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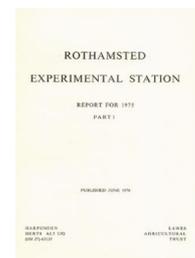
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Report for 1975 - Part 1

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Chemistry Department

G. E. G. Mattingly

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Introduction

This year the main lines of work of the Department have continued almost unchanged, though we report less research on field experiments than usual, partly because staff lost during the moratorium have not been replaced. We describe new experiments on the use of carbon disulphide to inhibit nitrification and lessen losses of nitrate from the soil. Preliminary results show that carbon disulphide, injected with aqueous ammonia under grass in November, effectively inhibited nitrification and increased grass yields at Rothamsted. Carbon disulphide had little effect, however, on yields on the sandy loam soil at Woburn. More work is planned with this promising material. We also summarise work that has been in progress for some years to predict, from a few relatively simple laboratory measurements, the maximum amounts of potassium that are available to crops from different soils during growth. Total potassium release is calculated from the simultaneous rates of release of potassium from three sources in the soil, corresponding to surface K, 'peripheral' K and 'matrix' K.

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In Part 2 of the Report we give recent measurements of losses of nitrogen, phosphorus and potassium by drainage. Losses of nitrate in drainage (1972-75) under arable crops at Saxmundham were about four times those under herbage crops. Losses varied greatly in different years; under arable crops, 53 kg N ha⁻¹ was lost during wet weather between October 1974 and May 1975 but only about 8 kg N ha⁻¹ during the dry winter of 1972-73. Negligible amounts of phosphorus (<0.1 kg P ha⁻¹) and potassium (0.2-4.2 kg K ha⁻¹) were lost in this way.

Results of experiments at Woburn, also given in Part 2, assess the value to crops of different amounts of soluble phosphorus in soils. On an old arable field yields of barley, potatoes and sugar beet were always much less than on a soil well supplied with residues of organic manures. Moreover, contrary to expectation, the crops on the site containing the most organic matter responded to fresh superphosphate at soil P levels much above those where response ceased on the old arable soil. These experiments illustrate the difficulties of relating crop yields unambiguously to soil analysis even on the same farm and show that the previous history of the site is sometimes more important than the treatments tested in determining the yields of the crops grown.

Experiments with nitrogen fertilisers

Alternative nitrogen fertilisers for winter wheat, 1974-75. Liquid NPK and N fertilisers are increasingly being used in the United Kingdom, especially on large arable farms, where shortage of labour often determines choice. Some farmers have asked how these liquids can best be applied, because spraying solution fertilisers, which saves time, rather than broadcasting or placing granular fertilisers, would be uneconomic if smaller yields resulted. Our earlier barley experiments showed that placement of liquid fertilisers, though slower than spraying, produced larger yields (*Rothamsted Report for 1973*, Part 1, 51-52). This work was later extended using liquid fertilisers for winter wheat. Three experiments on private farms in 1974, and three more in 1975, compared yields from spring applications of three liquid N fertilisers with those from granular ammonium nitrate.

In each experiment aqueous ammonia (28% N) was compared with aqueous urea (18% N); each was injected in bands that were 8-9 cm deep and either 25 or 50 cm apart. These two fertilisers were injected during April at growth stages 4-5 on the Feekes scale. On other plots, a solution (26% N) of ammonium nitrate and urea was sprayed over the wheat either partly at the same time as the injection and partly in May (at growth stages 6-7), or wholly in May. Yields from all three liquids were compared with those from ammonium nitrate granules ('Nitro-Chalk', 25% N), broadcast either partly in April (concurrently with the liquids) and partly in May, or wholly in May. Each of these eight fertiliser treatments were compared at rates supplying 50, 75, 100 or 125 kg N ha⁻¹.

In 1974 heavy rain in July caused severe lodging on two heavy land farms, hence maximum yields were obtained with only 50-75 kg N ha⁻¹; giving 100 or 125 kg N ha⁻¹ greatly decreased yields. On a farm on lighter land, yields were largest with 125 kg N ha⁻¹. Under these conditions the greatest need, for the efficient use of fertilisers, was to predict the best amount of N to apply and differences between the nitrogen fertilisers used were relatively unimportant. In 1975 little rain fell in June or July and there was no lodging. Best amounts of N ranged from 75 to 100 kg N ha⁻¹, but prediction was less important because yields were not diminished by excess N.

Because of severe lodging, produced by the two largest amounts of N at two of the 1974 centres, comparisons between these treatments are misleading. Consequently, Table 1 gives mean yields only from the four experiments where lodging did not complicate the interpretation of results. Yields with aqueous urea were slightly larger than with

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TABLE 1

Mean yields of winter wheat from four experiments comparing alternative nitrogen fertilisers, 1974-75

Yields of grain in t ha ⁻¹ at 85% dry matter		
Without nitrogen fertiliser 3.96		
With sub-surface applications of:	Fertilisers applied as	
	Aqueous ammonia	Aqueous urea
Injector knife spacing (cm)		
25	6.16	6.21
50	5.95	6.08
With surface applications of:	Ammonium nitrate/urea solution	Ammonium nitrate granules
Timing of N		
½ April, ½ May	5.71	6.26
All in May	5.70	6.12

aqueous ammonia and yields from each were a little larger when the bands were 25 rather than 50 cm apart. Injected in this way, yields from each fertiliser were a little larger than from comparable dressings of ammonium nitrate broadcast all at once in May, but a little smaller than from divided dressings of ammonium nitrate. Ammonium nitrate/urea solution, sprayed on one or on two occasions, scorched the leaves, especially at the second spraying and gave smaller yields than the two injected liquids or the broadcast granules. (Widdowson and Penny)

Late sprays of liquid N fertiliser and broad spectrum fungicide for winter wheat. An experiment at Saxmundham, which had tested amounts of spring-applied granular N fertiliser ('Nitro-Chalk') for successive wheat crops since 1970, was modified in 1974 to see (i) whether yields could be further increased by late sprays of liquid N fertiliser, and (ii) whether the wheat would make better use of this extra N if late-developing leaf diseases were controlled by a broad spectrum fungicide. The fertiliser solution, made from ammonium nitrate and urea, contained only 6% N to facilitate spraying the small amounts tested. The active ingredients of the fungicide were benomyl and mancozeb.

'Nitro-Chalk' was broadcast on whole plots in late April to supply 0, 50, 100 and 150 kg N ha⁻¹ and a 2 × 2 test (without and with) of the liquid fertiliser and fungicide was made on half-plots to make a single replicate of 16 half-plots. The liquid N fertiliser was sprayed to supply 25 kg N ha⁻¹ at each of growth stages 10.4 and 10.5.4 (Feekes scale). The fungicide was also sprayed at these stages and again at 11.1. The experiment was repeated in 1975, with 'Nitro-Chalk' applied cumulatively with that in 1974, but with the liquid N and fungicide treatments allocated to different half-plots.

Estimates at growth stage 10.5.4 in 1974 on all wheat given 'Nitro-Chalk' supplying either 100 or 150 kg N ha⁻¹ showed that mildew infection was slight and *Septoria* infection negligible. The mean percentage area of the second and third leaves affected by mildew was, however, decreased from 5.8 to 3.3 by the fungicide sprayed three weeks previously. Similar estimates at growth stage 10.5.4 in 1975 showed that mildew was even less prevalent than in 1974 and was again decreased by the fungicide. *Septoria* was more severe in 1975 but was not affected by the fungicide, probably because it was sprayed too late. Table 2 shows that in 1974 and again in 1975 the liquid N increased yield, whether or not the fungicide was also given. The fungicide doubled the effectiveness of the liquid N in 1974 but had no effect on the response to the liquid N in 1975, presu-

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TABLE 2

Mean yields of winter wheat from late sprays of liquid N fertiliser and broad spectrum fungicide

	Yields of grain in t ha ⁻¹ at 85% dry matter			
	Without liquid N fertiliser		With liquid N fertiliser	
	Without fungicide	With fungicide	Without fungicide	With fungicide
In 1974	4.94	5.09	5.21	5.71
In 1975	4.24	4.19	4.64	4.57

ably because it did not control *Septoria*. In both years the benefits from the liquid N increased with increasing amounts of 'Nitro-Chalk', probably because the larger leaf areas of the larger crops were better able to accept it. The liquid N increased mean yield by approximately 9% in both years.

The fungicide increased mean yield by 6% in 1974 although there was little mildew and negligible *Septoria*. Similar benefits from this type of fungicide, which could not be associated directly with the control of *Septoria*, have been reported recently (Mundy & Stevens, *Arable Farming* (December 1974), 13). In 1975, when *Septoria* was more severe, the fungicide did not control it and had no effect on yield. (Penny and Widdowson, with Jenkyn, Plant Pathology Department)

Late nitrogen foliar applications for winter wheat. The experiment on Gt Knott II (*Rothamsted Report for 1974*, Part 1, 80) in which N, as Ca(NO₃)₂, was sprayed (5% N solution) on winter wheat at rates up to 90 kg N ha⁻¹ at Feekes scale stages 6, 10 and 11.1, after spring 'Nitro-Chalk' dressings of 30 or 90 kg N ha⁻¹, was repeated, with some modifications, in 1975. Because of scorch damage in 1974, a glasshouse experiment was carried out during winter to compare the effects of urea and Ca(NO₃)₂ solutions and also to find the time of day when foliar spraying causes least damage. Calcium nitrate scorched leaves and depressed yields most and spraying at dusk (about 20.00 h) produced least scorch.

In a microplot experiment on Long Hoos III in 1975, urea was sprayed (5% N solution) in the late evening at the growth stages given above. None of the spray treatments gave a greater yield than equal amounts of N given in spring as 'Nitro-Chalk'. Crop responses to spraying at early stem extension (Feekes scale 6) were less than those from spring dressings. Spring dressings significantly increased yield when up to 120 kg N ha⁻¹ was given. Spraying 60 kg N ha⁻¹ at stages 10 or 11.1 (in addition to 90 kg N ha⁻¹ in spring plus 90 kg N ha⁻¹ sprayed at stage 6) produced grain yields that were 0.75 t ha⁻¹ more than those from 90 kg N ha⁻¹ in spring plus 90 kg N ha⁻¹ at stage 6.

The N concentration in grain increased with the amount of N given. 'Nitro-Chalk', applied in spring, gave higher % N in grain than equivalent split treatments; further nitrogen applications at stage 6 on the Feekes scale increased % N in grain very little but some large increases were obtained from the extra N given at stages 10 and 11.1. (Talibudeen, Penny and Page)

Aqueous ammonia and nitrification inhibitors for grass. The nitrification inhibitors 2-chloro-6-trichloromethylpyridine ('N-Serve', Dow Chemical Co.) and carbon disulphide (CS₂) were injected simultaneously with aqueous NH₃ under grassland both at Rothamsted and at Woburn in November 1974 and February 1975. The detection, measurement and movement of the inhibitors is described elsewhere in this Report

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(p. 177). Their effects on nitrification of NH_3 and on yields and % N in grass are given below.

Aqueous NH_3 (250 kg ha^{-1}) was injected either alone, or with 'N-Serve' (2.7 kg ha^{-1}) or CS_2 (15 kg ha^{-1}) and cross-sections of the injected bands of soil were removed from the field at intervals during the following three months. Sub-samples were extracted with 2M KCl. Nitrification of NH_3 , injected in November, was almost complete at Woburn after 60 days in bands without inhibitor but was slower at Rothamsted. Nitrification in bands given CS_2 was inhibited throughout the cross-sections from both sites and most of the applied N was recovered as ammonium N up to 60 days after injection. For the first 50 days no nitrate N was produced in bands given CS_2 at Rothamsted. Plots given 'N-Serve' had intermediate amounts of nitrate N at both sites. The effects of the inhibitors on nitrification in plots given NH_3 in February were not as easily monitored because nitrate was taken up by grass during growth. From April onwards, amounts of nitrate in these plots were less at Rothamsted where inhibitors had been applied, but not at Woburn.

TABLE 3

Effects of nitrification inhibitors on yields and % N in grass at Rothamsted and Woburn given 250 kg N ha^{-1} as aqueous ammonia in either November 1974 or February 1975

	No nitrogen	Fertiliser N applied in November 1974 as			Fertiliser N applied in February 1975 as		
		Aqueous ammonia	Aqueous ammonia + 'N-Serve'	Aqueous ammonia + CS_2	Aqueous ammonia	Aqueous ammonia + 'N-Serve'	Aqueous ammonia + CS_2
Rothamsted							
Yield, t ha^{-1} dry matter	4.6	6.6	7.3	7.1	6.4	7.0	7.0
% N in grass	0.98	1.41	1.50	1.58	1.83	1.75	1.75
Woburn							
Yield, t ha^{-1} dry matter	6.1	6.9	7.2	7.2	6.9	6.8	6.6
% N in grass	1.40	1.46	1.60	1.44	2.17	2.10	2.20

The grass was first cut in June (Table 3). Later yields were small on all plots because of drought. The inhibitors increased yields of the first cut at Rothamsted on plots given NH_3 in November or February. The % N in grass was increased by the inhibitors at Rothamsted on plots given NH_3 in November, but not on plots given NH_3 in February. At Woburn, however, the inhibitors had little or no effect on yield or on % N in grass presumably because ammonium N was taken up from the soil solution.

Carbon disulphide is much cheaper than patented nitrification inhibitors like 'N-Serve' but, unfortunately, CS_2 reacts rapidly with NH_3 . The use of trithiocarbonates, such as Na_2CS_3 , may avoid the need to inject CS_2 separately. It may also be possible to use trithiocarbonates to delay nitrification of anhydrous ammonia and granular nitrogen fertilisers. (Ashworth, with Briggs and Evans (Chemical Liaison Unit))

Reactions of aqueous ammonia with soil. Previous attempts to measure NH_3 sorption isotherms in mixtures of soil or clay with aqueous NH_3 gave results that depended on the ratio of amounts of solid and solution (*Rothamsted Report for 1972, Part 1, 47*). Reproducible isotherms have now been obtained, by first dispersing clay samples in water for 24 h, then adding aqueous NH_3 and stirring or shaking for several days. To measure the NH_3 sorbed, the equilibrated mixtures were centrifuged and aliquots of the

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supernatant solutions steam distilled. The amounts of NH_3 released were collected, titrated and compared with those released from a control aliquot.

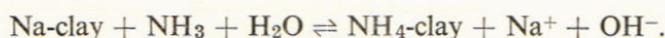
Clay fractions of three mineralogically different soils with the same cation exchange capacity (Batcombe, Bromyard and Speller soil series), saturated with Na, Ca or NH_4 , were used. Sorption was measured over the equilibrium concentration range 0–300 mmol NH_3 litre⁻¹. At 100 mmol litre⁻¹ the amount of NH_3 sorbed was about 70% of that sorbed at 300 mmol litre⁻¹. In all cases the Na-clay sorbed more NH_3 than the NH_4 -clay, and the Ca-clay sorbed an intermediate amount (Table 4).

TABLE 4

NH₃ sorbed on clay in equilibrium with aqueous solutions containing 100 mmol NH₃ litre⁻¹
mmol kg⁻¹ clay

Soil series from which clays were derived	Saturating cation		
	Na	Ca	NH_4
Batcombe	270	210	140
Bromyard	170	110	50
Speller	290	190	150

Apparently Na-clays sorb more NH_3 because some Na^+ ions are displaced from clay into solution according to the equation:



Presumably a similar process occurs with Ca-clays but displaced Ca^{2+} ions react with OH^- ions and are precipitated as CaCO_3 in the presence of CO_2 . With NH_4 -clays no net sorption can occur through this mechanism, and NH_3 is apparently sorbed only on pH-dependent charge sites.

To measure the amount of OH^- ion released as a result of this process of NH_3 sorption on Na-clays, two aliquots of the supernatant solution were taken. One was titrated without steam distilling, thereby measuring the NH_3 and OH^- ion contained, and the other was titrated after steam distilling, thereby measuring NH_3 alone. The amounts of OH^- ion measured were approximately equivalent to the amounts of Na^+ ion released, measured spectrophotometrically, and they also agreed with the difference (about 130 meq kg⁻¹ soil at equilibrium with 100 mmol NH_3 litre⁻¹) in NH_3 sorption by the Na- and NH_4 -clays. (Ashworth and Pyman)

Changes in soil nitrate concentrations under winter wheat. Soil nitrate measurements were made from April to August under commercial winter wheat on Long Hoos III, given 125 kg N ha⁻¹ as 'Nitro-Chalk' in spring. The techniques of measurements were described previously (Nair & Talibudeen, *Journal of Agricultural Science* (1973), **81**, 327–337). In 1975, more replicates were used to increase precision (four holes in ten fallow 2-m squares of cropped and fallow soil) and all measurements were made at only one depth, 15 cm. Surprisingly, nitrate concentrations decreased ten-fold during May in both cropped and fallow soil and reached minimum values in June. However, a few measurements made during May and June showed that nitrate concentrations remained high in the surface *centimetre* of soil. Nitrate levels increased through July, probably because of low rainfall (June, 25 mm, July, 21 mm) and high rates of evaporation from surface soil.

Throughout June and July, when the crops were healthy and grew well, N was taken up from soil nitrate concentrations as low as 2–4 mg N litre⁻¹ ($\text{pNO}_3 = -\log [\text{NO}_3] = 3.8\text{--}3.5$ in soil at field capacity). Moreover, these levels did not drop further, so the NO_3^- pool must have been continually replenished either by movement from the surface

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or from below, or by mineralisation of organic nitrogen. Maximum differences in NO_3^- concentrations between fallow and cropped sites, which represent the effect of crop uptake, occurred during early stem extension, panicle emergence and at the milk stage (Feeke's scale, stages 6, 10 and 11.1). Measurements made on Broadbalk (plot O7, section I) showed similar patterns of change of pNO_3 and of uptake by the crop. (Page and Talibudeen)

Leaching and movement of nutrients in soil

Simple equations for winter nitrate leaching. Data for the leaching of calcium nitrate, applied in early autumn to bare soil in Harwoods Piece (*Rothamsted Report for 1974*, Part 1, 78), were used to test an equation of Burns (*Journal of Agricultural Science, Cambridge* (1975), 85, 443-454) which considers a single percolation through many soil layers. Two further simple equations were tested which consider the effects of successive percolations in two-layer systems in which either temporary over-saturation (as suggested by Burns) or piston-flow occurs. All three equations much underestimated leaching if it was assumed that all soil water took part in the equilibrations between water and nitrate during leaching. Best results were obtained when only water at a suction of less than 2 atm was used in the equations. Differences between predictions from the different equations were less important than the assumptions about the amounts of water involved in nitrate movement. (Addiscott)

Phosphorus in soils and crops

Desorption of phosphate from some Rothamsted soils. Much work has been done on the measurement of adsorption isotherms of phosphate on soils from Rothamsted and elsewhere but desorption has been much less studied. Desorption isotherms, which are not necessarily the same shape as adsorption isotherms, are important because they govern the uptake of applied phosphate from soil, once adsorption or transformation to more insoluble forms is complete. They should be particularly relevant for studying the uptake of residual phosphate from soils.

TABLE 5

Analyses of soils from plot 4-0 from the Hoosfield Continuous Barley experiment, 1882-1965

Year	pH (in 0.01M CaCl ₂)	CaCO ₃ (%)	mg P kg ⁻¹ air-dry soil					
			Total P	Total isotopically-exchangeable P (144 h)			Maximum amount of P desorbed by	
				0.02M KCl	0.01M CaCl ₂	NaHCO ₃ - soluble P	0.02M KCl	0.01M CaCl ₂
1882	7.2	1.50	880	169	125	56	—	40
1913	7.2	0.74	1163	286	226	105	—	113
1946	6.9	0.25	1272	327	260	108	—	136
1965	6.9	0.16	1347	397	323	126	320 ^a	196

^a pH 7.2

Desorption isotherms were measured on soils taken between 1882 and 1965 from the Hoosfield Continuous Barley experiment (Table 5). Isotherms were obtained by measuring the phosphate concentrations in 0.01M CaCl₂ at increasing solution/soil ratios, which ranged from 0.01 to 50 litre g⁻¹. Most measurements showed that the concentration of phosphate in solution did not change after more than 24 h of desorption and that there is a limit to the amounts that can be desorbed at a given pH value. At solution/soil ratios

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of 0.5 and 1.25 litre g^{-1} phosphate desorption decreased very greatly between pH 3 and pH 10 whereas, at a solution/soil ratio of 20 litre g^{-1} , desorption passed through a minimum at pH 7. These effects of pH are different from those observed for oxide surfaces and for tropical soils, where adsorption always decreases and desorption increases between pH 7 and pH 10.

Solutions of lower ionic strength (0.001M $CaCl_2$) desorbed more phosphate (at any solution/soil ratio) although the maximum amount desorbed remained the same. Using 0.02M KCl in place of 0.01M $CaCl_2$ increased desorption and maximum desorption. When the desorption isotherms of several soils were compared with those obtained from desorption by a growing plant (Webber & Mattingly, *Journal of Soil Science* (1970), **21**, 111-120), the 'plant' desorption isotherms lie at higher solution phosphate concentrations so that the plant, in some way, renders the phosphate more easily desorbable.

The amounts of phosphate desorbed were always significantly less than the total isotopically-exchangeable phosphate. There is a unique linear relationship between maximum desorption and the amounts of isotopically-exchangeable phosphate in the Hoosfield soils. No desorption occurs until the soils contain about 80 mg kg^{-1} of isotopically-exchangeable phosphate and 80% of subsequent additions of isotopically-exchangeable phosphate can be desorbed. Bicarbonate-soluble phosphate, measured at the conventional solution/soil ratio of 0.02 litre g^{-1} , is greater than desorbable phosphate when the phosphate level is small. About 16% of the phosphate added since 1852 is recovered as $NaHCO_3$ -soluble P at pH 8.5 and the amount is linearly related to isotopically-exchangeable phosphate and represents about 43% of this 'pool'.

There is an approximately linear relationship between the increases in total and desorbable phosphate in the Hoosfield soils. The slope of the line relating these variables shows that about 30% of the increase in total phosphate since 1852 is desorbable whereas about 40% remains isotopically-exchangeable. In the soils studied so far the relationship between desorbable phosphate and the year the samples were taken is approximately linear. There is no unique desorption isotherm for the soils from the Hoosfield experiment and different curves were obtained for each year in which samples were taken.

It seems clear that simple solubility product considerations do not explain these results since a constant phosphate concentration is never achieved with increasing solution/soil ratio. Possibly several mechanisms, including adsorption and solubility phenomena, determine the phosphate concentration in solution. (Posner and Chater)

Effect of phosphorus on the amino-acid composition of barley grain. The effects of phosphorus on the amino acids in barley (cv. Julia) have been investigated using two samples of barley grain grown in 1971. These were analysed because adding P gave a large increase in yield in that year. Both were grown on calcareous soils from the Agdell experiment containing 2 and 34 mg bicarbonate-soluble P kg^{-1} and yielded 3.25 and 6.73 t grain ha^{-1} respectively. Barley was given 94 kg N ha^{-1} and total N of grain was 2.03% of dry matter on the soil without P and 1.71% on the soil with P; total uptakes of N were 56 and 98 kg N ha^{-1} respectively from the two soils. The amino-acid composition of the grain was little affected by P treatments or by the large differences in yield. Our results for the amino acid composition of Julia barley grain are very similar to those obtained by Rhodes and Mathers (*Journal of the Science of Food and Agriculture* (1974), **25**, 963) for the cultivar Maris Mink. (Nowakowski, Johnston and Lazarus)

Potassium in soils and crops

Potassium-calcium exchange in soils. Exchange isotherms were obtained at 30°C for surface soils and subsoils from the Aldeby, Beccles and Ragdale series which were

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collected, as part of a study of K release, from a catenary sequence at Harleston in south-east Norfolk. Standard free energy values, $(\Delta G_0)_{Ca \rightarrow K}$, calculated from the isotherms for the Aldeby and Beccles series were always much greater for surface than subsoils (mean difference 800 cal mol^{-1}) indicating increasing preference for K over Ca down the profile. The Ragdale series followed the same trend but the difference (200 cal mol^{-1}), was less pronounced. $(\Delta G_0)_{Ca \rightarrow K}$ was negatively correlated with surface area and positively correlated with surface charge density for the surface and subsoils of the three series examined in this catena. This indicates greater Ca selectivity with increasing surface charge density because divalent Ca will be adsorbed more strongly when adsorption sites are more closely packed. The negative correlation of ΔG_0 with surface area could also mean greater K selectivity as the surface area increases. This suggests that sites which are increasingly selective to K are becoming available as the surface area, of constant surface charge density, increases. Clay content and ΔG_0 were unrelated so that clay mineralogy must be the controlling factor. Detailed mineralogy of the clay fraction of these soil series has not yet been established but gross mineralogy indicates the presence of mica, montmorillonite, interstratified mica-montmorillonite, chlorite and kaolinite; montmorillonite is possibly the dominant clay mineral. A qualitative series for K preference in 1:1 and 2:1 minerals was suggested by Talibudeen (*Proceedings of the International Symposium on Soil Fertility Evaluation, New Delhi* (1971), **1**, 97-103)

vermiculite = chlorite > mica > montmorillonite > kaolin > amorphous oxides

We ascribe our results tentatively to increasing amounts of mica and chlorite in the subsoil. (Goulding and Talibudeen, with Hodge and Corbett, Soil Survey)

Potassium in soils available to crops. We reported earlier (*Rothamsted Report for 1972*, Part 1, 55) that soil potassium, released at very small ambient concentrations in the soil water, can be divided empirically into three parts, based on simultaneous rates of release which reflect the properties of different sources of K in soils. These correspond with 'surface' K (the fastest process, related to NH_4 -acetate exchangeable K), 'peripheral' K and 'matrix' K (the slowest process, by which K is derived from the mineral core).

We have recently achieved a mathematical resolution of this data that enables us to ascribe values to the amounts of K, K_{∞} , and the associated (apparent) diffusion constants, D, that relate to the sources from which the K is derived. We assume that the clay and fine silt fractions in the soil are the main sources of K release (*Journal of Agricultural Science Cambridge* (1968), **71**, 405-411) and thus derive an effective weighted mean radius for 'K-active' soil particles that is used for a spherical diffusion model for 'matrix' release. 'Peripheral' and 'surface' release is from layers that are very thin compared with the mean particle radius and which are calculated assuming K to be uniformly distributed in the particle. Fitting a 'planar' model for 'peripheral' release predicts observations reasonably well but for the surface layer it underestimates $K_{s\infty}$ by between 0 and 20%. Alternative models require more data for such analysis.

The mathematical analysis is based on equation (1), which expresses the contributions of the three processes to the flux of K in a given time t when the K concentration in the soil water is vanishingly small.

$$F(K) = f_s(D_s, K_{s\infty}, t) + f_p(D_p, K_{p\infty}, t) + f_m(D_m, K_{m\infty}, t) \quad (1)$$

The total K in the soil is

$$K_t = K_{s\infty} + K_{p\infty} + K_{m\infty} \quad (2)$$

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TABLE 6
 Typical parameters for potassium release from soils: Broadbalk and Hoosfield experiments

	Mean particle diameter $a = 9 \times 10^{-5}$ cm							
	Surface layer			Peripheral layer			Matrix core	
	Thickness l_s cm $\times 10^7$	Diffusion constant D_s cm ² s ⁻¹ $\times 10^{18}$	Total K $M_{s\infty}$ mg kg ⁻¹	Thickness l_p cm $\times 10^7$	Diffusion constant D_p cm ² s ⁻¹ $\times 10^{20}$	Total K $M_{p\infty}$ mg kg ⁻¹	Diffusion constant D_m cm ² s ⁻¹ $\times 10^{22}$	Total K $M_{m\infty}$ mg kg ⁻¹
<i>Broadbalk</i>								
Plot O3 Nil	4	4	140	8	9	160	80	11 000
O5 PKNaMg	9	110	210	18	46	370	50	12 000
<i>Hoosfield</i>								
Plot 1.0 Nil	2	6	210	5	4	380	70	11 000
7.2 FYM	18	140	500	—	—	—	110	12 000

Standard errors: for D/l^2 , ~35%; for D/a^2 , ~75%; for $M_{s\infty}$ and $M_{p\infty}$, ~20%; for $M_{m\infty}$, ~10%

Typical results from no K and K plots of the Rothamsted Classical experiments, analysed in this way, are summarised in Table 6. We can derive certain general conclusions: (1) D values of matrix K are least affected by K treatment and crop uptake, and are of the same order as those derived by us, and other workers, for K-bearing minerals of the mica family. Estimates of total soil K, the amounts of micaceous minerals and the particle size analysis of clay and fine silt particles should be adequate to calculate the contribution of matrix K to K release. (2) D_p and $K_{p\infty}$ values are increased significantly by K manuring. $K_{p\infty}$ values are of the same order as the surface K, $K_{s\infty}$. (3) K manuring increases D_s and $K_{s\infty}$ for surface K. Rate measurements for full exchange must be made to calculate these values precisely. (4) Where organic matter accumulates in the soil (e.g. from FYM additions or under grass), surface and peripheral K cannot be distinguished but the release of matrix K is unaffected. This suggests that organo-mineral surface reactions modify the physical nature of the peripheral layers.

A few relatively simple but precise laboratory measurements, outlined in (1)–(4) above, can be used to predict the *maximum* amount of K available to a crop during its period of growth. Work is now in progress on contrasting soil series. (Talibudeen, with Beasley, Computer Department, and Lane, Statistics Department)

Liming experiments

Long-term field experiments. After a sequence of barley crops (1970–73) the liming experiments at Rothamsted (Sawyers) and Woburn (Stackyard) were cropped with potatoes in 1974 and oats in 1975—both crops being tolerant of acid-soil conditions. Half of each plot was given 100 kg Mg ha⁻¹ before the potatoes were planted. The experiments therefore tested responses to phosphate, potassium and magnesium fertilisers at 4 pH levels. At both sites the responses in potatoes to phosphate and magnesium were large on the most acid plots and decreased with increasing pH, whereas potassium responses were largest at high pH. The magnesium effects were particularly striking with tuber yields being more than doubled at low pH but hardly increased at pH 7. Exchangeable Mg in the untreated plots was 25 mg kg⁻¹ air-dried soil at Rothamsted and 10 mg kg⁻¹ at Woburn at all pH levels.

The pattern of responses of the grain yields of oats in 1975 was similar to those of potatoes except that there were no significant responses to potassium. This was surprising since the control plots had not received potassium fertilisers for 12 years. These results

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(Table 7) suggest that recommended dressings of phosphate and magnesium should be larger for crops grown on acid soils. (Bolton)

TABLE 7
Effects of liming and P, K and Mg fertilisers on the yields of potatoes (1974) and oats (1975)

	Limestone, t ha ⁻¹ in 1962				Standard errors
	0	5	10	20	
Sawyers, Rothamsted pH (water) 1974	4.4	5.0	5.5	6.6	
	Potatoes, t ha ⁻¹ tubers				
With NPKMg fertiliser	53.2	56.7	60.5	56.3	} ±3.39
Without P	11.0	32.6	39.3	40.4	
Without K	35.7	22.0	23.3	10.2	
Without Mg	22.9	50.3	56.0	55.3	
	Oats, t ha ⁻¹ grain at 85% dry matter				
With NPKMg fertiliser	3.00	3.22	3.30	3.21	} ±0.312
Without P	1.76	2.29	2.83	2.44	
Without K	2.54	2.65	3.14	3.08	
Without Mg	1.25	2.63	2.99	2.92	
	Limestone, t ha ⁻¹ in 1962				
	0	5	12	19	
Stackyard, Woburn pH (water) 1974	4.7	5.5	6.3	6.8	
	Potatoes, t ha ⁻¹ tubers				
With NPKMg fertiliser	58.8	57.9	53.2	55.7	} ±3.42
Without P	13.6	32.4	41.0	45.3	
Without K	22.2	16.0	17.5	15.0	
Without Mg	13.2	37.0	37.1	39.0	
	Oats, t ha ⁻¹ grain at 85% dry matter				
With NPKMg fertiliser	2.27	2.71	2.44	2.41	} ±0.155
Without P	2.01	2.36	2.13	2.61	
Without K	2.23	1.97	2.25	2.29	
Without Mg	0.91	1.78	1.94	1.93	

A new field experiment at Woburn, superimposed on an old experiment which tested rates of K and Mg fertilisers, was started to investigate the effects of high rates of lime (over-liming) on a sequence of arable crops. It also includes two rates of nitrogen and three rates of Mg residues. Grain yields of spring wheat in 1975 were small because of drought and generally were unaffected by the N and Mg treatments. However, there was a significant interaction between nitrogen and liming which lessened yields at pH values between 5.0 and 6.1 when a high rate of nitrogen (100 kg N ha⁻¹) was also given. (Bolton and Penny)

Residual effects of potassium, magnesium and sodium fertilisers

Ryegrass has been grown for four years (1971-74) with NPK fertilisers given to all plots of a long-term experiment at Woburn where the annual treatment dressings were discontinued in 1967. (Some results for the 1967-70 period were given in the *Rothamsted Report for 1971*, Part 1, 67.) Analyses were made of two or three cuts of grass annually and of the soils, sampled 0-23 cm and 23-46 cm, after the experiment ended in autumn 1974.

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Residues of Mg fertilisers increased yields slightly in 1973 and increased Mg concentrations in the dry matter of all cuts. The average increase was from 0.12% to 0.18% Mg from the largest Mg dressings applied before 1967. Exchangeable Mg in all the subsoils and in the topsoils without added Mg fertiliser hardly changed after 1970 but there were large changes in the topsoils containing residues (Table 8). Average annual removals of 11.2 kg Mg ha⁻¹ from the plots without Mg fertilisers cannot be fully explained by changes in soil analysis and additions in the rain; about 8 kg Mg ha⁻¹ must derive from other sources, possibly non-exchangeable Mg in the clay minerals.

TABLE 8
Effects of residues of magnesium fertilisers applied in 1960-67 on exchangeable Mg in Woburn soils in 1970 and 1974

Total Mg added 1960-67, kg ha ⁻¹	Exchangeable Mg, mg kg ⁻¹ air-dry soil			
	topsoil (0-23 cm)		subsoil (23-46 cm)	
	1970	1974	1970	1974
0	16.4	16.1	9.5	7.4
375	46.5	30.0	39.1	38.6
750	74.4	45.6	75.7	75.8
S.E. ±	1.34	0.83	1.64	0.68

Despite annual applications of 160 kg K ha⁻¹ to all plots since 1971, slight residual effects of the old K treatments were apparent both in the crop and by soil analyses in 1974. More surprisingly, residues from sodium chloride applied in 1966 and 1967 significantly increased % Na in the grass in 1974 from 0.17% to 0.20%. Small but significant differences were also measured in exchangeable Na in the topsoils. Sodium in grass is nutritionally important for dairy cattle and this experiment shows that salt dressings can effectively increase sodium concentrations in grass for up to eight years. (Bolton and Penny)

Aluminium in soils and clays

Exchangeable aluminium related to soil pH and organic matter. Aluminium was extracted from the surface organic layer and the subsurface mineral layer of six acid plots from the Park Grass experiment by a method previously employed by Sivasubramanian and Talibudeen (*Journal of Soil Science* (1972), 23, 163-176) but using MNH_4NO_3 solution. Exchangeable Al was obtained by extrapolating the final constant rate of extraction to 'zero time'. The effluent pH was always greater than the initial pH because of the hydrolysis of adsorbed Al (*Rothamsted Report for 1974*, Part 1, 87-88 and this Report, Part 1, 95). However, the effluent pH decreased during extraction and finally became constant.

The total amount of Al extracted, and the rate of release of 'non-exchangeable Al', always increased as soil pH decreased, though pH decreased non-linearly. Both measurements were larger in the organic layer than in the mineral layer of soils, except for the soil from Plot 11 (N_3PKNaMg), where the reverse was observed. These results confirm that exchangeable and precipitated Al ions accumulate in soils as soil acidity increases and that soil organic matter retains increasing proportions of exchangeable Al. We are now investigating the hydrolysis constants of adsorbed Al on the mineral and organic surfaces of the soils by titrimetric methods. (Cabrera and Talibudeen)

Hydrolysed aluminium ions on montmorillonite. Work reported previously (*Rothamsted Report for 1974*, Part 1, 87-88) on soil from the Batcombe series suggested that the

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hydrolysis constants of aluminium ions adsorbed on the mineral surfaces of an acid soil (pH 3.7) could be significantly smaller than those of aluminium ions in solution (first hydrolysis stage $pK_1 = 5.0$ at 25°C). To test this, sodium montmorillonite, prepared from Wyoming bentonite, was converted to the Al-form at pH 3.0 and stored under absolute alcohol. Both forms were titrated in 10^{-3}N NaNO_3 with 10^{-1}N NaOH and HNO_3 from pH 4.0 \rightarrow 10.5 \rightarrow 4.0, using a radiometer automatic titrator in a CO_2 -free N_2 atmosphere. The titration curves were reproducible at titration speeds slower than one pH unit h^{-1} , with marked and reproducible hysteresis below pH 7 (although true equilibrium was not established even at speeds of one pH unit every 3 h). This hysteresis is probably caused by interlayer aluminium ion species that finally form insoluble $\text{Al}(\text{OH})_3$ on titration with the base and do not redissolve during acid titration.

The titration gave $870 \mu\text{-equiv g}^{-1}$ for the cation exchange capacity of the clay at pH 7.

The best fit to the observed titration curves on the basis of exchange between Na ions and hydrolysable Al ionic species was found with observed three-stage hydrolysis constants for Al^{3+} of $pK_1 = 5.5$, $pK_2 = 6.0$, $pK_3 = 6.5$. A similar result was observed for aluminium montmorillonite and aluminium Fithian illite by Colombera (PhD thesis, University of Western Australia, 1970). The region of the titration curve above pH 8.5, thought to represent the dissociation of SiOH edge sites on the clay, $\text{SiOH} \rightleftharpoons \text{SiO}^- + \text{H}^+$, gave a best fit dissociation constant of pK 10.0. More complex models that allowed for the variation of surface potential with changing surface charge density suggested by Bowden, Posner and Quirk (*Nature* (1973), **245**, 81-83) gave poorer fits to the observed data. (Pyman, Posner and Talibudeen)

Sulphur in crops

Sulphur deficiencies in perennial ryegrass. Grass was grown in pots in a growth cabinet with four rates of nitrogen (17, 67, 133 and 200 mg kg^{-1} soil) and four rates of sulphur (0, 8, 17 and 33 mg kg^{-1} soil) in a sandy loam from Woburn which contained only 10 mg kg^{-1} KH_2PO_4 -soluble sulphate S. The sulphur fertilisers increased yields of grass at the first cut only at the highest N level but, at the second and third cuts, at all N levels except the smallest. Yield responses occurred when the dry matter contained less than 0.20% S.

At the third cut, sulphur deficiency decreased concentrations of reducing sugars but had little effect on sucrose or fructosan in the grass dry matter. Only 44% of the nitrogen in the most sulphur deficient grass was protein N compared with over 80% in grass adequately supplied with sulphur. The non-protein N accumulated predominantly as amides, especially asparagine. Up to 88% of the total soluble N in the amino acid pool occurred in this form. When sulphur deficiency was corrected, the percentage of aspara-

TABLE 9
Effects of nitrogen and sulphur on yields and composition of perennial ryegrass
(third cut)

	133 mg N kg^{-1} soil			200 mg N kg^{-1} soil		
	8	17	33	8	17	33
Amount of S, mg kg^{-1} of soil						
Dry matter yield, g per pot	2.16	3.13	4.06	2.00	2.96	4.67
Total N, % in dry matter	1.90	1.55	1.39	2.45	2.00	1.72
Total S, % in dry matter	0.10	0.11	0.17	0.09	0.10	0.15
Reducing sugars, % in dry matter	1.7	3.0	3.4	1.2	2.4	5.1
Sucrose, % in dry matter	5.0	4.9	4.8	5.0	4.5	4.5
Fructosan, % in dry matter	15.4	15.4	16.1	15.9	13.5	12.1
Protein N as % of total N	61.9	74.6	80.9	44.5	53.5	77.6
Asparagine N as % of total N	26.0	9.9	0.5	39.8	28.2	4.2

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gine decreased and the percentage of glutamine and all the free amino acids increased. No free cystine or methionine was detected in any of the grass samples.

Although amounts of protein N were markedly affected by the treatments, proportions of the individual amino acids recovered from hydrolysed protein, including cystine and methionine, were similar for all the fertiliser treatments. The mean N:S ratio in the protein calculated from proportions of S-amino acids recovered was 15.3. Some results are given in Table 9. (Nowakowski, Bolton and Lazarus)

Sulphur deficiencies in spring wheat. Two pot experiments in growth cabinets, using the same sandy loam soil from Woburn as for the grass experiment described above, were made to provide wheat grain containing different concentrations of N and S for the Biochemistry Department. Yields without sulphur were small, especially when large nitrogen rates (up to 400 mg kg⁻¹ soil) were also given. With the largest amounts of sulphur (30 mg kg⁻¹ soil), yields were increased by nitrogen up to the largest dressings. There were marked effects of nitrogen on the appearance of the grain, 1000 grain weights and percentage small grain. These experiments were affected by severe *Fusarium* infections; sterilising the soil before planting by heating at 80°C overnight or spraying with benomyl did not control the infection. Yields of grain from one experiment are in Table 10; the other gave similar results. (Bolton)

TABLE 10
Effects of nitrogen and sulphur on the yield of spring wheat (Kleiber) in a pot experiment

S added, mg kg ⁻¹ of soil	Yields of oven-dry grain, g per pot			
	N added, mg kg ⁻¹ of soil			
	60	120	180	240
0	3.00	2.99	1.14	0.78
15	3.28	4.20	5.38	5.71
30	2.99	4.63	5.75	6.48

Saline soils

Sodium-calcium exchange as affected by organic manuring and soil salinization. A satisfactory expression of cation exchange equilibria, with special reference to Ca and Na, is of considerable practical value in the study of salt-affected soils. Such expressions can be used to predict the composition of adsorbed ions in soils in equilibrium with irrigation waters containing various proportions of Ca and Na salts. The few earlier studies on soils show that Na and Ca exchange can be satisfactorily expressed by the Gapon equation up to 60-70 exchangeable sodium percentage (ESP), and by double layer equations based on the Poisson-Boltzman equation. In soils containing much organic matter (>2% C) there is a strong preference for Ca adsorption (*Proceedings of the Soil Science Society America* (1964), 28, 32-35). Applying organic manures to salt-affected soils is common practice and should affect the cation adsorption/retention properties of soils.

We have examined the effect of soil salinisation and continuous organic manuring on cation exchange equilibria with reference to Ca and Na, using soils from microplot experiments (from Haryana Agricultural University, Hissar, India) where up to 200 t ha⁻¹ farmyard manure (FYM) were given in four years. These soils, which are derived from river alluvium, range in salinity from <1 to 15 mmhos cm⁻¹ EC_e.

The standard free energy (ΔG_0)_{Ca→Na} and the Gapon constant indicate that (1) surface soil is always more selective for Ca than the subsoil; (2) the activity coefficients of ad-

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sorbed ions and the free energy change of the exchange reaction are not consistently related to the organic carbon content of the soil; (3) although surface soils given FYM contain more organic matter, they do not show a proportionately greater preference for Ca than surface soils without FYM, which contain less organic matter; (4) the differences in $(\Delta G_0)_{Ca \rightarrow Na}$ between surface and subsoils without FYM are larger than for soils given FYM. This suggests that the quality of the organic matter (i.e. its stage of humification) as well as the amount of organic carbon influences selectivity for Ca. This factor has an important bearing on the relative merits of large additions of FYM, which are uneconomic, and green manuring in ameliorating soil salinity and alkalinity. Because there are only small differences in organic carbon in surface and subsoils from Haryana, we are examining Ca and Na exchange equilibria in surface and subsoils from the Rothamsted Classical experiments where differences in organic carbon are larger. (Poonia and Talibudeen)

Micronutrients

Heavy metals in sewage sludges. Two pot experiments were made to study effects of liming on heavy-metal toxicities in perennial ryegrass as part of joint work with the Pedology Department on the solubilities of heavy metals after incubation of metal-contaminated sludge at different pH values (Bloomfield). Yields of grass were decreased when 12% of sewage sludge, on a dry matter basis, was incorporated in Rothamsted soil, except when the pH was increased to 6.3. Concentrations of more than $350 \mu\text{g Zn g}^{-1}$, $160 \mu\text{g Ni g}^{-1}$ and $40 \mu\text{g Cu g}^{-1}$ in the grass dry matter were associated with lowered yields. The treatments had no effects on Cr or Pb concentrations in the grass. (Bolton)

Incorporating 12% of the same sludge into the more sandy Woburn soil decreased yields at pH values up to 5.7, but at pH 6.5, smaller additions of sludge (8% on a dry matter basis) did not decrease yields. When so much sludge was added, the pH of the sludge (pH 5.3) partly determined the pH of the soil:sludge mixtures. Acetic-acid extracts of metals in the soil-sludge mixtures did not reflect their availabilities to grass at different soil pH values. Ammonium acetate extracts, although slightly affected by soil pH, were still unsatisfactory for predicting the uptake of zinc by plants. (Lin and Bolton)

Mechanical fractionation of potato tubers

Pulps made by grating tubers on rollers with grooves 1 or 2 mm deep, running at surface speeds of $2-6 \text{ m s}^{-1}$, differed in texture, but no pulp from which an adequate amount of juice could be pressed, had enough 'body' to be retained in a belt-press of the type now used. Pre-pressing on a reciprocating conveyor produced pulp with the necessary 'body'. The press-cake coming from the belt-press contains 35-40% dry matter. Studies in collaboration with Lacey (Plant Pathology Department) show that such material cannot be preserved with propionic acid or ammonia. The dry matter content of batches of press-cake was therefore increased to 60% in a hydraulic press. There is no obvious mechanical obstacle to making a continuous press that would apply pressure more slowly, and reach a greater final pressure, so that material conservable as stock feed could be made in one operation. (Carruthers and Pirie)

Fodder fractionation. Because of the recent great increase in interest in fodder fractionation, extraction units are being installed in several institutes. The equipment hitherto used here is excellent for agronomic work, but wastes power by acting as a blower. Many different forms of a unit that is an amalgam of a screw expeller and a domestic mincer have been made. They extract juice from forage in one operation, seem to be more economical than the other units that have been tested and should be very much cheaper. (Pirie)

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Methods, apparatus and technique

Measuring areas on land-use maps. A technique was developed to measure areas on 1:63 360 maps using the 'Quantimet' Image Analysing Computer. The areas were measured on 'dyeline' prints of a tracing of the 'master' map with all the land-category boundaries included. The areas of each land-use unit were painted with black ink on the dyelines to give one map for each land-use category. Using this technique 330 maps were measured, each taking about 3 min. The standard error of a single measurement was equivalent to 100 acres for a mean area of 5000 acres, a coefficient of variation of 2%. (Bolton, with Jones and Turner, Plant Pathology Department)

Amino acid analysis

Buffer systems. With the buffer system used for analysing the free amino acids in plants (Lazarus, *Journal of Chromatography* (1973), **87**, 169), methionine sulphone arising from performic acid oxidation of grass protein could not be separated from aspartic acid. By reducing the pH of the buffer solution in the first chamber of the nine-chambered autograd of the Technicon Amino Acid Analyzer from 2.875 to 2.720 methionine sulphone and aspartic acid were completely separated. The resolution of all other amino acids was unaffected and the modified system was as suitable for analysing the free amino acids in plants as the earlier one. (Lazarus)

Chemical analysis

Automated cation analysis. Major items of equipment bought this year include a Hook and Tucker A40 Sampler, an Ismatec MP13 peristaltic pump and a Shandon Southern A3400 Atomic Absorption Spectrophotometer. These together form a second automated system for cation analysis which will enable us, more easily, to cope with the continually increasing demand for analyses. (Cosimini)

Nitrogen analysis. Two Technicon Digestor Blocks were purchased and installed together with individual extraction hoods and scrubber columns; these replace the gas-heated Kjeldahl racks used previously. Tests on the digester blocks show that the best results were obtained using 0.25 g plant material digested for 1 h with one autotab (1.5 g K_2SO_4 and 0.0075 g selenium) and 10 ml concentrated sulphuric acid. (Avery)

Radiochemical analysis

Liquid scintillation spectrometer performance. Work with nuclides of different β -energies in samples produced under various experimental conditions over the year, showed that, irrespective of energy, the counting efficiency increased by as much as 20% when the radioactivity in the samples is progressively decreased below 500 dpm for non-aqueous sample cocktails, or below 10 000 dpm for aqueous sample cocktails. This effect, which is serious where large changes in radioactivity are being assessed during an experiment, has been reported to Beckman-RIIC for joint investigation. (Smith and Talibudeen)

Computer programs

Quench correction. Programs were written to correct the observed count rate of a sample according to its measured degree of quench in the scintillation cocktail. The quenching may be caused by impurities, including water, in the sample or by its colour or turbidity. The corrections are derived from simultaneous counting of a calibrated sets of samples (of the nuclide/cocktail mixture being investigated) that are quenched artificially to different extents.

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Multiple-label experiments. A second program was written to separate the count rates of the constituent nuclides from the integral count of triple labelled samples containing ^{42}K , ^{45}Ca and ^{32}P , and corrects these count rates for decay. The program could be adapted for other mixtures of nuclides with suitably contrasting energies and half-lives. (Smith)

Staff and visiting workers

G. W. Cooke left at the end of February to take up his appointment as Chief Scientific Adviser to the Agricultural Research Council. He came to Rothamsted on a Ministry of Agriculture Scholarship in 1938 and was appointed Head of the Chemistry Department in 1956. We shall greatly miss his advice and guidance on agricultural problems. No successor has yet been appointed and G. E. G. Mattingly has been Acting Head since 1 March 1975. H. A. Smith retired in April after 46 years on the staff. R. W. H. Brown, I. B. Carruthers and D. Cox left.

The following visitors worked in the Department during the year: Mr. J. H. Ahmed (Bahrain), Mr. A. A. Blandin (France), Dr. F. Cabrera (Spain), Mr. A. T. Halm (Ghana), Mr. M. C. Igbokwe (Nigeria), Dr. A. I. Jose (India), Dr. V. Kudiyarov (USSR), Dr. I. Latkovics (Hungary), Mr. Char-fen Lin (Taiwan), Mr. R. Mukuka (Zambia), Mr. S. Osafo-Kroffah (Ghana), Dr. S. R. Poonia (India), Professor A. M. Posner (Australia), Mr. M. A. F. Pyman, Professor L. F. Welch (USA) and Mr. K. N. Wickramasinghe (Sri Lanka). M. J. Emerson, D. W. J. Green and R. Nankervis were sandwich course students.

G. W. Cooke attended a meeting of the Scientific Board of the International Potash Institute in Berne as a guest of the Institute. N. W. Pirie was invited by the Royal Society to visit the Democratic Republic of Vietnam, Bangladesh and India, and by the Club of Rome to visit Milan. Pirie also attended the Conference on the Atmosphere in Chapel Hill, North Carolina, sponsored by the National Institute of Health.

Publications

GENERAL PAPERS

- 1 COOKE, G. W. (1975) The energy costs of the nitrogen fertilisers used in Britain, the returns received and some savings that are possible. *Journal of the Science of Food and Agriculture* **26**, 1065-1069.
- 2 COOKE, G. W. (1976) A review of the effects of agriculture on the chemical composition and quality of surface and underground waters. In: *Agriculture and water quality. Ministry of Agriculture, Fisheries and Food. Technical Bulletin No. 32*, 5-57.
- 3 JOHNSTON, A. E. (1976) Additions and removals of nitrogen and phosphorus in long-term experiments at Rothamsted and Woburn and the effect of the residues on total soil nitrogen and phosphorus. In: *Agriculture and water quality. Ministry of Agriculture, Fisheries and Food. Technical Bulletin No. 32*, 111-144.
- 4 MATTINGLY, G. E. G. (1975) Labile phosphate in soils. *Soil Science* **119**, 369-375.
- 5 PIRIE, N. W. (1975) Leaf protein: a beneficiary of tribulation. *Nature, London* **253**, 239-241.
- 6 PIRIE, N. W. (1975) Introductory remarks. In: *A discussion on the recognition of alien life. Proceedings of the Royal Society, London, (B)* **189**, 139-141.

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- 7 PIRIE, N. W. (1975) Agricultural science (plant). *McGraw-Hill Yearbook of Science and Technology*, pp. 90-92.
- 8 PIRIE, N. W. (1975) Preface to: *Food protein sources*. xv-xx. International Biological Programme 4. Cambridge University Press.
- 9 PIRIE, N. W. (1975) The *Spirulina* algae. In: *Food protein sources*. International Biological Programme 4. Cambridge University Press, pp. 33-34.
- 10 PIRIE, N. W. (1975) Leaf protein. In: *Food protein sources*, International Biological Programme 4. Cambridge University Press, pp. 133-139.
- 11 PIRIE, N. W. (1975) Methods and merits of fodder fractionation. *Journal of the Science Society of Thailand* **1**, 103-113.
- 12 PIRIE, N. W. (1975) The potentialities of leafy vegetables and forages as food protein sources. *Baroda Journal of Nutrition* **2**, 43-58.
- 13 PIRIE, N. W. (1975) Some obstacles to eliminating famine. *Proceedings of the Nutrition Society* **34**, 181-186.
- 14 PIRIE, N. W. (1976) Leaf protein. *Encyclopaedia of Food Science*. Westport, Conn., USA: AVI Publishing Company.
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- 16 PIRIE, N. W. (1975) Food related measures: new sources. In: *Nutrition in the community*. Ed. D. S. McLaren. Chichester: John Wiley & Sons Ltd., pp. 159-168.
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