

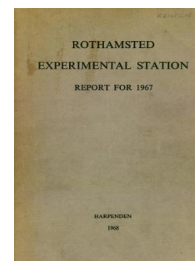
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CHEMISTRY DEPARTMENT

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Our research is mainly concerned with chemical problems affecting the fertility of soils. Field experiments on the nutrition of crops not only provide the evidence needed to decide how to use fertilisers and manures efficiently but also the soils and plant material for study in the laboratory. Things done, or material added, to soil for one crop can have lasting effects of great importance. Hence, most of our newer field experiments are intended to last through at least one sequence of crops, and some are planned for much longer. For studying residual effects we also make much use of the Classical and Long-term experiments at Rothamsted, Woburn and Saxmundham. We still do some experiments that last only one year, particularly with nitrogen fertilisers, which, in the United Kingdom, have large immediate effects but (proportionately) small residual ones. Such single-year experiments are of little use for advice on using phosphate and potash fertilisers (the residual effects of which may be greater than their immediate ones) unless these can be well related to chemical and physical properties of soil, and to previous use of the land.

Experiments with organic manures

An experiment was started in 1965, on sandy loam soil at Woburn long in arable cropping, using crop yields and soil analyses to evaluate cumulative effects of organic matter. Four organic manures are used each year and ploughed-in during autumn:

Farmyard manure (FYM) at 20 tons/acre
 Green manure grown when practical
 Chaffed straw } supplying 3 tons dry matter/acre
 Sedge peat }

Long leys (grass treated with N fertiliser, or clover plus grass) were established in 1965. Italian ryegrass was the green manure in 1965 (the wheat that followed was killed by wheat-bulb fly and was replaced by barley). Trefoil was undersown in barley in 1966 and followed by potatoes in 1967.

Plots given only fertiliser serve as controls; they get P, K and Mg equal to the amounts in the organic manures and equivalent to either PKMg in peat or straw (with supplementary P) or to PKMg in FYM. The total nutrients applied are balanced to allow for different amounts removed; the net amounts applied by spring 1967 were:

	P	K (lb/acre)	Mg
Green manure, peat, straw or equivalent fertilisers	92	270	34
FYM or equivalent fertilisers	259	651	101

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Crops in 1966 and 1967. The largest plot yield with the 1966 barley, which was sown late and grew badly, was 36 cwt/acre. Potatoes in 1967 grew better, but even so the best yield was only 11 tons/acre. Table 1 shows yields

TABLE 1
Yields of barley and potatoes on Stackyard Field, Woburn with and without green or organic manures

	Barley, 1966 (cwt grain/acre) at 85% dry matter	Potatoes, 1967 (tons/acre)
(a) Inorganic manuring (PKMg) equivalent to straw + superphosphate		
Without organics	32.9	6.97
Straw (3 tons/acre)	27.9	8.91
Peat (3 tons/acre)	31.3	7.83
Green manures	27.8	11.06
(b) Inorganic manuring (PKMg) equivalent to farmyard manure		
Without organics	31.3	9.62
FYM (20 tons/acre)	35.5	10.43
Standard error	±1.06	±0.780

of barley (with 67 lb N/acre) and potatoes (with 157 lb N). Barley without organic manuring yielded similarly with the large and small amount of PKMg. FYM gave an extra 4 cwt/acre of barley grain, peat had no effect, and both straw and green manure (ryegrass) gave about 5 cwt/acre less than inorganic fertilisers. The differences probably reflect immobilisation of N by straw and ryegrass residues, and the little extra N (<22 lb/acre) released from FYM.

Green manures, straw and FYM all had much larger effects on potatoes than barley. The fertilisers equivalent to PKMg in FYM produced larger yields than the smaller amounts equivalent to nutrients in straw. FYM gave slightly (but not significantly) more potatoes than equivalent fertilisers. Peat and straw gave 1 and 2 tons/acre respectively more than equivalent inorganic nutrients.

The most outstanding effect in 1967 was the vigorous growth of potatoes after trefoil and the 3-4 tons/acre more tubers than with the equivalent inorganic fertilisers. Before ploughing the trefoil in November 1966 its roots and tops contained 60-80 lb N/acre. The gains from trefoil residues were equivalent to the increases in potato yields from 100 lb N/acre broadcast before planting. (Mattingly)

Experiments on nitrogen fertilisers

Anhydrous and aqueous ammonia. Anhydrous ammonia (82% N) was again compared with "Nitro-Chalk" (21% N) for grass and spring wheat (*Rothamsted Report* for 1966, p. 41), an aqueous solution of ammonia (containing 29% N) was also tested for grass. Aqueous ammonia is not under pressure, is easier to handle than anhydrous ammonia and need not be injected so deeply into soil to avoid losses. (Because it is more dilute, the aqueous fertiliser is also much easier to apply properly in experiments, as

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the application machines can be calibrated with a simple volumetric device.)

Grass. One experiment on permanent grass at Rothamsted compared yields from aqueous and from anhydrous ammonia injected either in November or in March, and from "Nitro-Chalk" broadcast all at once in March or divided into three equal amounts applied in March, in June and in August. Table 2 shows the total yields from three cuts.

TABLE 2

Comparisons of aqueous and anhydrous ammonia on permanent grass

Yields of dry grass (cwt/acre). Total yield without nitrogen = 45.8 cwt/acre

lb N/acre	Ammonia in autumn		Ammonia in spring		"Nitro-Chalk" dressing	
	Anhydrous	Aqueous	Anhydrous	Aqueous	Single	Divided
112	58.1	66.2	70.7	61.3	66.5	69.9
224	64.4	81.4	74.9	72.8	69.2	93.1
336	77.8	89.3	80.7	84.8	78.4	93.3
448	81.2	99.3	81.8	95.1	96.8	96.8
Standard error			±3.41			

Aqueous ammonia usually gave larger yields than anhydrous ammonia, and as large as equivalent single dressings of "Nitro-Chalk". Applying either form of ammonia during autumn gave encouraging results; yields from injecting aqueous ammonia then were slightly larger than from injecting it in spring.

With 112, 224 or 336 lb N/acre, the largest yields came from divided dressings of "Nitro-Chalk", but with 448 lb N/acre, yields from single and divided dressings of "Nitro-Chalk" and from aqueous ammonia were the same. Thus, where a large amount of N is needed, a large single dressing may be an efficient way of supplying it for an entire growing season.

Another experiment with grass measured the effects of cultivating with the injection tines. Slits made in autumn slightly increased yields, whereas those made in spring decreased them.

Wheat. One experiment at Rothamsted and one at Woburn compared anhydrous ammonia with "Nitro-Chalk" for spring wheat. Both fertilisers greatly increased yields. At Rothamsted yields from the two fertilisers were nearly the same, but at Woburn were larger with "Nitro-Chalk". (Widdowson, Penny and Flint)

Isobutylidene diurea (IBDU). The slow-acting N fertiliser IBDU made in Japan (*Rothamsted Report* for 1966, pp. 43-44) was again tested on grass, and on conifer seedlings and transplants (of Sitka spruce, *Picea sitchensis*).

Grass. Ammonium nitrate and IBDU (30% N) were broadcast and raked 2 in. deep into the seed-bed prepared for sowing S22 ryegrass at the end of March. Both fertilisers were tested when supplying 100, 200 or 300 lb N/acre and IBDU was tested as powder, and as small, medium and large granules (0.5-0.8, 0.8-1.5 and 1.5-2.4 mm diameter respectively). The grass was cut in June, July, September and November. Ammonium

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nitrate, IBDU powder and small granules increased yields similarly at each rate (Table 3). The medium-sized granules were inferior to these

TABLE 3
Comparisons of fine, medium and coarse IBDU for ryegrass

Fertiliser-N applied (lb N/acre)	Total yield of dry matter from 4 cuts cwt/acre		
	Mean of ammonium nitrate, and powder and small granules of IBDU	Medium granules of IBDU	Large granules of IBDU
	Yield without nitrogen 24.6		
100	55.7	47.2	39.0
200	72.7	68.7	55.2
300	80.3	79.8	65.4

forms when supplying 100 lb N/acre, but equal at 300 lb N/acre. The large granules always produced the least yield. (Gasser, Penny and Flint)

Conifers. The experiments with one-year Sitka spruce seedlings, started in 1966 at Wareham and Kennington Extension, compared two granule sizes of IBDU (0.8–1.4 and 1.5–2.4 mm, both with 30% N) with formalised casein (11% N) and "Nitro-Chalk" (21% N). Four amounts of each were tested. IBDU and formalised casein were dug in early in February before sowing; "Nitro-Chalk" was split into four topdressings applied at the beginning of June, July, August and September. In 1967 similar experiments were started at the same nurseries on transplanted one-year seedlings uniformly manured in the seed-bed.

At Kennington Extension the summer rain was close to the 21-year average, but Wareham had 5 in. in May (the average is 2.2 in.). Table 4 shows, for *seedlings*, responses to N were large at both nurseries; the best

TABLE 4
Effect of four nitrogen fertilisers on height of Sitka spruce seedlings and transplants at two nurseries in 1967

	Height (in.)			
	Seedlings		Transplants	
	small N	large N	small N	large N
<i>Wareham</i>				
without N	0.4		5.1	
IBDU (0.8–1.4 mm)	1.0	1.2	9.9	10.6
IBDU (1.5–2.4 mm)	1.3	1.8	8.9	9.8
Formalised casein	1.6	1.9	10.2	10.2
"Nitro-Chalk"	1.8	2.9	9.1	10.0
Standard error	±0.17	±0.17	±0.44	±0.44
<i>Kennington Extension</i>				
without N	1.4		10.4	
IBDU (0.8–1.4 mm)	2.4	2.3	13.4	13.7
IBDU (1.5–2.4 mm)	2.6	2.5	12.9	14.2
Formalised casein	2.5	2.5	13.7	15.4
"Nitro-Chalk"	3.0	3.1	13.2	15.2
Standard error	±0.13	±0.13	±0.48	±0.48

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treatments increased seedling height 7-fold at Wareham and more than doubled it at Kennington Extension. The finer IBDU (0.8–1.4 mm) was least effective, coarser IBDU (1.5–2.4 mm) behaved like formalised casein, but—in contrast to 1966—“Nitro-Chalk” was much better than the other three sources of N.

All large amounts of N doubled the height of *transplants* at Wareham; at Kennington Extension the best treatments increased height by nearly a half. Differences between sources of N were smaller and less consistent than with seedlings, and “Nitro-Chalk” was no better than the slow-release forms.

On the light sandy soil of Wareham all nitrogen treatments decreased soil pH. The sites had received a small basal dressing of lime, and on the plots without nitrogen the pH was 5.0 (in CaCl₂). In the seed-bed experiment (after two cropping seasons) the small amounts of N of the slow-release fertilisers decreased pH by at least half a unit and the larger amount of N by a whole unit or more. “Nitro-Chalk” also decreased pH, but to a lesser extent. The pH values in the transplant experiment (after one season) followed a similar trend but were less consistent. There is ample evidence that Sitka spruce seedlings grow best at pH 4.5 (Benzian, *Bull. For. Commn., Lond.* (1965), No. 37, Vol. 1), and the large decreases in soil reaction associated with nitrogen dressings make it difficult to interpret the results. On the sandy loamy soil of Kennington Extension (pH of the site is about 4.2) the decreases were very small—ranging from 0.1 to 0.3 pH unit.

The speed at which nitrogen is released from the four fertilisers was followed during the growing season by sampling *seedling* tops (cut at ground level) at five times (July, early and late August, September and

TABLE 5

Effect of four different nitrogen fertilisers on dry matter of Sitka spruce seedlings and %N in crop at different stages of growth in two nurseries, 1967

	Dry matter of tops (mg/plant)			%N in dry matter		
	July/ Aug.	Aug./ Sept.	Nov.	July/ Aug.	Aug./ Sept.	Nov.
<i>Wareham</i>						
Without nitrogen	8	16	24	(1.3)*	(0.9)	(1.2)
IBDU (0.8–1.4 mm)	25	92	154	2.0	1.1	0.9
IBDU (1.5–2.4 mm)	29	124	226	2.2	1.5	1.1
Formalised casein	30	139	234	2.4	1.4	1.1
“Nitro-Chalk”	26	146	257	2.6	1.8	1.3
<i>Kennington Extension</i>						
Without nitrogen	29	112	149	2.2	1.4	1.2
IBDU (0.8–1.4 mm)	41	172	314	2.7	2.0	1.6
IBDU (1.5–2.4 mm)	40	184	369	2.5	2.0	1.8
Formalised casein	40	179	324	2.6	1.9	1.7
“Nitro-Chalk”	40	208	416	2.6	2.3	1.9

* Brackets indicate there was not enough material for accurate analyses.

November). In Table 5 the results at first and second sampling dates are averaged, as are those at the third and fourth. At Wareham the finer IBDU (0.8–1.4 mm) produced plants with smallest weights and smallest N concentrations, presumably because N was lost during the very wet May.

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The coarser IBDU behaved like formalised casein. Except for dry weights at the first sampling, "Nitro-Chalk" was better throughout. At Kennington Extension differences between fertiliser forms were small, particularly effects on N concentrations. At Wareham the largest N concentrations (with "Nitro-Chalk") were less than the smallest (with IBDU 0.8-1.4 mm) at Kennington Extension.

In a small trial with *seedlings* at Wareham still coarser IBDU (2.5-4.0 mm) was better than the 1.5-2.4 mm fraction, but the plants were smaller than those given "Nitro-Chalk":

g N/sq. yd	Height of seedlings (in.)			With "Nitro-Chalk"
	Without N		0.8	
	With IBDU			
	1.5-2.4 mm	2.5-4.0 mm		
12	2.6	3.3		4.3
24	3.7	4.0		4.8

(Benzian and Freeman)

Thiourea ((NH₂)₂CS) has been suggested as a possible source of N in fertilisers; it inhibits the nitrification of the ammonia produced when it decomposes and lessens loss by leaching. It may decompose more slowly than urea. Very few experiments with it have been reported, but Fuller (*J. agric. Fd Chem.* (1963), **11**, 188) found that it was better than other sources of N tested (including ammonium sulphate) on both light and heavy soil; it also had residual effects where other N fertilisers had none.

In experiments using soil from Geescroft at Rothamsted, thiourea was added in various amounts up to the equivalent of 500 lb N/acre, and the mixtures were incubated at 50% of water-holding capacity for 1, 2, 4, 8, 16 and 24 weeks when they were analysed. Small amounts lasted in the soil for 7 weeks. With thiourea at 100 lb N/acre the ammonia released maintained its concentration (about 29 ppm N) for 4 weeks and then declined, whereas nitrate concentrations increased to a maximum of 140 ppm of NO₃⁻-N after 24 weeks. Ammonia concentrations produced with 500 lb N/acre continued to increase throughout the experiment and exceeded 200 ppm of NH₄⁺-N after 24 weeks; by contrast nitrate-N was 30 ppm at 2 weeks, declined to 12 ppm at 8 weeks and recovered to 40 ppm by the end of the experiment (24 weeks). Hence, although thiourea can inhibit nitrification of the ammonia produced when it hydrolyses, to do so large amounts of it must be mixed with the soil. Should thiourea become cheap enough, and similar effects obtain in field soils, it will be worth more testing as a fertiliser. The need to use large dressings to inhibit nitrification is not necessarily a disadvantage, because if it does last long as a fertiliser only one large dressing would be needed for crops with a long growing season. (Hamlyn and Gasser)

Timing and placing of nitrogen fertilisers. An experiment with spring wheat in the glasshouse used pots 6 in. wide and 27 in. deep to test the effects of placing N at various depths, and of giving it at different times. Maximum yield and N-uptake were obtained when plants sampled at 42

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“boot” stage had about 15% of their total nitrogen present as mineral-N (i.e. about 5000 ppm, mostly nitrate-N); at anthesis these plants had about 10% of their N in mineral form (i.e. about 2000 ppm, mostly nitrate-N). When large dressings were given in halves, one at sowing and the other at “boot” stage, the second half altered the crop composition within 15 days to that typical of the large total dressing. Nitrogen increased grain more when put below the surface than when put on the surface of the soil. The late (“boot” stage) dressings increased N in grain (average for the treatment was 2.37% N in grain) more than early dressings (2.03% N in grain grown with dressings given at sowing; without N fertiliser the grain contained 1.63% N). Fertiliser recoveries, calculated from N balance sheets for crops harvested at various stages, were:

	% fertiliser-N recovered	
	Range	Average
“Boot” stage	62-85	70
Anthesis	55-96	78
Maturity	69-95	86

The percentage recovered was greater from the larger amounts and the later dressings.

The efficiency of fertiliser N is likely to be enhanced by splitting dressings, giving some “early” and some “late”, because crops then take up more. On soils containing much mineral-N at sowing, late dressings will be more efficient than early ones. (Spratt and Gasser)

Experiments on the residual effect of crops and manures

Fertilisers and organic manures leave residues that affect future crops and alter the need for fresh fertiliser dressings. Legumes leave extra nitrogen in the soil, and other crops leave residues rich in carbon that, temporarily at least, immobilise nitrogen. All such effects need allowing for when deciding the manuring of crops, and we are studying some in crop-sequence experiments of various durations.

Effects of previous cropping, and of nitrogen fertiliser on barley yields. A 3-year experiment at Rothamsted described by Widdowson, Penny and Williams (*J. agric. Sci., Camb.* (1965), 65, 45-55) compared concentrated and dilute compound fertilisers, and several nitrogen fertilisers, used with a crop rotation of kale, Italian ryegrass and barley. Barley was then grown to measure residual effects, and yielded much less after ryegrass than after kale or barley. This was thought to be because the ryegrass roots on plots not given N-fertiliser immobilised much mineralisable soil-N while decomposing. Another experiment was made to test this further.

In 1965 spring wheat, Italian ryegrass and kale were each grown without N and with either 112 or 224 lb N/acre, and followed in 1966 by barley grown without N, and with either 56 or 112 lb N/acre. Barley yielded 7.6 cwt more grain/acre after kale without N than after wheat without N, but where kale and wheat had 224 lb N/acre it yielded only 2.1 cwt more after

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kale. Table 6 shows that this advantage was not lost by applying N for the barley. Barley after ryegrass yielded less than after wheat and much less than after kale; the difference was least where most N was applied for the ryegrass in 1965 (224 lb N/acre) and for the barley (112 lb N/acre). Applying 224 lb N/acre to each of the three preceding crops increased

TABLE 6
*Effects of crop sequence and nitrogen fertiliser used on Stackyard
Field at Rothamsted on barley yields in 1966 and in 1967*
Yields of barley grain (cwt/acre at 85% dry matter)

Crop in 1965	N applied, lb/acre			Standard error
	0	56	112	
	1966 grain yields			
Wheat	16.1	27.9	36.3	±1.02*
Kale	21.6	33.6	40.3	
Italian ryegrass	11.8	25.9	35.1	
Standard error		±1.32†		
	1967 grain yields			
Wheat	17.5	33.1	41.5	±1.15*
Kale	14.7	32.4	42.8	
Italian ryegrass	20.4	40.1	45.1	
Standard error		±1.32†		

* For horizontal and diagonal comparisons.

† For vertical comparisons.

barley yields in 1966 from 4 to 9 cwt grain/acre; the largest gain was after wheat, which removed least N. The nitrogen applied to the barley increased yields least after kale and most after ryegrass, and as much whether or not the previous crops had been given N.

In 1967 barley was grown again without nitrogen and with either 56 or 112 lb N/acre, applied in all combinations with the previous treatments. Barley yielded almost 5 cwt/acre more where ryegrass than where kale or wheat were grown in 1965, whereas yields after kale and wheat were the same. The gain from growing grass was least (3 cwt grain/acre) where it had not been given N and most (6 cwt grain/acre) where it was given 224 lb N/acre; the same amount of nitrogen given for the wheat or the kale did not increase barley yields, nor did the N given for the 1966 barley. The nitrogen given in 1967 greatly increased yields (the response to 112 lb N/acre was 25.6 cwt grain/acre), more after kale than after wheat or ryegrass. This increase was diminished by the nitrogen given in 1965, and also by that given in 1966.

Although the grass roots initially immobilised much nitrogen, some or all of it became available two years later, and the shortage of nitrogen in 1966 where grass was grown in 1965 was temporary. (Widdowson and Penny)

The idea that barley yields less after grass than after wheat or kale because the soil under grass mineralised less N when ploughed than soil under kale or wheat stubbles was confirmed by sampling the soils from this and a similar experiment. Samples taken during two successive Novembers where grass, wheat and kale had been harvested were incubated out-of-doors during the winter, and then used to grow ryegrass in the glass-house.

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Little or none of the fertiliser-N applied in March for the field crops remained in the surface soil in November. Each year ryegrass grown in pots in the glasshouse yielded less dry matter, and contained less N, with soil taken from land under grass than from land under wheat or kale. Yields of ryegrass, and the amount of N taken up in the glasshouse during 1966, were both increased by fertiliser-N given to all three crops in 1965, but during 1967 only by fertiliser applied for wheat and kale in 1966. Of nitrogen added to the soil in the glasshouse, ryegrass recovered less from soil that had previously grown grass than from soils that had grown either wheat or kale. (Gasser and Mitchell)

The effects of leys on mineralisable nitrogen in soils. Results of the Ley-Arable Experiments at Rothamsted, summarised later in this report (p. 316), show that when leys are ploughed the soils provide more nitrogen for following crops than is left after a sequence of arable crops. Winter wheat is the first test crop and follows four sequences, each of 3 years, either lucerne, or grass leys manured with nitrogen, or grass-clover leys, or three arable crops (ryegrass-clover ley, sugar beet and oats). Samples of the soils sown with wheat were taken in January 1967, incubated and their mineralisable-N was measured. Measurements were made on both fresh (i.e. wet) soils and on sub-samples that were air-dried; small and large core samples were also compared. The dried soil gave more mineral-N on incubating, but in each set of figures the differences were similarly associated with previous treatment. Table 7 gives averages of the two methods. Small core samples (12 cores/plot) produced less mineralisable nitrogen than large single cores per plot, for no known reason.

TABLE 7

Comparisons of mineralisable-nitrogen and yields of wheat without N-fertiliser in the Rothamsted Ley-Arable Experiments

	Treatment cropping, 3 years of			
	Lucerne	Ley with N fertiliser	Ley with clover	Arable crops
Mineralisable-N (ppm of NH_4 -N + NO_3 -N)				
Highfield	35	42	33	29
Fosters	24	22	28	18
Yields of wheat grain (cwt/ acre at 85% dry matter)				
Highfield	47	54	59	44
Fosters	66	56	55	42

Soil after the sequence of arable crops has less mineralisable-nitrogen than soils after leys. Highfield soil contained much more than Fosters (Highfield was old grassland until ploughed for this experiment in 1948 and still contains much more organic matter than Fosters Field, which has been arable for very many years (*Rothamsted Report* for 1964, pp. 41-44)). Wheat grown without N fertilisers in 1967 yielded less after arable crops than after leys on both fields (Table 7). Mineralisable-N in soil and yields showed no other correlation on either field. Although wheat yielded most

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on Highfield after the grass-clover ley, and after lucerne on Fosters Field, mineralisable-N was less in these than in soils where other crops were grown for the three years previously.

The lack of agreement between analyses of incubated soil and wheat yields does not suggest that such analyses are useful in forecasting how much nitrogen will be available to crops. Also the amounts of N released depended on size and kind of sample and, as previously, dried soil had more mineralisable-N than fresh soil. Results from these field experiments show that a knowledge of previous cropping and manures is likely to be a more reliable guide than measuring mineralisable nitrogen in deciding on the nitrogen manuring of crops. (Blakemore and Gasser)

Residual and cumulative effects of phosphate fertilisers on acid soils at Rothamsted. The immediate and residual effects of phosphate fertilisers on yields of barley, potatoes and swedes in tests made from 1960 to 1965 were described in last year's report (pp. 45-46). Table 8 shows the

TABLE 8
Total phosphorus removed by potatoes, barley and swedes in 1960-1965 and analyses as means of soil samples taken in 1961, 1963 and 1965

Phosphate fertiliser	P applied (lb P/acre)	Total P removed (lb P/acre)			P soluble in	
		Potatoes (tubers)	Barley (grain and straw)	Swedes (roots)	NaHCO ₃ (ppm)	CaCl ₂ (μM/litre)
None	—	42	74	20	7.6	0.31
Superphosphate (annually)	12	50	82	45	11.3	0.44
	24	54	81	60	14.2	0.54
Nitrophosphates with						
5% of total P soluble in water		57	81	65	15.3	0.66
26% of total P soluble in water		57	86	62	15.3	0.68
50% of total P soluble in water		57	83	63	15.8	0.69
Gafsa rock phosphate	147	53	88	59	13.3	0.55
Basic slag	1959	57	89	59	14.3	0.59
Potassium meta-phosphate		57	88	61	14.4	0.58
Super-phosphate		57	89	64	15.7	0.62
Standard error (without P)		±0.9	±1.4	±1.5	—	—
Standard error		±1.2	±1.8	±1.9	—	—

amounts of P removed in 6 years, and mean amounts of P soluble in 0.5M-NaHCO₃ solution and in 0.01M-CaCl₂ solution in soil samples taken in 1961, 1963 and 1965. Swedes recovered less phosphorus from rock phosphate, basic slag and potassium metaphosphate than from superphosphate or the nitrophosphates; potatoes recovered less from rock phosphate than from the other fertilisers. Soils given superphosphate or nitrophosphate contained a little more soluble phosphate than soils given rock phosphate, basic slag or metaphosphate. The residues of the phosphates tested in these experiments were valued from effects on yields, P uptakes and soil analyses. Averaging all these assessments, and taking

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superphosphate residues as standard (= 100), the other phosphates were worth:

Nitrophosphate	100-102
Potassium metaphosphate	95
Basic slag	94
Gafsa rock phosphate	92

Rock phosphate probably had a large residual value because: (i) the soil was acid throughout the experiment (pH about 5.5); (ii) fertilisers and soil were well mixed before cropping; (iii) the soil was not saturated with fluorapatite, even after liming.

The value of soil analyses in assessing phosphate residues was found by calculating the percentage of the total variance in swede and potato yields that was accounted for by a regression on phosphorus soluble in sodium bicarbonate. Table 9 shows that a surprisingly large proportion of variance

TABLE 9
Percentage of total variance in yield or P uptake accounted for by regression on NaHCO₃-soluble soil P

Crop		1961	1963	1965
Potatoes	{ yield	(38)*	64	70
	{ uptake	(62)*	70	83
Swedes	{ yield	92	42	76
	{ uptake	92	34	87

* Yields and uptakes were small on some plots due to acidity.

for potatoes and swedes was accounted for by variations in soluble soil phosphate, especially in 1965. Much less of the variance in barley yields (8-28%) and uptakes (26-50%) was accounted for by soil analyses, and details are not given here. Yield and soluble soil phosphate were related by the following figures, averaging results obtained in 1961, 1963 and 1965.

	Increase in yield per ppm of NaHCO ₃ -soluble P
Potatoes	0.24 ± 0.037 tons/acre
Barley grain	0.22 ± 0.08 cwt/acre
Swedes	1.16 ± 0.148 tons/acre

(Mattingly)

Residues of superphosphate and FYM at Saxmundham. The values of phosphate residues accumulated from dressings given between 1899 and 1964 are being explored in Rotation II Experiment; 1967 results are given in full later in this Report (p. 241). Turnip yields (harvested in July) were doubled by the residues from 10 tons/acre of FYM given once in 4 years (for 64 years), trebled where 5 cwt/acre (7½ cwt/acre since 1921) of superphosphate was also given with the FYM, and were nearly quadrupled by giving fresh phosphate to plots with residues. Sugar beet grew until October (twice as long as the turnips) and made more use of the meagre supply of soil P. The yields of untreated plots (8.3 tons/acre) were doubled (16.9 tons/acre) by residues from a dressing of FYM and of superphosphate once in 4 years; giving fresh phosphate in addition produced an extra 1½ tons/acre of roots. The results with turnips and sugar

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beet in 1967 and with potatoes in 1966 (*Rothamsted Report* for 1966, p. 251) all show that fresh superphosphate broadcast before sowing produces small but consistent increases in yields of root crops on this soil, even where it contains 38–40 ppm of P soluble in 0.5M-NaHCO₃ solution. (Mattingly and Johnston)

The effect of fertiliser residues in Agdell Field on the responses of grass to fresh fertilisers. The Classical Experiment on Agdell field, which continued from 1848 to 1951 and was described by Warren (*Rothamsted Report* for 1957, pp. 252–260), compared none, PK and NPK fertilisers in two variants of the Norfolk Four Course Rotation: swedes, barley, clover or beans (versus a fallow) and wheat. Residues from the fertilisers, applied once in 4 years, accumulated in the soil. By 1951 each of the 6 plots contained different amounts of P and K because the “NPK” plots received more than the “PK” plots (part of the N was applied as rape cake containing P and K), and more P and K was removed from the clover than from the fallow plots. In 1958 half plots were sown with grass to measure P and K uptake from the residues. The grass, Italian ryegrass from 1958 to 1959 and cocksfoot from 1960 to 1963, was liberally dressed with N after each cutting for silage. Only one cut was taken in 1963, and the plots then ploughed because much of the cocksfoot was killed by the winter.

Between 1958 and 1963 the grass extracted about one-tenth of the total P that had accumulated in the surface 9 in. of soil from past dressings. This removal diminished the NaHCO₃-soluble P in the soil. The grass took up much more K than P; the extra K taken up from the residues was at least twice as much extra exchangeable K as the soil contained in 1958, so some must have come from reserves of fixed K. The exchangeable K in all the soils diminished to about the same amount, so any K residues remaining were in the “fixed” form.

Before grass was sown in 1964 the plots were further subdivided, so that, in addition to testing residues, the response to different amounts of fresh P and K in the soil could be measured. (The new dressings were 200, 400 and 800 lb/acre of P and 230, 460 and 920 lb/acre of K.) Basal phosphate was given to sub-plots testing potassium, and basal potassium to sub-plots testing phosphate. To maintain these comparisons, the amounts of P and K removed by the grass each year were replaced next spring with P or K fertilisers, except subplots testing P_0 where P was not given and K_0 where K was not given.

The new dressings were applied over the ploughed land in March 1964 and seed of timothy grass sown in May. Large benefits from all amounts of new P and K fertilisers showed as soon as the grass germinated, but dry weather later checked growth, and only one cut was taken in 1964 (results are in *Rothamsted Report* for 1964, p. 59). In 1965 and 1966 the grass grew well, producing over 5 tons/acre of dry matter in both years. In 1967 only one cut was taken before the plots were ploughed and cultivated to kill couch grass; timothy was resown in the autumn.

Responses to newly applied fertilisers were big in 1964, when the grass behaved like an annual arable crop, but in each of the next three years the only responses were to the smallest amounts of P and K. Table 48

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10 shows total yields for 1964–67, with effects of new P and K given as means with the three amounts tested. Little of the residual P was taken up by the grass between 1958 and 1963; during 1964–67 the remaining residues produced an extra 46–105 cwt/acre of dry matter. The average annual

TABLE 10
Effects of new fertiliser dressings, and of P and K residues on yields of timothy in the Agdell Experiment

Yields of dry grass, (cwt/acre), totals for 1964–67

Plot nos. Fertilisers	Old treatments, 1848–1951					
	Rotation with fallow			Rotation with clover		
	1 NPK	3 PK	5 None	2 NPK	4 PK	6 None
<i>Treatment to grass in 1964–67</i>						
With basal N and K						
Without new P	245	186	140	199	169	94
effect of P residues	105	46	—	105	75	—
With new P	270	249	243	253	228	245
effect of new P	25	63	103	54	59	151
With basal N and P						
Without new K	221	190	193	182	215	173
effect of K residues	28	—3	—	9	42	—
With new K	259	239	249	258	245	238
effect of new K	38	49	56	76	30	65

recovery of P during the first (1958–63) and the second (1964–67) period of the test suggested that 40–50 years more cropping will be required to recover all the phosphate residues. Residual P decreased the effect of new P; with new P yield was increased to nearly the same amount on all plots.

Any K residues in 1964 must have been in “fixed” forms, because exchangeable K in the six plots was the same. In 1964–67 without fresh K the old PK plot with fallow and the old NPK plot with clover yielded the same as the corresponding plot without residues; the extra uptake of K was small, only 50 lb K/acre in four years. Thus if any residue remains from the K fertilisers applied between 1848 and 1951 it releases K too slowly to increase grass yields. The old NPK plot with fallow, and the old PK plot with clover, produced 28 and 42 cwt/acre of extra dry matter respectively, and the fixed K residues responsible provided an extra 130 lb K/acre. Fixed K cannot be measured, so we cannot estimate how much remains in these soils and how long the grass may take to recover it. With new K the yields on all plots were almost the same. (Johnston and Penny)

Effects of nitrogen and potassium fertilisers on the composition of ryegrass

Soluble carbohydrates. In last year's Report (p. 54) we showed that grass given much N on potassium-deficient soils grew little after the first cut because the root system was very small. An experiment using this potassium-deficient soil to grow ryegrass in the glasshouse tested effects

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of N and K fertilisers and showed how soluble carbohydrates in leaves, stubble and roots were altered by different amounts of ammonium nitrate and potassium chloride.

Table 11 shows that nitrogen had little effect on the simple sugars

TABLE 11
The effects of N and K fertilisers on the soluble carbohydrates produced by ryegrass

Fertiliser supplying (as ppm of weight of soil used)		Total amounts (mg/pot) in leaves + stubble + roots		
N	K	Simple sugars	Fructosan	Total soluble carbohydrates
40	0	867	579	1446
40	60	1532	1642	3174
40	120	1709	2423	4132
40	240	1499	2738	4237
80	0	804	306	1110
80	60	1797	1467	3264
80	120	2641	2736	5377
80	240	2703	4432	7135
160	0	919	261	1180
160	60	1537	712	2249
160	120	2485	1159	3644
160	240	3688	3753	7441

produced by grass grown without K fertiliser, but diminished fructosan. With each of the amounts of nitrogen supplied, increasing the K greatly increased the soluble carbohydrate. Fructosan is the main reserve carbohydrate in grass, and the small amount in the crop given most N but no K probably explains why the grass in the field failed to grow after the first cut in 1966. (Nowakowski)

Protein and free amino acids. Potassium increased yields of both cuts (especially the second) and of the stubble and roots (Table 12). With each

TABLE 12
Effects of N and K fertilisers on yield and composition of ryegrass

Fertiliser supplying (as ppm of weight of soil used)		Yield of dry matter (g/pot)	Per cent in dry matter		Percentage of total N		
N	K		K	N	Protein-N	α -amino-N	Amide-N
40	0	3.4	0.51	1.58	85	4.5	1.5
40	240	6.0	2.79	0.93	90	2.9	0.7
80	0	4.3	0.45	2.72	80	6.9	2.1
80	240	10.5	1.68	1.10	89	2.7	0.4
160	0	4.7	0.47	4.43	64	8.3	3.7
160	240	14.7	1.08	1.70	90	3.3	0.4

amount of N applied, K increased the protein-N. Grass not given K accumulated free amino acids and amides, and giving K increased the proportion of aspartic acid, glutamic acid, serine, proline and 4-amino-*n*-butyric acid in the total α -amino-N. (Nowakowski with Byers, Biochemistry Department)

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Experiments with nutrient cations

Liming experiments. The experiments with beans at Rothamsted and Woburn described by Moffatt (*Rothamsted Report* for 1966, pp. 243-246) ended in 1964, and three successive barley crops have been grown on the plots. Yields diminished during the three years, especially on the most acid plots and those not given phosphate fertiliser (Table 13). At both Rothamsted and Woburn the largest yields of 39-43 cwt grain/acre were on plots with soil pH 6.5-7.5. Without phosphate most yield was obtained at pH 7 at Woburn, but at Rothamsted in two of the years most was obtained at pH 5.7. In 1967 fungus diseases attacked roots and leaves, especially at Rothamsted, and these accounted for the small yields

TABLE 13
Yields of barley in liming experiments at Rothamsted and Woburn,
1965 to 1967

		(cwt/acre of grain at 15% moisture)									
		Rothamsted (Sawyers)				Woburn (Stackyard)					
Mean soil pH		4.8	5.7	6.7	7.5	5.3	6.5	7.2	7.5		
lb N/acre											
Rothamsted		Woburn									
Without phosphate											
1965	56	56	24.2	41.2	41.1	40.7	35.5	38.9	41.1	41.2	
1966	56	112	18.5	33.9	36.7	37.0	34.9	39.1	40.2	39.9	
1967	84	112	7.7	30.6	27.3	23.8	23.1	29.4	33.3	32.7	
With 22 lb P/acre/annum											
1965	56	56	27.6	42.4	42.4	41.8	40.4	40.6	43.2	43.5	
1966	56	112	25.0	36.3	39.4	39.4	38.9	39.9	41.9	42.0	
1967	84	112	15.2	38.0	39.6	37.5	34.9	37.6	36.1	37.4	
		Standard error		±3.7				±0.9			
		(mean for 3 years)									

from limed plots without phosphate. If the decline in yield reflects increasing prevalence of disease the results suggest that applying phosphate lessens its effects. (Bolton)

Long-term experiments at Woburn with potassium, magnesium and sodium. The experiment at Woburn begun in 1960 (*Rothamsted Report* for 1966, pp. 51-52) grew barley in 1967, which was cut green in July. The soils were then sampled, and amounts of K, Mg and Na removed in all the crops grown since 1960 were compared with amounts applied as fertilisers, and the changes in exchangeable cations assessed during the whole period.

The amounts of magnesium remaining in the soil balanced the differences between amounts removed in crops and amounts added. There was no evidence that non-exchangeable magnesium became available to the crops, even though magnesium fertilisers increased yields and amounts of exchangeable Mg in the topsoil of plots given none decreased to 15 ppm.

Average amounts of potassium added and removed in crops were:

lb K/acre	
Added	Removed
0	64
118	135
237	190

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Exchangeable potassium in the soil changed less than expected from these figures, both in plots not given potassium and those given 237 lb K/acre. The average annual release of non-exchangeable potassium was 39 lb K/acre in plots given none, and plots given 237 lb lost some. Subsoil analyses suggested that the "lost" potassium was fixed in non-exchangeable forms rather than leached below 18 in.

Sodium chloride was applied only to kale and barley in 1966 and 1967. In plots without added potassium 31% of the added sodium was removed in the crops and 45% was in the soil after cropping. With the double amount of potassium only 10% of added sodium was removed in the crops (although yields were larger) and 79% remained in the soil. Much of the applied sodium was recovered from the subsoil (9–18 in.), suggesting that the "lost" sodium was leached below 18 in., and not fixed in a non-exchangeable form in the topsoil.

Ryegrass was planted in autumn 1967 to remove cations from the fertiliser residues accumulated during the last 8 years. (Bolton and Penny)

Sodium in soils. Leaching soils with *N* ammonium acetate removes sodium adsorbed on the exchange complex, together with what is dissolved in soil water. The latter depends on the concentration of free anions. The amount of sodium in the soil solution at a standardised 0.01 molarity can be measured by equilibrating soils with 0.01 *M*-calcium chloride containing a range of sodium concentrations. For each solution the sodium activity ratio $\left(AR^{Na} = \frac{a_{Na}}{\sqrt{a_{Ca} + Mg}} \right)$ is plotted against the amount of sodium removed from or adsorbed by the soil (Na_e). The equilibrium activity ratio, and the ratio at which there is no change in sodium concentration in the equilibrating solution, are compared with the graph of AR^{Na} plotted against ΔNa_e , to show how much sodium would be in the soil solution at 0.01 molarity (Tinker, *Trans. int. Soc. Soil Sci. Aberdeen* 1966 (1967), p. 222).

Such measurements on five neutral soils not given inorganic fertilisers showed that 12–34% of the NH_4^+ -exchangeable sodium was unadsorbed. Similar measurements showed that much less NH_4^+ -exchangeable potassium (about 5%) was unadsorbed. Because so much of the exchangeable sodium is in soil solutions, much sodium may be leached, and the compositions of soil solutions and rainfall may be related. AR^{Na} in Rothamsted rain (1965–67) was in the range 0.025–0.004 mole/litre^½, in the soils it was 0.019–0.005 mole/litre^½. Hence AR^{Na} in soils, and to a lesser extent exchangeable sodium, is likely to depend on the composition of rain falling just before sampling.

The sodium in soils derived from rain can be estimated independently by measuring chloride, assuming that the Na/Cl ratio in rain is constant and that all the chloride present is from rain. Chloride was measured in the same five soils and the equivalent sodium calculated using an Na/Cl molar ratio of 0.82 (average of Rothamsted rain); 14–28% of the exchangeable sodium had come from the rain, which was similar to the amounts measured in the solutions containing $CaCl_2$ discussed above.

Potassium activity ratios in rain (average 0.0013 mole/litre^½) are similar

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to those in soils at Rothamsted, Woburn and Saxmundham which have not been given fertilisers for many years. (Bolton)

Magnesium deficiencies. Leaf symptoms of magnesium deficiency were common on crops in 1967, appearing during warm dry weather in June after a cold wet spring. (Rain at Rothamsted was 2.91 in. more, and sunshine 40 hours fewer, than average in May.)

The Intensive Cereals Experiment at Woburn is on the sites of the old Permanent Wheat and Barley Experiments. Potatoes or grass breaks are grown in the rotation; leaves of the wheat and potatoes on some plots were chlorotic, and growth was poorest where the symptoms were worst. In early June mid-stem leaves of wheat contained 0.04% Mg in the plants from the most chlorotic plots and 0.09% Mg on plots without symptoms. Chlorotic potato leaves contained 0.11% Mg, healthy leaves 0.20%. Concentrations of N, P, K, Ca and Mn were satisfactory according to published analyses for "normal" plants, and did not reflect the differences in growth. Clearly, magnesium deficiency was the main cause of the chlorosis on both crops.

Some potato leaves were also chlorotic in the "Reference" plots at Rothamsted, especially in those given both potassium fertiliser and FYM. In June the leaves contained 3.5–5.2% K and 0.24–0.29% Mg.

Potato leaves are said to become chlorotic when magnesium constitutes less than 10% of the total Ca + K + Mg in the dry matter (Marel & Broek, *Z. Pfl-Ernähr. Düng. Bodenk.* (1959), **84**, 244–254). In these leaves 7.5–10.9% of the total cations was magnesium. In an adjoining experiment, where the same variety of potatoes was planted on the same date, less potassium was given and there were no symptoms of Mg-deficiency. Leaves contained from 0.47 to 1.36% Mg, which was equivalent to from 11 to 32% of the total cations. However, these plants died earlier than those containing more potassium and less magnesium; yields were not increased by magnesium fertilisers. (Bolton)

Potassium in soils

Harwell Series soil. This soil has unusual properties for potassium-calcium exchange (*Rothamsted Report* for 1965, p. 63), and its abnormal K-fixation and K-release characteristics are an extreme example of the way British soils behave. The K–Ca exchange isotherm shows the K⁺ ion to be strongly preferred to Ca⁺⁺ up to 40% saturation of the cation-exchange capacity (CEC) with K; the activity coefficient of adsorbed K⁺ decreased from 0.88 at 40% saturation to 0.16 when the soil was nearly unsaturated. Adsorbed K⁺ exchanges isotopically less easily below 40% K saturation, which is attributed to the presence of clinoptilolite in particles coarser than 0.3 μ.

In "exhaustion" experiments the soil (with 20% of its CEC saturated with K (equivalent to 345 ppm K) released 13290 ppm K when leached with 4 litres M-CaCl₂ during 611 hours and 2346 ppm K when cropped with ryegrass for 3½ years in the glasshouse. In the CaCl₂ extraction the K concentration in the equilibrium solution dropped from $5 \times 10^{-3}M$

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initially to $4.6 \times 10^{-4}M$ finally; with glasshouse cropping, the corresponding figures in $0.01M$ - $CaCl_2$ solution were $6 \times 10^{-3}M$ to $1.5 \times 10^{-4}M$ respectively.

Last year (*Rothamsted Report* for 1966, p. 65) we reported that the $<0.3 \mu$, $0.3-5 \mu$ and $<53 \mu$ fractions of this soil (separated after Na saturation) were being cropped in the glasshouse with and without partial K saturation. The results of a year's cropping and the K content of the fractions show that much less K^+ was exchanged into the coarser than into the finer particles. The bigger the particles, the less K was released to ryegrass and the stronger the fixation. This effect was so great that none of the added K^+ in the K-treated $<53 \mu$ fraction could be removed by ryegrass. Treating the soil with K diminished the amount that could be taken up by ryegrass from the untreated fraction during a year's cropping, but it would have been released in a long experiment.

These results conform with the presence of montmorillonite (predominant in the $<0.3 \mu$ fraction), which does not show hysteresis in cation exchange from the Ca to the K form, but the CEC of the "Harwell" soil decreased by almost a quarter in making the change. The coarser particles of this soil (excluding the sand) are responsible for most of the "fixation" and continued release of potassium. (Talibudeen with Weir, Pedology Department)

Exchange equilibria involving aluminium ions. In *Rothamsted Report* for 1965 (p. 65) we showed Al^{3+} ions were adsorbed more strongly than Ca^{2+} ions. Adsorption of aluminium by clays and soils was in the order: Vermiculite (Montana) \gg Park Grass soil $>$ Deerpark soil $>$ Illite (Fithian) $>$ Montmorillonite (Wyoming) $>$ Kaolinite (St. Austell). This preference for aluminium ions is directly related to the surface density of negative charges on the clay or soil and to the proportion of "vermiculite" (measured by the decrease in CEC on heating the clay after saturating it with potassium). Removing organic matter by treating with sodium hypochlorite decreased the CEC of Park Grass and Deerpark soils by 4 me/100 g, but Ca:Al isotherms show this caused little change in aluminium preference.

The integral distribution coefficient of an ion exchanger containing components of known exchange characteristics in equilibrium with solutions of known cation composition was calculated from the weighted contribution of each component to the total negative charge of the exchanger. Calculated values of this coefficient for Ca:Al exchange in Park Grass and Deerpark soils agree much better with observed values based on hypothetical vermiculite:illite mixtures than with vermiculite:montmorillonite mixtures; this suggests what minerals may be in these soils. K:Al exchange equilibria show that potassium is adsorbed the more strongly, and the soils and clays are in the order Park Grass, Deerpark $>$ vermiculite, illite \gg montmorillonite. The shape of the conventional isotherm suggests that in all materials, except montmorillonite, some isotopically exchangeable potassium cannot be easily replaced by aluminium, indicating partial or complete blocking of exchangeable K^+ by Al^{3+} when very little of the CEC is occupied by K. Such conditions can easily occur in severely leached acid soils and be important practically.

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From the results of work on Ca:Al and K:Al exchange we deduce that K^+ is more strongly bound than Ca^{2+} in the order: Vermiculite > Park Grass > Deerpark \gg Illite > Montmorillonite. This is confirmed by our general conclusions from work on other soils (Deist and Talibudeen, *J. Soil Sci.* (1967), **18**, 125-137). (B. Coulter and Talibudeen)

Experiments on partial sterilisation of soils

Partial sterilisation of soils has formed a part of Rothamsted's work for well over half a century. E. J. Russell studied it before he came here in 1907 and (with H. B. Hutchinson) published papers in 1909 and 1913 (*J. agric. Sci., Camb.*, **3**, 111 and **5**, 152) in which many of the changes caused in soils were described and discussed. The purpose of partial sterilisation is simply to increase soil productivity by preventing disease, but its effects are complicated. After partial sterilisation the numbers of bacteria in soil at first diminish but soon increase greatly. Much ammonia is liberated from organic nitrogen in the soil, ammonia and sometimes nitrite accumulate, nitrification is suppressed and soluble manganese increases in many soils, which may be toxic to following crops. The effect on root diseases may last for only one crop, but sometimes much longer.

Work on the nutrition of wheat at Woburn has been increasingly interfered with by soil-borne pests and diseases, so we attempted to eliminate them and to measure the effects of nitrogen fertiliser on sick and on healthy crops by treating some plots with formalin. The first of these experiments at Woburn was described in the *Rothamsted Report* for 1964 (pp. 65-66), and the work has now been extended to Rothamsted and Saxmundham.

Interpreting the results of experiments on partial sterilisation is complicated by the extra nutrients, and particularly the extra nitrogen, that are released after disinfecting the soil. Several departments now have field experiments testing partial sterilisation, and a better understanding of the biological and chemical changes is needed. Earlier work to find how chemicals used as nematicides affect mineral N in soil was described by Gasser and Peachey (*J. Sci. Fd Agric.* (1964), **15**, 142), and new experiments on the chemical changes in soil have begun in collaboration with the Pedology Department.

Field experiments on cereals with formalin and nitrogen

Rothamsted. The experiments started in 1965 with spring wheat (*Rothamsted Report* for 1965, p. 49) on Little Knott (a field mainly used to grow cereals for 20 years) and Pastures (ploughed from 10-year-old grass in February 1964) were continued. Formalin was applied in September 1966, either before (to the stubble) or after ploughing and cultivating the sites, in all combinations with the formalin previously applied. Cappelle Desprez wheat was sown in October. On Little Knott there were dramatic differences in height and vigour between adjacent plots. Table 14 shows that these differences came mainly from the harmful effects of applying formalin the year before (Spring 1966) and the beneficial effects of fresh nitrogen.

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On Pastures the treatments produced larger differences in growth than in 1965 or in 1966, but applying formalin the year before was less harmful than on Little Knott. On Little Knott freshly applied formalin increased yields when it was applied after ploughing, but on Pastures field a stubble drench gave larger yields (results obtained from this experiment by Salt,

TABLE 14
The effects of applying formalin and nitrogen for winter wheat at Rothamsted in 1967

Year applied	cwt grain/acre at 15% moisture content				
	Little Knott Field Formalin		Pastures Field Formalin		
	Without	With	Without	With	
1965	23.6	24.2	30.4	29.6	
1966	30.0	17.7	31.6	28.4	
1967*	23.1	24.6	29.1	30.9	
N. applied (lb/acre)	Formalin in 1967*				
	Without		With		
	Without	With	Without	With	
0	13.0	16.8	20.4	31.9	
56	21.6	27.3	28.5	35.2	
112	30.1	25.9	33.9	27.9	
168	27.8	28.5	33.6	28.6	
Formalin applied					
To stubble		22.7	22.6	28.8	32.1
To seedbed		23.5	26.7	29.4	29.7

* Applied autumn 1966.

Plant Pathology Department, pp. 137, help to explain this). As in previous experiments, formalin increased yields most on plots not given fertiliser N; on Pastures, wheat on plots given formalin plus 112 or 168 lb N/acre lodged, and yields of grain, though not of straw, were diminished.

Yields were consistently larger on Pastures than on Little Knott, and the difference was not eliminated by applying either formalin or nitrogen, or both. Though maximum yields were similar on Little Knott and Pastures, only 4 of 32 plots on Little Knott yielded more than 35 cwt grain/acre, whereas 9 plots did on Pastures. (Widdowson, Penny and Flint)

Saxmundham. In 1966 the largest yield of barley grain obtained on Rotation I Experiment at Saxmundham was 34.2 cwt/acre (from 12 tons/acre FYM); the largest from NPK fertilisers alone was 32.4 cwt grain/acre (*Rothamsted Report* for 1966, pp. 248-250). A new experiment in 1967 examined some of the factors that may be limiting yields there. These treatments were tested in all combinations:

- (1) a soil drench with formalin in February;
- (2) 8 tons ground chalk/acre (intended to improve soil structure);
- (3) 67 or 135 lb N/acre (as calcium nitrate);
- (4) N applied either to seed-bed (in March) or as a top-dressing (in May);
- (5) a tall (Maris Badger) and short (Deba Abed) barley variety.

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With enough nitrogen, yields of barley grain were large and neither formalin nor lime significantly increased them; Deba Abed yielded significantly more than Maris Badger. Pests and diseases that attack roots seem not to be the cause of poor barley yields at Saxmundham.

Table 15 shows that nitrogen greatly increased yields and, in contrast

TABLE 15

The effects of different amounts and times of nitrogen fertilisers on yields of barley grain (cwt/acre at 85% dry matter) at Saxmundham in 1967

Variety	Yields without nitrogen { Deba Abed 16.1 Maris Badger 27.7 lb N/acre applied			
	67		135	
	March	May	March	May
Deba Abed	29.8	46.5	44.1	42.7
Maris Badger	33.5	41.9	37.9	38.2
	Standard error ± 1.36			

with the results from previous barley experiments on heavy soils, May top-dressings gave much larger yields than seed-bed dressings. In March more than 135 lb N/acre was needed for maximum yields, but in May 67 lb N/acre was probably enough, for it gave the largest yields (presumably because the larger amount lodged the barley). In wet springs much of the nitrogen applied early to poorly textured clay soils may be wasted. (Widdowson, Penny and Flint)

An experiment with formalin on timothy and meadow fescue at Rothamsted. A formalin drench applied in February was tested in all combinations with none, 67, 135 and 202 lb N/acre applied in March before the grasses were sown. At the first cutting (in July) formalin significantly increased yields both with and without fertiliser N, but most where none was given and least with the most N. (Widdowson, Penny and Flint)

Field experiments with methyl bromide. Three small experiments at Saxmundham tested the effect of disinfecting soil with methyl bromide

TABLE 16

Effects of nitrogen fertilisers and methyl bromide on yields per acre of sugar beet, potatoes and barley at Saxmundham

N. applied lb/acre	Methyl bromide ml/sq. ft	Sugar beet		Potatoes, tubers (tons)	Barley, grain† (cwt)
		Roots (tons)	Tops		
0	0	14.9	8.0	8.5	17.6
56	0	17.7	6.8	9.6	31.8
112	0	17.9	10.4	8.9	34.9
168	0	20.4	11.1	9.7	38.9
84	3.3	19.9	7.1	11.8	36.1
(84)*	0	(17.8)	(8.6)	(9.2)	(33.4)
	Standard error	± 1.58	± 1.17	± 1.19	± 2.45

* Data in brackets are simple averages of yields with 56 and 112 lb N/acre.

† At 85% dry matter.

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before sowing barley, sugar beet and potatoes. The land used had been fallowed in 1966, and we had no reason to expect large gains from a sterilant; the experiments were made to see whether soil-borne pests and diseases are a major cause of the poor yields often obtained in the Rotation Experiments at Saxmundham. Yields are shown in Table 16. None of the experiments was accurate. Methyl bromide increased the yields of sugar beet, potatoes and barley, although not significantly so. Some at least of the extra yield must have come from the mineral nitrogen methyl bromide released from the soil. The gains from disinfecting the soil were not large enough to suggest that soil-borne pests and diseases cause large losses of these three crops when they are grown in satisfactory rotations. (Williams and Cooke)

Greenhouse and laboratory work on nitrogen released in partially sterilised soil. Several ways were tried of partially sterilising a sandy loam soil from Woburn which has often grown cereals: the soil received a 2.5-megarads dose of gamma-rays, or 1000 ppm of methyl bromide, or formalin for 72 hours. Mineral nitrogen was released two or three times more quickly in treated than in untreated soil. After allowing volatile sterilants to escape, wheat and ryegrass were grown in the soil in pots in a glasshouse, with and without calcium nitrate supplying either 177 or 354 mg N/pot. Table 17

TABLE 17

The effects of partial sterilants and N fertiliser on yields and N uptakes of ryegrass and wheat in a pot experiment

Nitrogen applied (mg/pot)		Sterilant				Standard error per pot
		None	Gamma radiation	Methyl bromide	Formalin	
<i>Yields of roots and tops in grams dry matter/pot</i>						
0	Ryegrass	3.0	7.1	5.2	5.0	} ±0.51
177		13.8	16.5	14.8	14.8	
354		17.6	20.2	17.9	17.0	
0	Wheat	3.0	5.5	3.9	4.4	} ±0.72
177		10.2	13.1	9.7	11.2	
354		14.0	14.7	11.8	12.7	
<i>Nitrogen in roots and tops, mg/pot</i>						
0	Ryegrass	31	75	59	53	} ±8.9
177		186	221	212	218	
354		337	393	369	390	
0	Wheat	34	79	65	61	} ±7.5
177		174	239	223	217	
354		323	388	365	372	

shows that irradiated soil produced more dry matter of both crops than soil untreated or treated with methyl bromide or formalin, which increased yield only when little or no N was given. Crops grown in irradiated soil contained more nitrogen than those in untreated soil or soil treated with methyl bromide or formalin. Both methyl bromide and formalin

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gave crops richer in nitrogen than crops from untreated soil; this advantage persisted even with plants given the largest amount of fertiliser-N, though not accompanied by an increase in yield. The increased yields of both crops apparently reflected the extra soil N mineralised by the sterilisation treatments, and there was no indication that partial sterilisation improved growth by controlling soil-borne pathogens. Inoculating treated with untreated soil did not alter the results.

Yields of wheat from pots given the most fertiliser N and treated with methyl bromide or formalin were probably decreased because non-volatile degradation products of these chemicals remained in the soil after treatment. Soil treated with methyl bromide contained 121 ppm bromine, determined by X-ray-fluorescence spectroscopy. All the residual bromine was removed by leaching with $N-K_2SO_4$ solution; presumably it was retained in the soil as bromide ions. (Jenkinson, Pedology Department, with Nowakowski and Mitchell)

The effects of formalin on the mineral-N and mineralisable-N were also measured in some of the soils from field experiments.

Rothamsted. Formalin applied before sowing grass on Fosters field increased mineral-N from 7.4 to 8.9 ppm 6 weeks later (just before sowing the grass), and changed the proportions of ammonium and nitrate:

	ppm	
	NH_4^+-N	NO_3^--N
Without formalin	2.9	4.5
With formalin	4.9	4.0

When the fresh soils were incubated for 24 days at 25°, formalin-treated ones produced 40 ppm N and untreated ones 23 ppm.

Saxmundham. Treating with formalin increased mineral-N in the field 6 weeks later from 4.9 to 6.1 ppm N; after incubating soils for 24 days at 25° C it increased N mineralised from 16 to 25 ppm (averaging plots with and without lime). Applying lime decreased the N mineralised by 1.6 ppm (averaging plots with and without formalin). (Gasser, Widdowson and Penny)

Soil structure

We continued work that attempts to show how soil structure alters nutrient uptake. Three field experiments now measure slaking and shrinkage in cultivated soils, and the results of physical tests on very many soils are being related to their physical and chemical properties.

Consolidation of ploughed land. A micro-survey apparatus, similar to that of B. Wilton (*J. agric. Engng Res.* (1964), 9, 214), was used to compare the behaviour of the surface soils on Fosters Field at Rothamsted (Clay Loam on Clay-with-Flints), Stackyard Field at Woburn (Sandy Loam over Lower Greensand), and Harwood's Field at Saxmundham (Chalky

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Boulder Clay). Duplicated measurements were made on uncovered and covered strips of soil cultivated by hand 9 in. deep. The uncovered soil slaked most at Saxmundham, where the mean fall of the surface was 1.4 in., compared with 1.1 in. at Rothamsted and 0.7 in. at Woburn. The rates of slaking cannot be compared strictly, because measurements began at different times and rainfall also differed. Work began at Saxmundham earlier, but less rain fell there than at the other two sites between April and June; nevertheless, Saxmundham soil slaked and subsided more quickly.

The covered soil (protected from rain) shrank most at Saxmundham (0.9 in.) and least at Woburn (0.3 in.), shrinkage at Rothamsted was 0.5 in. The surfaces of covered and uncovered soils at all three sites tended to move similarly. Covered soils absorbed water from moist air and swelled in much the same way as unprotected soil swelled when wetted by rain. Wind removed covers from two strips at Rothamsted in October, and the soil beneath was wetted by rain. Slaking in these strips was proportional to slaking in the uncovered strips *at the same time*; the previously covered soil did not slake completely in one wetting. The porosity of all the soils in these experiments will be measured next spring. (Williams)

Stability of soil aggregates

Table 18 shows the correlation coefficients between physical tests and soil composition, calculated for a group of 189 widely differing soils. Losses of pore space caused by instability in water, by dry mechanical slaking and by total (water and mechanical) slaking were measured on artificially prepared

TABLE 18
Correlation coefficients between results of physical tests on soils and their composition

Soil composition	Water slaking instability (%)	Dry slaking instability (%)	Total mechanical instability (%)	Breaking strength (Kgm)
G + CS + FS (6-0.02 mm)*	0.72	0.79	0.58	-0.62
G + CS (6-0.2 mm)*	0.63	0.69	0.49	-0.57
% Organic carbon	-0.63	-0.36	-0.62	-0.13
% Total nitrogen	-0.68	-0.48	-0.63	-0.03
% Silt (0.02-0.002 mm)	-0.48	-0.59	-0.38	0.40
% Clay (<0.002 mm)	-0.55	-0.61	-0.40	0.62

* G : gravel, 6-2 mm.

CS : coarse sand 2-0.2 mm.

FS : fine sand 0.2-0.02 mm.

aggregates by the methods of Williams & Cooke (*Soil Sci.* (1961), **92**, 30-39). Breaking strength of soil cylinders produced by the tests on mechanical slaking was measured.

Instability and breaking strength of crumbs was more closely related to percentage of gravel and coarse plus fine sand than to coarse sand and gravel alone. Increasing percentages of organic carbon (Walkley-Black method) increased resistance to water and mechanical slaking. Breaking strength of clods was little affected by percentage of organic carbon, but was greatly increased by increasing percentage of clay and diminished as

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coarse sand increased. Stability to water diminished as percentages of coarse and fine sand increased, and increasing organic matter made the soils more stable to wet slaking, whereas changes in proportions of silt and clay had less effect. By contrast, soils were made more stable mechanically by increases in silt and clay than by increases in organic matter. The percentages of total N were sometimes better correlated than percentages of organic carbon with soil behaviour (perhaps because nitrogen content is a better indicator of the recent history of soil).

Partial regression analyses were made on the results of each of the physical tests and soil properties, and equations accounting for the largest percentage of total variance associated with each test were calculated in terms of the mineral and organic-matter fractions. The partial regression coefficients, with associated levels of t , which measure their relative importance, are given, together with the regression equations in Table 19.

TABLE 19
Regression coefficients and equations relating soil physical tests and soil composition

Physical test (y variate)	Soil composition* (x variate)	b	SE	t	Regression equation
% Water slaking instability (I/WS)	% OC	-5.95	0.866	6.87	I/WS = 2.48 - 5.95% OC + 0.47% MP
	% MP	0.468	0.047	10.02	
% Dry mechanical instability (I/DS)	% MP	0.338	0.019	17.38	I/DS = 1.42 + 0.34% MP
% Total mechanical instability (I/MS)	% OC	-3.11	0.426	7.30	I/MS = 56.43 - 3.11% OC + 0.13% MP
	% MP	0.132	0.023	5.74	
Breaking strength (Kgm) (B/S)	% OC	-24.27	2.111	11.49	B/S = 22.31 - 2.43% OC - 0.20% MP
	% MP	-2.03	0.114	17.82	

* % OC = % organic carbon (Walkley & Black) % MP = Mineral particles 6 mm-0.02 mm.

The percentages of the range of particles that includes the gravels, coarse sands and fine sands (6-0.02 mm) were more useful than other physical or chemical soil descriptions in determining whether soil aggregates were stable to water or to mechanical force, or whether clods were easily crushed. Organic-matter content was the only other soil property measured that was worth including in the equations. (Williams)

Apparatus and experimental methods

Flame spectrophotometric analysis. When estimating barium in extracts made from micas, aluminium suppresses barium emission. We confirmed the report by I. Rubeska and B. Moldan (*Analytica chim. Acta* (1967), **37**, 421) that a mixture of lanthanum and oxine prevents this. (Salt)

Technicon AutoAnalyzer. This instrument has been used for over a year, mostly to measure P in crops and soils, but also total N in Kjeldahl digests and nitrate in soil and plant extracts. It is very quick, and results are reproducible. Cations, alone or together, do not interfere with measuring P within the concentrations found in plant material or soil extracts.

D. N. Fogg and N. T. Wilkinson's method (*Analyst* (1958), **83**, 104), which was always used in the AutoAnalyzer, was compared with five manual methods for estimating phosphorus in solution. With 0-100 ppm

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of P the solutions needed no dilution, and the AutoAnalyzer was more accurate than other methods. Another manifold was used in the range 0–2 ppm of P; diluting the prepared solutions doubled the standard error. Of the manual methods W. C. Hanson's (*J. Sci. Fd Agric.* (1950), **1**, 172) using vanadomolybdate yellow was best. E. Truog and A. H. Meyer's 1929 method (*Ind. Engng Chem. analyt. Edn*, **1**, 136) long used in the Chemistry Department, was worst.

The AutoAnalyzer was much used to measure phosphorus in extracts of soils made with 0.5M-sodium bicarbonate solution and 0.01M-calcium chloride solution. The two methods used in the AutoAnalyzer were Fogg and Wilkinson's (tested above) and J. Murphy and J. P. Riley's (*Analytica chim. Acta* (1962), **27**, 31), modified to make it stable and prevent reagents precipitating in the mixing coils. Both were compared with Truog and Meyer's old method, used manually on extracts made from 22 soils taken from sites in many parts of Britain. Results with soils containing much soluble P (more than 30 ppm of P soluble in bicarbonate solution, and more than 4 μ M P/litre in calcium chloride solution) agreed well. With soils containing little P, the Fogg and Wilkinson method found significantly more P in extracts made with calcium chloride, and slightly more in bicarbonate extracts, than the other two methods, which agreed well. The heating needed to develop the colour in Fogg and Wilkinson's method probably hydrolysed organic phosphorus extracted from the poorer soils, and so gave the larger amounts.

Total phosphorus in soils was extracted after fusing with sodium carbonate; using Fogg and Wilkinson's method in the AutoAnalyzer gave results agreeing well with those obtained manually. The same method was also satisfactory for measuring total P in extracts of dry-ashed plant materials. Soil extracts were analysed at 20 samples/hour and plant-ash extracts at 60/hour.

Total nitrogen in Kjeldahl digests of plant material, measured by using J. A. Varley's method (*Analyst* (1966), **91**, 116) in the AutoAnalyzer, agreed well with results obtained by distilling manually and titrating. Varley's method was modified by including a sodium citrate-sodium tartrate reagent stream in the manifold to prevent copper being precipitated. Forty samples an hour were analysed.

Nitrate-N and nitrite-N were measured in extracts of soils made with 1N-potassium sulphate, and in extracts of plant material made with 0.1N-potassium sulphate. M. H. Litchfield's method (*Analyst* (1967), **92**, 132), used in the AutoAnalyzer to deal with 20 samples/hour, gave results agreeing well with those obtained by manual distillation and titration. Nitrate plus nitrite were determined in the extracts by reducing nitrate to nitrite before measuring the colour. To correct the nitrate figure because of nitrite present in the extracts, nitrite alone was estimated in 40 samples per hour.

When the method used to analyse Kjeldahl extracts was used to analyse ammonium-N in soil and plant extracts made with potassium sulphate solution the values obtained were too large. The colorimetric reaction used on the AutoAnalyzer is not specific for ammonium-N, and amino-acids and amino-sugars in the extracts interfere. (Salt and Messer)

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Total nitrogen in 11 soils with 0.08–0.4% N, measured by J. M. Bremner's Kjeldahl method (*J. agric. Sci., Camb.* (1960), **55**, 11–33), agreed well with measurements by an automated Dumas method. One gram of <2 mm soil, ground to pass a 0.5-mm round-hole sieve, was used for the Dumas method; other conditions were as used for plant material (*Rothamsted Report* for 1965, pp. 66–67). Copper in the post-heater tube had a much shorter life when soils were analysed. (Hamlyn and Avery)

Spectrophotometric analysis. The old medium quartz spectrograph, now converted to direct reading, was originally fitted with a blue-sensitive photomultiplier tube (Mazda Type 27 M3). Replacing this tube by an EMI (Type 9592B) has extended measurements to the red end of the spectrum. A new power supply unit was built. (Smith)

Polarographic analysis. The sensitivity of the D.C. Polarograph fitted with "Univector" attachment described in *Rothamsted Report* for 1965 (p. 68) was further increased by amplifying with a Chandos "Ultra Galvanometer" coupled to a "Servoscribe" recorder. As little as 0.01 ppm of copper, nickel, cadmium and zinc was measured accurately, and the method was used to examine distilled, tap and drainage waters. Little solution is needed (<2 ml), and a pen recording is used. (R. J. B. Williams)

Measuring nitrate in field crops. Diphenylamine dissolved in strong sulphuric acid has long been used as a semi-quantitative field test of nitrate in plant sap. Diphenyl benzidine is a more sensitive reagent (I. M. Kolthoff & G. E. Noponen, *J. Am. Chem. Soc.* (1933), **55**, 1448) and was used in the field to measure 10 ppm or less of nitrate-N in plant sap. The sap, produced by squeezing about 20 mg of stem or petiole tissue in a narrow glass tube with a plunger, is absorbed on a small disc of glass-fibre filter and the reagent is added. The reaction and colour production are not complicated by fragments of tissue carbonising. By matching the colours produced with standards, 1–10 ppm of nitrate-nitrogen can be determined. Using the diphenylamine reagent in the same way covers the range 20–1000 ppm of nitrate in plant sap. The method was used to detect the very small amounts of nitrate in tissue from N-deficient crops, and the response to top-dressing. We hope to develop it as a check on nitrogen manuring. (R. J. B. Williams)

Staff and visiting workers

O. Talibudeen returned from a year at the Rubber Research Institute in Malaysia. R. K. Cunningham returned in October from 3 years at the University of the West Indies and left in November to join the Overseas Development Ministry. J. D. H. Williams resigned his temporary appointment to join the Canadian Department of Agriculture. A. R. Bromfield was appointed to a supernumerary post for work overseas.

Visiting workers included Dr. M. Kozak (Hungary), Mr. A. Schmitt (Switzerland), Mr. E. D. Spratt (Canada) and Mr. S. Sivasubramaniam (Ceylon).

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B. Benzian was a guest of the International Potash Institute at a Colloquium on Forest Fertilisation which the Institute arranged in Finland. J. K. R. Gasser was a guest of the Institute of Soil Fertility in Groningen (Holland) at a symposium on Nitrogen in Soil. G. E. G. Mattingly was invited by the Joint FAO/IAEA Division of Atomic Energy in Food and Agriculture to a meeting in Vienna on Plant Nutrient Supply and Movement.

J. Bolton was awarded the Ph.D. degree of London University.