferentially by the soil, but after soil organic matter was removed by mild oxidation, K was greatly preferred. Increasing the equivalent ion ratio of K : Al in the soil solution from 9.0 to about 12.5, increased the %K saturation from 15% to 40% in untreated and oxidised soils, greatly increasing K-selectivity. At equivalent ion ratios exceeding 12.5, K selectivity decreased as more K was adsorbed. At K : Al ratios in solution similar to those expected in the field, soil organic matter increased the activity of the K in the soil relative to that of Al. (In Exhaustion Land soil from Rothamsted, which has < 1% organic C, K is preferred to Al more than in Park Grass soil, which contains > 3% organic C.)

Soil organic matter was fractioned by NaOH extraction and by centrifuging. Three groups of  $pK_a$  values in the range 2.1-5.9 resembled those given in the literature for fractionated soil organic matter extracts, and indicate functional groups that alter the relationship between free and combined aluminium. (Sivasubramaniam and Talibudeen)

A glasshouse experiment measured the effect of ranges of K and Al concentrations (0-10<sup>-4</sup> M K and 0-2.5  $\times$  10<sup>-3</sup> M Al) maintained in soil solutions for 10-12 months on the growth and nutrient composition of tea seedlings; changes in the soil : water complex during cropping were compared with those predicted by laboratory work. An acid soil (pH 3.9 in 0.01 M CaCl<sub>2</sub> solution) from the Exhaustion Land at Rothamsted was used. Blocks of small and large tea seedlings (Camellia sinensis) 36 weeks old were used, part of these were harvested after six months. Increasing K concentration increased height and the largest Al concentration decreased it; these effects were not significant in blocks planted with large seedlings. but were significant for small seedlings; with the largest Al concentration, increasing the K concentrations greatly increased height. Leaf number was significantly increased by the largest K concentration only with the most Al. Increasing Al decreased number of leaves significantly for small but not for large plants. %K in the dry matter of the first mature leaf increased with increasing K concentration but was not affected by Al concentration; %Al in leaf was not altered by change in either K or Al concentrations. Only the largest concentration of soil K increased the dry yield of plants; the largest amount of Al decreased it. %K in stems and leaves was increased by increasing K concentration but not affected by concentration of Al.

When K : Al ratios in the soil solution are less than a critical value, dry matter yield, plant height, number of leaves and %K in tea seedlings are adversely affected by increasing soil Al concentrations and are increased by increasing K concentrations. The critical K : Al ratio was between 66

4.0 and 6.0; there was no significant interaction between Al and K uptakes, but Al uptake increased linearly with P uptake (mole ratio Al :  $P = 2.79 \pm 0.277^{***}$ ). (Sivasubramaniam, Talibudeen and Mitchell)

#### Herbicides

Simazine and beans. On Barnfield simazine again decreased yields, and did so more on the plot given only fertilisers than on the plots given FYM + fertilisers. (One lb/acre of simazine was used in both years as this is recommended for medium to heavy soils.)

	Yields of beans cwt/acre				
	Without simazine		With simazine		
Annual manuring (1876–1969)	1968	1969	1968	1969	
None PKNaMg fertilisers 14 tons/acre FYM + PK fertilisers	25·7 30·8 31·9	19·2 23·7 22·1	7·6 16·7 29·6	6·5 12·8 21·0	

After the results for 1968 were known, the interaction of simazine and soil organic matter on the yield of beans was studied by using an experiment started at Woburn in 1963 to study organic matter and soil structure (Rothamsted Report for 1966, 38). Annual dressings of peat given to some plots had caused large differences in the %C in the soil by autumn 1968 but, because the same dressings of fertilisers were used on all plots, there were no large differences in soluble soil P and K. Bicarbonate soluble P was 84 to 89 ppm P, ammonium acetate soluble K was 169 to 184 ppm, much smaller differences than on Barnfield between the fertiliser and FYM plots and unlikely to affect bean yields. The amount of simazine recommended for use on light soils is 0.75 lb/acre in 20-100 gallons of spray. None, 0.42, 0.84 and 1.68 lb/acre were tested. All the cultivations, including drilling the seed about 3 in. deep, and harvesting, were done by hand. Weeds were well controlled by all amounts of simazine right through to harvest. Two periods of heavy rain, one late April, the other early May, washed enough simazine into the root zone of the beans to affect their early growth on some plots. With the most simazine given, early growth on plots containing the least soil organic matter was diminished by about half. Table 15 shows that this had persisted to harvest, for grain yields were almost halved on the most affected plots. Simazine applied at about the recommended amount caused an appreciable yield loss where soil was poor in organic matter. However, the most simazine did not affect yield on plots containing most soil organic matter. Without simazine, yield increased with increase in soil organic matter and the larger yields were as good as any at Woburn in 1969.

Simazine will be applied again in 1970 and the residues from the largest amount given in 1969 will be tested. All our results show that, when beans are sprayed with simazine in experiments where previous treatments have altered soil organic matter, yield may be affected by the interaction of simazine and soil organic matter. Also, yields from soils containing little

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#### TABLE 15

#### Effect of simazine and soil organic matter on beans at Woburn in 1969 Simazine %C in air dry soil\*

added 1969							
lb/acre	0.66	0.74	1.15	1.55	2.28		
Yields of g	grain at 15	% moist	ure conte	nt: cwt/a	cre		
0 0·42	19·7 17·6	18·9 20·2	$21.0 \\ 23.7$	22·5 22·6	$24 \cdot 8$ 23 · 9		
0·84 1·68	12·7 11·8	12·9 15·0	19·3 19·2	$22 \cdot 2$ 20 \cdot 0	22·9 23·1		

\* Samples taken autumn 1968 0-12 in. deep, %C by Walkley-Black multiplied by factor 1.3.

organic matter will probably be less when simazine is used than when weeds are killed mechanically.

After harvest but before the land was ploughed, samples of (almost air-dry) soil were taken 0–2 in. and 2–4 in. deep, rubbed through a 2 mm sieve and subsampled for bioassay tests with turnips. Apparent simazine concentrations in the 0–2 in. samples are given below. ('Normal' arable top soil from Woburn has about 0.8 %C.)

	%C in air-dry soil 0–12 in.						
lb/acre	0.66	0.74	1.15	1.55	2.28		
	Apparent simazine concentrations in ppm in 0-2 in.						
0.42	0.2	0.1	_	_			
0.84	0.2	0.3	_		_		
1.68	>0.8	>0.8	0.5	_	-		
	0.42	ded in 1969         0.66           Jb/acre         0.66           Ap           0.42         0.2           0.84         0.2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ded in 1969 $\gamma_{10}$ in an 20 cm 0 12 in           lb/acre $0.66$ $0.74$ $1.15$ $1.55$ Apparent simazine concentration in ppm in 0-2 in. $0.42$ $0.2$ $0.1$ $$ $0.84$ $0.2$ $0.3$ $$ $$		

Only the two soils with the least carbon contained simazine in the 2–4 in. samples, approximately 0.2 ppm from the two largest amounts applied. (Johnston and Briggs)

Sorption of herbicides by soil. In attempts to develop general principles of sorption of chemicals by soils, work continued on the relation between chemical structure and sorption of herbicides, their metabolites and other compounds. Sorption isotherms on four Rothamsted soils were determined for various anilines or their carbamate, anilide or urea derivatives; also some work was done with nitrobenzenes, phenols and catechols. Sorption increases linearly with increases in soil organic matter, and the organic matter/water partition coefficient (Q) is approximately constant whatever the origin of the soil. Several substituted phenylureas were synthesised to test a hypothesis based on the formation of donor-acceptor complexes. The Hammett constant,  $\sigma$ , for the substituent on the phenyl ring was the best predictor of sorption; 70% of the variation in log Q is explained by  $\sigma$ , which measures the relative power of substituent to withdraw or give electrons. Substituents on the side-chain nitrogen produced similar effects related to their inductive effect measured by the Taft constant,  $\sigma^*$ .

Increasing the length of alkyl chains produces a regular increase in log Q; this is independent of electronic effects. Work with a series of specially synthesised alkyl-N-phenylcarbamates indicated that the effect on 68

sorption of adding an extra methylene group is similar in widely different molecular environments. There seem to be two different effects in sorption of herbicides by soil: an electronic effect independent of water solubility, and a hydrophobic bonding effect measured by octanol/water partition and inversely related to water solubility. A more theoretical approach based on linear free-energy relationships now being developed predicts a linear relationship between the Hammett constant and log Q. (Briggs)

#### Sorption of 6-chloropicolinic acid by soils

The nitrification inhibitor, 'N-Serve' (Registered trademark of The Dow Chemical Company, Midland, Michigan), hydrolyses in soil to 6-chloropicolinic acid (6-CPA), whose sorption by 42 samples from 18 soil types was investigated. The soils used were from Rothamsted and Woburn and other places in England, two lateritic soils from Jamaica and four from Ceylon, and an acid loam from Georgia, USSR. There were calcareous and non-calcareous sandy loams and clay loams, pH ranged from 3-2 to 7-8 and organic carbon from 0.78% to 43.3%. Solutions of <sup>14</sup>C-carboxyl labelled 6-CPA in water adjusted to pH 7 with NaOH were mixed in centrifuge tubes with the soils, incubated at various temperatures for different times, mixed again, centrifuged, and the radioactivity remaining in the supernatant fluid measured; apparent sorption was calculated.

As the pK of 6-CPA is 3.55 at about pH 4.5, it is 90% ionised and, at pH 5.5, almost all ionised. The anion should be repulsed by negatively charged parts of clay and organic matter and attracted to the lipophilic parts of the organic matter. The net effect is slightly positive or 'negative' sorption in neutral soils. The 6-CPA anion is also attracted to the positive surfaces of hydrated iron and aluminium oxides. The un-ionised molecule probably is not repulsed by any part of the soil surface and is capable of hydrogen bonding to either organic or mineral surfaces, and is more lipophilic than the anion. The net effect is increasing sorption with decreasing pH (usually coupled with increasing organic matter) and with increasing amounts of hydrated iron and aluminium oxides in the soils. KCl decreases sorption in soils with much hydrated iron and aluminium oxides because 6-CPA is displaced by chloride. For soils that sorb 6-CPA strongly, as concentration of 6-CPA in solution increases relative to the surface available, per cent sorption decreases because the surface approaches saturation. Moist and oven-dried soils have less immediately available surface for sorption than air-dried soils, and 3 mm aggregates less than 60-mesh soils.

The similarity in sorption of 6-CPA at 7°C and 25°C when incubating for 24 hours suggests the bonding mechanisms are not significantly affected by temperature over the range investigated. Temperature has a substantial effect on apparent sorption during four weeks' incubation; changes in the soil surface and composition, or in the forms or amounts of 6-CPA or decomposition products present, can be caused by differences in incubation temperature. Even at 7°C, there was no consistent pattern of apparent sorption of 6-CPA during 24 hours incubation compared with four weeks. Analyses of soil solution mixtures incubated for four weeks at

7° and 25°C indicated decomposition of 6-CPA especially at low initial concentrations and with neutral or alkaline soils. (Goring)

#### Apparatus and methods

Measuring chloride in plants. Our standard method, using a Volhard titration after ashing the plant material with added alkali, is tedious for many samples. A potentiometric titration with 0.01 N silver nitrate was developed to measure chloride directly in a suspension of 200 mg plant dry matter in 2 ml of alcohol and 2 ml 0.1 N nitric acid, heated for 10 minutes and cooled. The alcohol (added first) eliminates wetting problems and makes the silver chloride less soluble. To avoid having a salt bridge in addition to a silver micro-electrode in the small titration vessel, a Pt electrode fused into the tip of the burette (containing AgNO<sub>3</sub>) was used as the standard electrode (Sanderson, P. H., Biochem. J. (1952), 52, 502). The burette tip was inserted into the suspension while titrating and stirring with a magnet. The end point was nearly always at the same potential (220 mv). The new method was much faster and at least as accurate as the old one. Using 200 mg dry matter, the standard errors of single measurements were equivalent to  $\pm 0.016\%$  Cl, and with 500 mg,  $\pm 0.006\%$  Cl in sugar beet tops (mean 1.22%) and roots (mean 0.042%) respectively. (Bolton)

**Comparison of grass species as test crops in glasshouse experiments.** Perennial and Italian ryegrass have been much used to remove nutrients (N, P, K, Mg, Mn) from soils. Yields during autumn and winter, even with supplementary lighting, are much less than during spring and summer. Three experiments in 1968–69 compared the growth of and N-uptake by nine grasses grown between March and June without supplementary lighting, with grass grown between October and January both with and without artificial light; perennial (S23) and Italian ryegrass (S22) were the standards. Timothy, meadow fescue, New Zealand crested-dogstail and cocksfoot consistently yielded less, and Westerwolds ryegrass (*Tewera tetraploid*) and, to a lesser extent, Italian ryegrass (S22) yielded more than S23. Some results with four grasses, summarised in Table 16, show that

#### TABLE 16

### Mean yields (dry matter, g/pot) and nitrogen uptakes (mg N/pot) from three cuts of four grass species from three experiments

	March-June		(With artificial lighting)		October–January (Without artificial lighting)	
	DM	N-uptake	DM	N-uptake	DM	N-uptake
Westerwolds ryegrass Italian ryegrass (S22) Perennial ryegrass (S23) Timothy (S51)	6·7 5·7 4·9 3·3	96·2 92·2 97·4 86·2	$2 \cdot 2$ $2 \cdot 2$ $1 \cdot 7$ $1 \cdot 1$	41 · 9 44 · 5 41 · 1 27 · 0	1.5 1.6 1.2 0.6	48.8 50.1 36.8 22.8
Standard error	$\pm 0.16$	$\pm 1.50$	±0.06	$\pm 1.48$	$\pm 0.03$	±1.46

most species and varieties took up the same or less nitrogen than S23 during spring or winter under artificial lighting. Although yields were 70

increased considerably and consistently by lighting, N-uptake was not. Westerwolds and Italian ryegrass took up more N than other grasses without extra light than with artificial lighting. In winter, without lighting, Italian ryegrass took up more N than S23 and two other strains of perennial ryegrass (S24 and S321), meadow fescue, Westerwolds ryegrass and Italian ryegrass all removed more nitrogen than S23. Either Italian ryegrass or Westerwolds ryegrass seem more useful test crops than perennial ryegrass in experiments during winter. (Mitchell)

#### Staff and visiting workers

J. Ashworth, V. Cosimini, Brenda Messer and K. W. Petts were appointed to the staff, and P. H. Le Mare to a three-year Fellowship sponsored by Overseas Development Ministry.

Visiting workers included Dr. C. A. I. Goring (USA), Dr. A. Islam (Pakistan), Mr. L. Lawal (Nigeria), Dr. O. G. Oniani (USSR), Mr. S. Sivasubramaniam (Ceylon), Dr. H. Glebowski (Poland).

J. Bolton attended a Symposium on 'Sulphur in Agriculture' at Wexford (Eire) in October. G. W. Cooke attended a Colloquium on the Transition from Extensive to Intensive Agriculture, arranged by the International Potash Institute in Israel during March, as a guest of the Institute. In October he visited the Rubber Research Institute of Malaya at the invitation of the Director. J. K. R. Gasser visited Agricultural Research Institutes in Czechoslovakia at the invitation of the Director of the Institute of Plant Nutrition, Prague and with the help of a grant from the Royal Society. A. R. Bromfield went to Samaru, Nigeria, to start research on sulphur in local soils and crops; the work will last for several years.

J. K. Coulter (now Tropical Soils Adviser) was awarded the Ph.D. degree of London University for work done in the Department.