

Rothamsted Repository Download

A - Papers appearing in refereed journals

Mattingly, G. C. G. 1977. Chemistry Department Rothamsted Experimental Station 1976. *Report - Agricultural Research Council and Ministry of Agriculture Rothamsted Experimental Station*. 1976 (1), pp. 81-103.

The publisher's version can be accessed at:

- <https://dx.doi.org/10.23637/ERADOC-1-133>
- <http://www.era.rothamsted.ac.uk/eradoc/OCR/ResReport1976p1-81-103>

The output can be accessed at: <https://repository.rothamsted.ac.uk/item/8wq8g>.

© Please contact library@rothamsted.ac.uk for copyright queries.

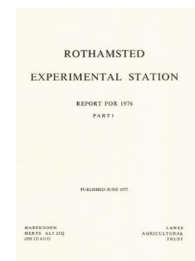
Thank you for using eradoc, a platform to publish electronic copies of the Rothamsted Documents. Your requested document has been scanned from original documents. If you find this document is not readable, or you suspect there are some problems, please let us know and we will correct that.



ROTHAMSTED
RESEARCH

Report for 1976 - Part 1

[Full Table of Content](#)



Chemistry Department

G. E. G. Mattingly

Chemistry Department, G. E. G. Mattingly (1977) Report For 1976 - Part 1, pp 81 - 103 - DOI:
<https://doi.org/10.23637/ERADOC-1-133>



This work is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/).

CHEMISTRY DEPARTMENT

G. E. G. MATTINGLY

Staff

Acting Head of Department G. E. G. Mattingly, PH.D.*Senior Principal Scientific Officer*

O. Talibudeen, PH.D.

Principal Scientific Officers

J. Bolton, PH.D., F.R.I.C.

G. G. Briggs, PH.D.

A. R. Bromfield, M.SC.

A. E. Johnston, B.SC.

T. Z. Nowakowski, PH.D.

A. Penny, B.SC.

F. V. Widdowson, B.SC., F.R.A.G.S.

R. J. B. Williams, B.SC.

Senior Scientific Officers

T. M. Addiscott, PH.D.

J. Ashworth, PH.D.

Higher Scientific Officers

E. Bird

Margaret Chater

V. Cosimini, L.R.I.C.

W. Lazarus, B.SC.

Brenda Messer

J. D. D. Mitchell, B.SC.

M. Roberts

G. A. Rodgers, PH.D.

G. J. Smith

Scientific Officers

R. J. Avery

P. C. Brookes, PH.D.

J. B. Butler, M.SC.

Mrs. Avis A. Evans

K. W. T. Goulding, M.SC.

M. V. Hewitt

Mrs. Iren Jasko, DIPL.CHEM.

Mrs. Joyce W. Munden

M. B. Page, B.SC.

P. R. Poulton

Assistant Scientific Officers

K. F. Buckingham

P. A. Cundill

A. J. Dean

M. J. Emerson

A. J. Pope

S. D. Prior

D. J. L. Robinson

D. A. Smith

C. D. Tearle

V. H. Thomas

Temporary Workers

Blanche Benzian, B.SC.

F. Cabrera, PH.D.

M. C. Igbokwe, B.SC.

M. Miyaguchi, DR.AGR.

N. W. Pirie, M.A., F.R.S.

K. N. Wickramasinghe, B.SC.

Secretary

I. Patricia Bond

Clerical and other Staff

Mrs. Mary I. Fearn

H. Goodenough

Mrs. Barbara D. Moseley

Foreman (Saxmundham)

V. C. Woolnough, B.E.M.

Introduction

Work was started in 1975 to investigate the value of carbon disulphide to inhibit nitrification and so minimise losses by leaching from fertilisers containing ammonia or urea. Field experiments this year confirmed that carbon disulphide delayed nitrification of aqueous ammonia injected into grass at Rothamsted almost completely for two months but it was again less effective on the lighter soil at Woburn. Trithiocarbonates, which generate carbon disulphide in soil, behaved similarly. Nitrapyrin (2-chloro-6-trichloromethylpyridine) was relatively ineffective for several months after injection but then inhibited nitrification well into May. The mode of action of the two classes of nitrification inhibitors is, therefore, different and, used together, they appear to offer interesting possibilities for controlling nitrification for periods up to six months after their application. Inhibitors were also tested in experiments on winter wheat, forage maize and potatoes. Growth of all crops, however, particularly grass, was restricted by the prolonged drought during 1976 so there was little opportunity to assess the effects of inhibitors on the rates of growth of the crops; most of these experiments will be repeated in 1977.

ROTHAMSTED REPORT FOR 1976, PART 1

This year, too, the exceptional soil moisture deficit resulted in larger but less variable soil nitrate concentrations than in previous years in the 0–25 cm soil layer under winter wheat. The 'work function', calculated from measurements made with ion-selective electrodes of the differences between $(pNO_3)_{\text{fallow}} - (pNO_3)_{\text{crop}}$, where $pNO_3 = -\log_{10} [NO_3^-]$, provides a better indication of the uptake of nitrogen by wheat than differences in the nitrate content (in mg N litre⁻¹) of soil water under fallow and crop.

A model has been developed to predict the amount of solute (e.g. nitrate or chloride ions) in each layer of a soil profile after rainfall or evaporation. It gives good agreement between the predicted and measured distribution of these ions in the soil and is now being developed further to allow for the changes in concentrations of nitrate that result from biological processes.

In 1976 we recorded the shortest period of continuous drainage at Saxmundham (128 days) since records began ten years ago and the smallest losses of nitrate (about 7 kg N ha⁻¹) under both arable and herbage crops between 1 October 1975 and 30 September 1976. Yields of winter wheat (Cappelle-Desprez) at Saxmundham between 1974–76 were, for the first time, almost the same as on comparably manured soils at Rothamsted, perhaps because losses of nitrate by leaching were smaller during much of this period than formerly.

Last year we summarised work to predict the maximum amounts of potassium that are available to crops from different soils during growth. Extended to unmanured and PK-treated soils from Rotation I at Saxmundham (in conjunction with the Pedology Department), this research shows that about 55% of the 'native' soil K and 70% of the added K could be extracted from the fine clay (<0.2 μm) by a Ca-saturated resin in 200 h. Over very long periods, however, only 30% of the native soil potassium would come from this fraction, the rest being derived from the coarse fractions, especially the fine sand (20–50 μm).

Liquid NPK fertilisers applied in several ways to potatoes at Rothamsted and Woburn produced smaller yields at both farms in 1974 than equivalent amounts of granular fertiliser broadcast before planting. Placing fertiliser containing more than 188 kg N ha⁻¹ on either side of the seed checked early growth at Rothamsted in 1974 but not at Woburn. In the wetter spring of 1975 there was no damage from placing fertiliser near the seed on either farm. Spraying the liquid fertilisers on the surface of soil before planting gave the smallest yields in both years.

In Part 2 of the Report another joint paper with the Pedology Department shows that the carbon and nitrogen contents of soils from the Hoosfield Continuous Barley experiment have remained almost unchanged since 1882 on the unmanured plot (1–O) or on plots given PK (4–O) or NPK (4–A). Farmyard manure (FYM), applied each year since 1852, had trebled the carbon and nitrogen in the soils by 1975 and decreased the bulk density from 1.52 to 1.29 t m⁻³. Any improvements in the structure of this soil, however, did not increase barley yields, which were no larger than on plots given optimal NPK (plot 4–A).

A second paper, also in Part 2, summarises crop yields and soil analysis from 1852–1975 in the adjacent Hoosfield Exhaustion Land experiment, which now measures the value of residues of farmyard manure and PK fertilisers last applied in 1901. The more productive varieties of barley (Julia) grown from 1970–75 and given only N fertiliser yielded 1.83 t ha⁻¹ of grain (at 85% dry matter) on plots unmanured from 1852–1901, 4.75 t ha⁻¹ on plots containing residues of farmyard manure and 4.22 t ha⁻¹ on plots containing residues of PK fertilisers. Residues from farmyard manure or fertilisers, last applied 75 years ago, are still adequate to maintain about national average yields of barley on this soil and, at present rates of removal of phosphorus by the barley crop, could last for another 70 years. (On soils from the Hoosfield Continuous Barley experiment, which

CHEMISTRY DEPARTMENT

have received PKMg fertilisers or farmyard manure each year since 1852, Julia barley yielded about 5.4 t ha⁻¹ during the same period when given optimum N.)

Before 1958, when the crops were small, all the phosphorus taken up by barley came from the pool of isotopically-exchangeable P. After 1958, larger crops were grown and the decrease in the isotopically-exchangeable P accounted for only 40% of the P in the crop. The NaHCO₃-soluble P in the soils decreased, however, by only 40 and 20% during the two periods respectively. Between 1902-51 and 1952-74 the decrease in exchangeable potassium in the soil accounted for 70 and 15% respectively of the potassium in the crop. This experiment, which is unique in the world, shows how much phosphorus and potassium must have come from non-exchangeable reserves, especially during the last 25 years.

Experiments with nitrogen fertilisers

Nitrification inhibitors

Field measurements of nitrification inhibition. This year we used carbon disulphide, CS₂, and trithiocarbonate ions CS₃²⁻, which generate CS₂ in soil, with nitrapyrin (2-chloro-6-trichloromethylpyridine) to inhibit nitrification in bands of NH₄-N injected as aqueous NH₃ or aqueous urea fertiliser. In field experiments with grass and winter wheat at Rothamsted and Woburn, the extent of nitrification was measured using 2 M-KCl to extract NH₄- and NO₃-N from soil cores, taken with a hand sampler inserted vertically into the injection slit to 20 cm depth.

Analyses of the KCl extracts showed that all the materials inhibited nitrification at both sites, but more effectively on the heavier soil at Rothamsted. After injecting 375 kg NH₃-N ha⁻¹ under grass in mid-November 1975, CS₂ (12.5 kg ha⁻¹) or equivalent Na₂CS₃ delayed nitrification at Rothamsted almost completely until mid-January 1976 after which time nitrification proceeded almost normally. In contrast, nitrapyrin (1.25 kg ha⁻¹) was relatively ineffective until January, by which time the cross-sectional area of injected N had contracted, through nitrification at its periphery, to coincide with that of nitrapyrin. It then continued to inhibit further nitrification until May.

Nitrification was very slow after injecting into grass in February 1976, presumably because of drought. Inhibition by (NH₄)₂CS₃ was extremely effective, and was still clearly apparent from analyses of soil cores taken in June. Few measurements were made of inhibition by CS₂ or nitrapyrin, after injection in February.

Soil cores were also analysed after injecting 100 kg NH₃- or urea N ha⁻¹ for winter wheat in March at Rothamsted. There was a lag of only three weeks before nitrapyrin (1.25 kg ha⁻¹) became fully effective, presumably because the bands of injected N and nitrapyrin were already of similar size. Its effects on soil NO₃-N could still be detected in June. In contrast, CS₂ (11 kg ha⁻¹) or (NH₄)₂CS₃ (equivalent to 8 kg CS₂ ha⁻¹) was effective for only five weeks, and ineffective after the end of April. Presumably CS₂ diffuses away much faster in arable soils than under grassland, which may account for its short-lived effect.

Measurements of NO₃-N concentrations in stems of grass and winter wheat (Table 1)

TABLE 1
Effects of nitrification inhibitors on the NO₃-N in the stems of grass and winter wheat
(mg litre⁻¹)

Crop	Injection date	Sampling date	Inhibitor			
			None	Nitrapyrin	CS ₂	CS ₃ ²⁻
Grass	14 Nov 1975	27 Feb 1976	430	350	180	180
Winter wheat	9 Mar 1976	5 May 1976	380	25	55	210
		19 May 1976	10	2	40	25

ROTHAMSTED REPORT FOR 1976, PART 1

gave results consistent with soil measurements and confirmed the relative effectiveness of the materials under the different conditions. Because of low rainfall during winter and drought in summer, none of the materials had much effect on yields of grass or winter wheat given injected N fertiliser and these experiments will be repeated in 1977. (Ashworth and Matula, with Briggs and Evans, Chemical Liaison Unit)

Glasshouse experiments with carbon disulphide. The effects of CS_2 on growth and %N in grass given aqueous NH_3 were measured. Ryegrass (cv. S22) was sown after adding known amounts of CS_2 (0.04–2.0 g kg^{-1} soil) and aqueous NH_3 by pipette, into the centre of pots of Rothamsted or Woburn soil (500 g), down a hole which was afterwards plugged with soil. On both soils, total dry matter yield from three cuts (c. 4 g) and recovery of added N (c. 65%) were not altered by CS_2 but, with Rothamsted soil, yields at the first cut were smaller, with compensatory growth later, where 0.2 g CS_2 kg^{-1} soil, or more, was applied. This result is consistent with those from field experiments at Rothamsted on grass given aqueous NH_3 , in which nitrification was delayed until after the first cut (Ashworth & Flint, *Journal of Agricultural Science, Cambridge* (1974), **83**, 327–333).

Although CS_2 inhibited nitrification until after the second cut using Woburn soil, it did not decrease yield at any cut. These results suggest that grass is more able to take up $\text{NH}_4\text{-N}$ from Woburn than from Rothamsted soil, presumably because the latter, which contains more clay, holds $\text{NH}_4\text{-N}$ more strongly.

This change in the rate of growth of grass was reproduced in a second glasshouse experiment with ryegrass on Rothamsted soil using CS_2 (0.5 g per pot) or equivalent Na_2CS_3 as inhibitor. This experiment tested the effects of incorporating Na_2CS_3 and urea in a solid matrix with 'plaster of Paris'. The product, which gave off CS_2 , was used without delay. When mixed uniformly with soil, its effects on the distribution of yield throughout the experiment were similar to those from CS_2 or Na_2CS_3 solution added by pipette. Solid urea applied to the soil surface delayed germination and early growth, especially when Na_2CS_3 , which depressed overall yield, was also incorporated. Although Na_2CS_3 is stable in solution, contact with solids catalyses its decomposition to CS_2 and H_2S and it will clearly be difficult to produce, for practical use, stable granular N fertilisers incorporating CS_3^{2-} .

The addition of Na_2CS_3 appeared to have phytotoxic effects in a pot experiment with barley. Seeds germinated but died within three days, where a mixture of aqueous NH_3 and Na_2CS_3 solution had been injected by pipette. It is likely that H_2S was the phytotoxic agent because, in separate tests, Na_2S solution and Na_2CS_3 solution caused similar symptoms, although barley seedlings recovered from the effects of Na_2S . Aqueous emulsions of CS_2 had no deleterious effect. No phytotoxicity from Na_2CS_3 or $(\text{NH}_4)_2\text{CS}_3$ has been noticed in any field experiment, where vapour concentrations, however, are unlikely to exceed 100 mg kg^{-1} even at the centre of an injected band of soil, in contrast to 1000 mg kg^{-1} in pots. (Ashworth, Hewitt and Mitchell)

Effects of nitrification inhibitors on the composition of permanent grass. Because of the increasing use of fertiliser N on grass, an experiment was done on permanent grassland (Highfield IX) to investigate the effects of large single dressings of N on dry matter yields and composition of grass soon after applying the fertiliser. Aqueous urea was injected on 26 February 1976 to supply 250, 375 or 500 kg N ha^{-1} , alone or with ammonium trithiocarbonate (ATC). Equivalent amounts of 'Nitro-Chalk' were applied, in divided dressings for each cut, to provide a standard.

Table 2 shows that, at the first cut (4 May), the amount of urea N applied had no effect on dry matter yields and little on % total N, irrespective of whether ATC was applied, presumably because growth was limited by drought. However, grass given urea plus ATC

CHEMISTRY DEPARTMENT

gave slightly smaller yields, probably because it inhibited nitrification. On plots given 375 kg urea N alone, 60% of the N extracted by KCl from core samples of soil taken from injection slits on 2 May was present as $\text{NO}_3\text{-N}$ but only 6% where ATC had been applied.

Protein N decreased with increasing amounts of applied urea N, whether or not ATC was used. At each level of urea N, grass given ATC contained less $\text{NO}_3\text{-N}$ than grass grown without inhibitor. However, the effect of ATC was less marked where the largest amount of urea N was applied. This may be due to 'self-inhibition' of the $\text{NH}_4\text{-N}$ produced by urea hydrolysis. Previous work has shown that nitrification in bands is slow when large amounts of urea are injected (Penny, Widdowson & Ashworth, *Journal of Agricultural Science, Cambridge* (1977), **88**, 319-331).

With each amount of urea N, the total free amino-acid and amide N fractions were greater in grass given urea plus ATC than in grass given urea only, largely because of an increase in amide N. However, the concentrations of individual amino acids (not shown in Table 2), were little affected by the amounts of urea N applied.

TABLE 2

Effects of applying increasing amounts of aqueous urea, with and without trithiocarbonate, to permanent grass on yields and various nitrogen fractions in grass of the first cut

	Aqueous urea								
	Control	'Nitro-Chalk'	Without inhibitor			With inhibitor			
			250	375	500	250	375	500	
N given (kg ha^{-1})	None	100	250	375	500	250	375	500	
Dry matter yield (t ha^{-1})	1.01	3.04	2.94	3.06	3.29	2.65	2.87	2.74	
Total N, % of dry matter	2.63	4.13	4.26	4.57	4.59	4.34	4.56	4.93	
% of total N:									
Protein N	87.8	81.1	80.0	78.1	70.4	79.0	77.4	75.1	
Nitrate N	0.2	3.0	4.5	6.2	5.7	2.2	3.8	4.3	
Total free amino acid and amide N	3.1	6.6	8.7	8.9	9.3	9.9	9.7	9.9	

All grass samples contained an unusually large proportion of free proline, ranging from 5.5 to 9.2% of total N in the combined free amino-acid and amide fraction. Normally, this proportion ranges from 1 to 4%. The accumulation of free proline under exceptionally dry conditions is consistent with the early work of Kemble and MacPherson (*Biochemical Journal* (1954), **58**, 46-49) on perennial ryegrass and the more recent findings of Barnett and Naylor (*Plant Physiology* (1966), **41**, 1222-1230) for Bermuda grass (*Cynodon dactylon*) which show that free proline accumulates in grasses under water stress.

The only practical implication of these results, which were obtained during the exceptionally dry summer of 1976, is that ATC can be expected to decrease the concentration of nitrate in grass given a single application of injected aqueous urea. However, further experiments are obviously needed under more normal growing conditions before making any definite recommendations for practical agriculture. (Nowakowski, Ashworth and Lazarus)

Nitrogen in cereal grain and straw. Cereal experiments (124 on winter wheat, 41 on spring wheat, 235 on barley), conducted during the last 20 years, are being re-examined to see how % N in grain (and in some straw) has been affected by the amount and timing of N fertilisers, by different crop sequences, and by some environmental factors, such as weather and soil texture. The experiments were done at Rothamsted, Woburn, Broom's Barn and Saxmundham Experimental Stations and on commercial farms within a 25-mile radius of Rothamsted. Some preliminary results, given in *Rothamsted Report for*

ROTHAMSTED REPORT FOR 1976, PART 1

1974, Part 1, 80–83, showed that % N (which is proportional to % protein) in cereal grain often increased with applied N, even after there was no further response in yield.

An appraisal of the data is now being made by a 'two-stage' procedure: *Stage 1*. Each experiment is characterised by name of site, year, variety, surface-soil texture, subsoil texture, soil wetness class; winter leaching, spring leaching, amount and date of maximum potential soil water deficit, radiation; soil N index (*Ministry of Agriculture, Fisheries and Food* (1973), *Bulletin* No. 209), number of current N levels tested; precision (expressed as coefficients of variation) of grain yield, % N in grain and, where applicable, straw yield and % N in straw. The above data are listed for all three cereals. Sowing date, soil pH and total soil N—the latter confined to experiments on commercial farms—are listed for barley only. *Stage 2*. The experimental factors comprise one-year manurial residues (farmyard manure, amounts of fertiliser N) and current manuring treatments (farmyard manure, amounts of fertiliser N, times, methods and forms) and crop sequences. The largest amount of fertiliser N applied was 275 kg N ha⁻¹ to spring and winter wheat and 200 kg N ha⁻¹ to barley. Among the crop sequences examined were (1) frequency of cereal cropping, (2) comparisons between arable rotations and short- and long-term grass and (3) contrasts of cropping residues from legumes, grass and legume/grass mixtures.

The computer-listing of stages 1 and 2 has been completed for all three cereals. A preliminary examination of the wheat data shows that grain yields (at 85% dry matter) and N concentrations in dry matter of grain ranged, for spring wheat, from 1.0 to 6.3 t ha⁻¹ and 1.6 to 3.1% N, and for winter wheat from 1.0 to 9.5 t ha⁻¹ and 1.2 to 3.0% N respectively. The exceptionally high value of 3.0% N for winter wheat, which falls outside the range of the remainder, is for a 1973 grain sample from a farmyard manure + N plot on Broadbalk field at Rothamsted. This value has been confirmed by analysis of N in flour from an independent sample (Mr. B. A. Stewart, Flour Milling and Baking Research Association).

The largest amounts of protein ($5.7 \times$ Kjeldahl N) produced in this series of experiments were 925 kg ha⁻¹ for winter wheat and 660 kg ha⁻¹ for spring wheat. (Benzian, with Lane and Simpson, Statistics Department)

Nutrient uptake and soil nitrate depletion by winter wheat

Weekly soil nitrate measurements were made during April–July 1976 under winter wheat and in adjacent fallow soil (given 100 kg N ha⁻¹ as 'Nitro-Chalk' in April) 0–50 cm below the surface, with a nitrate ion-selective electrode (Page & Talibudeen, *Plant and Soil* (1977) in the press). Wheat shoots were sampled at 3–4 day intervals and analysed for dry weight and for concentrations of N, P, K, Mg and Ca in the crop.

Soil nitrate. Soil nitrate concentrations decreased with depth. The numerical difference, $(pNO_3)_{\text{fallow}} - (pNO_3)_{\text{crop}}$ (where $pNO_3 = -\log_{10}[NO_3^-]$) was greatest in the 12.5–25 cm zone. This parameter is directly proportional to the work done by the crop in taking up soil nitrate and these observations imply that more work is done by roots in the 12.5–25 cm zone in removing similar amounts of NO₃⁻-N than in other zones. This difference in pNO_3 was larger in the four weeks before harvest than in the four weeks after N application, although total N uptake, indicated by differences in the soil nitrate concentration, was very similar during both periods.

The very dry summer of 1976 resulted in larger and less variable soil nitrate concentrations in the 0–25 cm zone than observed during 1972–75. The maximum differences between $(pNO_3)_{\text{fallow}}$ and $(pNO_3)_{\text{crop}}$ occurred at Feekes stages 6, 10 and 11.1, indicating periods of maximum uptake by the crop. Weekly changes in the work function, $(pNO_3)_{\text{fallow}} - (pNO_3)_{\text{crop}}$ measured at 12.5–25 cm or in the 0–25 cm or 0–50 cm profile,

CHEMISTRY DEPARTMENT

correlated better with weekly crop N uptake than did differences between the $\text{NO}_3\text{-N}$ content (expressed in ppm) of soil water under fallow and crop. This suggests that this work function is a better indicator of the pattern of plant N uptake than the $\text{NO}_3\text{-N}$ content of soil water.

Crop growth and nutrient uptake. Shoot dry weight increased to a maximum at Feekes stage 11.3 (about 15 days before maturity) and then decreased slightly although the ear weight remained constant. Mg, N and P concentrations in the shoots decreased to minima at Feekes stages 10.1, 10.5 and 11.3 respectively, but increased subsequently because the concentrations in the ears increased during grain filling. Total uptake values showed that these nutrients were translocated to the ears during grain filling, mainly by losses from the foliage, and uptakes in the shoots reached maxima at Feekes stages 11.2, 11.1 and 11.3 respectively. K and Ca uptakes reached maxima earlier, at Feekes stages 10.1 and 10.5 but both nutrients were subsequently lost, mainly from the foliage. (Page, Smalley and Talibudeen)

Leaching and movement of nutrients in soil

Modelling solute leaching in structured soils. A computer model has been developed in which the soil (at field capacity) is treated in layers. As a working approximation, soil pores are divided into two categories, (i) those in which solute and water move in piston flow each time rain falls, and (ii) those in which they are retained in the layer. The amount of water held by each category is defined with reference to the soil moisture characteristic. Equalisation of solute concentration between categories (i) and (ii) is assumed to occur after each rainfall 'event', and gives 'hold-back' of solute for subsequent release. The model permits solute and water to move through the large pores of an indefinite number of layers during heavy rain. It predicts the amount of solute in each layer of a profile after any number of rainfall or evaporation 'events', and can either store water and solute in the bottom layer for withdrawal up the profile when evaporation occurs, or subtract any previous evaporation from rainfall and predict the solute concentration in each aliquot of drainage from the bottom layer.

In an earlier experiment, nitrate applied to field plots in early October was either put on the surface or incorporated to a depth of about 13 cm. The plots were sampled, 0-13 cm and 13-26 cm, at intervals. Comparing the measured concentrations in each layer with those predicted by the model showed that when the first two samplings, which were made within ten days of the plots being power-harrowed, were omitted, the regression of nitrate concentration (mg kg^{-1} dry soil) measured (F) on that predicted (P) was

$$F = (1.037 \pm 0.100)P + 2.6; r = 0.973$$

for surface-applied nitrate, and

$$F = (1.088 \pm 0.126)P + 4.0; r = 0.961$$

for incorporated nitrate. Dividing the 13 cm layers into 6.5 or 3.25 cm sub-layers improved the relationship.

When Cl concentrations in drainage after Cl application to the 20 and 40 in drain gauges were plotted against cumulative drainage (this Report, p. 88), the model predicted with reasonable accuracy the overall shapes of the curves and the positions of subsidiary peaks.

The model has been further developed to allow for any mineralisation of soil nitrogen which may occur between rainfall events by means of a simple first-order rate equation. The temperature coefficient of the rate constant is given by an Arrhenius-type equation, and a laboratory experiment is in progress to obtain the necessary constants for Rotham-

ROTHAMSTED REPORT FOR 1976, PART 1

sted soils. It is also being adapted to model the leaching of adsorbed solutes, e.g. pesticides. (Addiscott)

Nitrate N in borehole waters at Rothamsted and Woburn. Concentrations of nitrate N in borehole waters sampled at Rothamsted Farm between 1 October 1975 and 30 September 1976 varied from 4.1 and 7.0 mg litre⁻¹ with a mean concentration of 5.9 mg litre⁻¹. At Woburn the corresponding values were 2.5–7.0 mg litre⁻¹ and 5.0 mg litre⁻¹. Concentrations at both sites showed less variation than during the period 1968 to 1974 when nitrate N at Rothamsted varied from 4.9 to 11.8 mg litre⁻¹, with a mean value of 6.0 mg litre⁻¹ and at Woburn from 0.01 to 8.5 mg litre⁻¹, with a mean value of 4.2 mg litre⁻¹. Rainfall at Rothamsted from 1 October 1975 until 30 September 1976 was 391 mm of which only 23% fell between the beginning of May and the end of August when evaporation was large. At Woburn, the rainfall was 328 mm during the same period of which 22% fell between May and August. Above average rainfall after the beginning of September did not increase the NO₃-N content of borehole waters sampled at either site in October 1976. (Williams)

Chloride leaching in uncropped drain gauges. The 20 in and 40 in-deep 'Classical' drain gauges originally constructed by Lawes and Gilbert in 1870 with undisturbed soil monoliths of 0.001 acre (4.05 m²) surface area have been used to study leaching patterns of chloride applied in October 1974 as CaCl₂ at a rate of 254 kg ha⁻¹ Cl (equivalent to 100 kg ha⁻¹ nitrate N). The chloride applied to the 40 in gauge was labelled with ³⁶Cl. Daily measurements of total Cl and ³⁶Cl have been made in the rain and drainage waters. Further unlabelled chloride applications were made in autumn 1975 to both gauges.

The autumn and winter of 1974–75 were very wet and some added chloride was measured in the drainage soon after application when about 25 mm of drainage had occurred. Chloride concentrations increased to maxima in both gauges at between 50 to 150 mm drainage. Graphs of Cl concentrations against amounts of drainage were not smooth but showed several well-defined peaks depending on the pattern of rainfall. 'Tailing' of the chloride concentration graph occurred in both gauges, especially the 40 in gauge where all the ³⁶Cl had not leached during the subsequent 1975–76 winter which was drier than average. (Bolton, with Rose, Physics Department)

Rainfall, evaporation and drainage at Saxmundham

For the period from 1 October 1975 until 30 September 1976 the rainfall at Saxmundham Experimental Station was 500 mm. This amount is 129 mm less than the 40-year average; only the monthly rainfall in November 1975 and in July and September 1976 exceeded their long period means. Only 30% of the total rainfall fell from the beginning of May until the end of August. Evaporation (E₀), measured by pan evaporimeters, was 740 mm between 1 April and 30 September, when the accumulated moisture deficit was 276 mm.

The period of *continuous* drainage on Harwood's Field lasted from 28 November 1975 until 3 April 1976 (128 days) and was the shortest since records began in 1967. From 1 April until 1 October there were 176 days without drainage, 14 more than in 1974 which had the most drainage-free days since 1968.

Losses of NO₃-N were correspondingly small. From 1 October 1975 until 30 September 1976 losses were 7.2 kg ha⁻¹ under both arable and herbage crops and the losses during the period of continuous drainage, mentioned above, were 5.6 kg ha⁻¹ under arable crops and 5.0 under herbage. These are the smallest losses of NO₃-N in drainage at this site since records began in 1968. Concentrations of 20–40 mg litre⁻¹ NO₃-N in moderate flows of drainage collected in September and the beginning of October this year indicate

CHEMISTRY DEPARTMENT

that much residual nitrate remained in the soil and will be susceptible to leaching later in the year. (Williams)

Atmospheric ammonia as a source of terrestrial combined nitrogen

Ammonia released into the atmosphere from agricultural, domestic and industrial sources exists either as free ammonia gas or is converted by reaction with other gases (primarily SO_2) into particulate ammonium compounds. Some of the atmospheric ammonia (i.e. NH_3 gas and NH_4 particulate material) is deposited on the soil and quantitative estimates of the amounts returned are necessary for the construction of nitrogen balance sheets. This ammonia may also be important agriculturally in areas where nitrogen fertilisers are not used. Two mechanisms are responsible for the input of atmospheric ammonia to soils: (i) NH_3 and $\text{NH}_4\text{-N}$ are dissolved or suspended in and deposited by rain. The amounts of nitrogen returned in this way at Rothamsted are well documented. (ii) Some of the total ammonia is returned through the process of dry deposition from the atmosphere onto soils. Previous determinations at Rothamsted over 60 years ago (Hall & Miller, *Journal of Agricultural Science, Cambridge* (1911), **4**, 46-68) suggest that dry deposition adds 2 kg $\text{NH}_3\text{-N ha}^{-1} \text{ year}^{-1}$ to the soil. However, Eriksson (*Handbuch der Pflanzenernährung und Düngung* (1968), Vol. II, 774-792) gives a much higher theoretical value (13 kg $\text{NH}_3\text{-N ha}^{-1} \text{ year}^{-1}$) for Rothamsted.

Preliminary results from present work, using selective materials to sorb either particulate NH_4 compounds alone, or particulate $\text{NH}_4\text{-N}$ and NH_3 gas together, indicate that soils still receive only 1-3 kg $\text{NH}_3\text{-N ha}^{-1} \text{ year}^{-1}$ from deposition of atmospheric ammonia and that 80-90% of the total nitrogen deposited in this way is in the form of particulate NH_4 compounds while the remainder is probably gaseous ammonia. Weekly dry deposition values vary in inverse proportion to the rainfall, although concentrations of atmospheric ammonia show little correlation with rainfall. The amount of dry deposition (1-3 kg $\text{NH}_3\text{-N ha}^{-1} \text{ year}^{-1}$) is low compared with values from certain areas of the world where atmospheric ammonia concentrations are high due to intensive agricultural or industrial activity, and reflects the small total atmospheric ammonia concentration (c. 3 $\mu\text{gm NH}_3\text{-N m}^{-3}$ air) at Rothamsted. (Rodgers)

Root growth of herbage crops at Saxmundham

The pin-board monolith method was used to sample roots of lucerne and grass sown in 1970 on soil which had received either NPK fertilisers or farmyard manure (FYM) and had grown only arable crops since 1899 in the Rotation I experiment at Saxmundham Experimental Station. In November 1973 monoliths were excavated to a depth of 61 cm along 30 cm of crop row for both manure treatments; in addition, two monoliths were taken, each 61 cm across the direction of drilling and 30 cm deep, from the lucerne and grass on the FYM plot to investigate the distribution of roots along and across the rows. In October 1976 the same grass sward, in which the original rows were no longer visible, was re-sampled across the direction of drilling. The monoliths were the same length but only 30 cm deep because, at the previous sampling, few grass roots were found below 25 cm. Lucerne, which had been resown in spring 1976, was not sampled. In addition, soil moisture and bulk density were measured at different depths. The roots, freed from soil by washing, were sub-divided into 10 cm depths.

Before 1964, ploughing depth was probably not greater than 15 cm but it was increased in winter 1964-65 to about 25 cm and then maintained at this depth during the next five years. In 1973 the monoliths still contained some large clods of dense, unaltered subsoil which must have been incorporated in the plough layer by deeper ploughing in 1964-65;

ROTHAMSTED REPORT FOR 1976, PART 1

very few roots of either grass or lucerne had penetrated these clods. Similar clods were found in the monoliths taken in 1976.

Soil moisture contents at both sampling times were very similar (33% v/v in October 1973 and 31% v/v in November 1976). In 1973 mean densities for the top 40 cm of soil were much the same for both manurial treatments and crops and averaged 1.56 g ml⁻¹ (range 1.53–1.59). In 1976 soil under grass was further consolidated where NPK fertilisers were given; densities were 1.60 or larger, but FYM-treated soil was much less dense, 1.46 g ml⁻¹. Air-filled pore space (Table 3) had increased considerably in FYM-treated soil under grass by 1976 but had changed little on NPK-treated soil. Earthworms, which are rarely seen in this soil under arable cultivation, have increased greatly in numbers since herbage crops were grown and their presence may explain the increase in porosity associated with the FYM treatment.

TABLE 3

Air-filled pore space at various depths in FYM- and NPK-treated soils growing grass and lucerne, Rotation I experiment, Saxmundham

Year	Depth (cm)	Air-filled pore space (% v/v)			
		Lucerne		Grass	
		NPK	FYM	NPK	FYM
1973	5	8.9	10.6	5.3	4.8
	15	10.1	8.8	5.0	8.2
	25	1.6	7.5	4.8	3.8
	40	2.7	4.3	5.6	1.5
	Mean 0-40	5.7	7.8	5.2	5.2
1976	5	ns	ns	4.7	11.4
	15	ns	ns	8.4	11.0
	25	ns	ns	3.8	13.0
	Mean 0-30	-	-	5.6	11.8

ns = not sampled

In 1973, but not in 1976, the stubble and any stems and leaves in it were separated from the roots; yields ranged from 1.9 to 4.5 t dry matter ha⁻¹. The yields of grass and lucerne roots in 1973 and of grass roots in 1976 at different depths are in Table 4. In 1973 the total yield of roots of lucerne was about 30% larger than that of grass. More than 95% of grass roots, but only 65% of lucerne roots in the 0-50 cm depth, were in the top 10 cm. Lucerne roots left to decompose *in situ* could well provide channels for weaker roots to penetrate to greater depths. The amounts of grass roots sampled in October 1976 (5.25 t

TABLE 4

Weights of lucerne and grass roots (t ha⁻¹) in 1973 and 1976, Rotation I experiment, Saxmundham

Depth (cm)	1973				1976	
	Lucerne		Grass		Grass	
	NPK	FYM	NPK	FYM	NPK	FYM
0-10	5.96	4.44	6.42	3.93	4.69	2.30
10-20	1.47	1.38	0.19	0.19	0.45	0.23
20-30	0.82	1.00	0.02	0.02	0.11	0.07
30-40	0.24	0.28	0.01	0.00	ns	ns
40-50	0.10	0.20	0.00	0.00	ns	ns
Total	8.59	7.30	6.64	4.14	5.25	2.60
0-10 cm as % of total	69.3	60.8	96.8	95.0	89.3	88.5

ns = not sampled

CHEMISTRY DEPARTMENT

ha⁻¹ on NPK-treated soil and 2.60 t ha⁻¹ on the FYM plot), were less than those measured previously to a depth of 30 cm but a similar percentage (90%) of the total amount of roots was found in the 0–10 cm horizon.

Both in 1973 and 1976 weights of grass roots were larger in NPK- than in FYM-treated soil; this was also the case with lucerne in 1973. In 1969, before the herbage crops were sown, the FYM-treated soil contained more NaHCO₃ soluble P and exchangeable K, 31 mg P and 242 mg K kg⁻¹ respectively, than the NPK-treated soil, 18 mg P and 157 mg K. The smaller root systems on the FYM-treated soil may have developed because this soil contained more available nutrients or, perhaps, had a better structure so that nutrients moved more readily through the soil during depletion at the root-soil interface. (Williams and Johnston)

Continuous cereals at Woburn

Winter wheat and spring barley has been grown continuously and in rotation in the Intensive Cereals experiment at Woburn since 1966; some yields were summarised briefly (*Rothamsted Report for 1974*, Part 1, 83) and the full results are now being prepared for publication. The rotation was: all grass ley, potatoes, cereal, cereal, cereal, so that yields of the first, second and third cereal after a break crop can be compared with the yields of wheat and barley grown continuously. Nutrient composition of the crops has been determined and the balance between nutrients applied and removed related to changes in amounts of plant nutrients in soil. All plots received 55 kg P and 110 kg K ha⁻¹ each year and N was tested at 63, 126, 189 and 252 kg N ha⁻¹ to wheat and 50, 100, 150, 200 kg N ha⁻¹ to barley.

Both cereals yielded most when grown immediately after potatoes; 100–126 kg N ha⁻¹ was sufficient to give almost maximum yields. Best yields of the second barley crop, which were obtained with 150 kg N ha⁻¹, were almost equal to the maximum yield of the first barley after the break crop. The second wheat crop, however, yielded about 1 t grain ha⁻¹ less than the first even when given optimum amounts of N. Best yields of the third cereal after the break and of wheat or barley grown continuously were very similar; these were only about 0.4 t ha⁻¹ less than the maximum for barley but 1.1 t ha⁻¹ less for wheat.

Percentage N in grain and straw of both wheat and barley increased with increasing N dressings; there was most N in the harvested crops given the largest N dressing. Nitrogen fertilisers had little effect on % K in either wheat or barley grain but, unexpectedly, they greatly increased % K in the straw of both cereals from 0.8 to 1.5% K in wheat and from 1.0 to 1.8% in barley straw. For wheat given most N, % K varied with the number of wheat crops after the break. The first wheat crop contained most K (1.5%) in the straw and, as the number of continuous wheat crops increased, the % K in straw diminished. All straw samples had much the same % K when least N was given. The effect of the rotation on % K in barley straw was much smaller than that for wheat straw.

There were large differences in the amounts of K removed in the grain plus straw because yield and % K in straw both increased with increasing N dressings. These differences in K uptake had caused measurable differences in the exchangeable K in the soils by 1974.

Both crops were sampled in May and June 1976, at growth stages 6 and 10 on the Feekes scale, to see how soon % K in wheat and barley was affected by the amount of N applied. For both crops, % K in dry matter increased at both sampling dates with the amount of N applied and N and K uptake were linearly related in green wheat and barley at both stages of growth. (Igbokwe and Johnston)

The yield of continuous wheat at Saxmundham, 1974–76

The site used from 1966–70 by Slope, Etheridge and Williams to value the effects of a two-year break on the yield of successive crops of winter wheat (*Rothamsted Report for*

ROTHAMSTED REPORT FOR 1976, PART 1

1972, Part 2, 160–165) was used from 1971–73 to grow winter wheat again (*Rothamsted Report for 1973*, Part 1, 48–49) to see whether yields could be improved by changing seed rate and row spacing at three levels of N. Yields were largest when 210 kg seed ha⁻¹ was sown in rows 15 cm apart and 150 kg N ha⁻¹ was given. The site was used again to grow winter wheat from 1974–76; four-fifths of the experiment was used to test all combinations of two varieties (Maris Huntsman v Cappelle-Desprez), without and with chlormequat chloride (CCC), and three amounts of nitrogen (50, 100 and 150 kg N ha⁻¹) applied either once (nominally late April) or twice, in equal dressings in April and May. All these plots were sown with a drill having coulter 13 cm apart. These treatments were arranged so that any effects on yield from increasing numbers of consecutive wheat crops could also be measured. In 1974, the 6th, 7th, 8th and 9th continuous wheat crops were grown; by 1976, these had become the 8th, 9th, 10th and 11th crops. In addition, wheat was sown with the Smythe drill; it was the 5th, 6th and 7th continuous wheat crop in 1974, 1975 and 1976 respectively.

In autumn, basal fertiliser (0–20–20) at 1260 kg ha⁻¹ was ploughed in and a 20–10–10 fertiliser broadcast at sowing to minimise or prevent N deficiency during the winter. Additionally, and to maintain continuity, plots sown by Smythe drill during 1971–73 were retained, but split lengthwise to test the value of autumn-applied N. (The Smythe drill was the traditional means of sowing wheat at Saxmundham; it has coulter spaced 20 cm apart.)

In 1974, with ample rain, 150 kg N ha⁻¹, applied in spring, severely lodged both Cappelle-Desprez and Maris Huntsman. CCC diminished lodging in Maris Huntsman, but not in Cappelle-Desprez, and 150 kg N ha⁻¹ gave a larger yield than 100 kg N ha⁻¹ only where CCC had been applied to Maris Huntsman. In 1975 and 1976 the wheat did not lodge; yields were always largest with 150 kg N ha⁻¹, and were larger with CCC than without on both varieties and in both years.

TABLE 5

Effects of variety, nitrogen, chlormequat chloride (CCC) and timing of nitrogen on the yield of winter wheat at Saxmundham, 1974–76

Variety	Cappelle-Desprez			Maris Huntsman			Mean
	50	100	150	50	100	150	
N given (kg ha ⁻¹)							
	Yields of grain in t ha ⁻¹ at 85% dry matter						
CCC							
Without	3.81	4.83	5.51	4.09	5.25	5.61	4.85
With	4.16	5.12	5.65	4.23	5.22	6.04	5.07
Timing of N							
All April	3.96	4.83	5.55	4.12	5.14	5.84	4.91
½ April, ½ May	4.02	5.13	5.61	4.21	5.32	5.82	5.02
Mean	3.99	4.98	5.58	4.16	5.23	5.83	4.96

Table 5 shows that the largest mean yield was from Maris Huntsman given 150 kg N ha⁻¹ in spring together with CCC. The only benefit from giving N in two dressings rather than in one occurred in 1975, when wet weather delayed the application of the N and dry weather afterwards diminished the effectiveness of all but the first half of the divided dressings.

Yields from the experiment may be compared with those from Broadbalk field at Rothamsted, which has a well-structured clay-loam soil, more suited to long runs of wheat, than the intractable sandy clay-loam at Saxmundham. Long runs of wheat, up to 11 consecutive crops, have yielded as well at Saxmundham as at Rothamsted (Table 6) although, in each year, yields were smallest on plots which had grown wheat

CHEMISTRY DEPARTMENT

TABLE 6

Yields of continuous winter wheat (Cappelle-Desprez) at Rothamsted (Broadbalk Field) and at Saxmundham on plots given comparable treatment, 1974-76

	Row width (cm)	Total N given, kg ha ⁻¹ *			
		50	100	150	200
Rothamsted					
Without autumn N	17	2.96	3.94	4.51	5.16
Saxmundham					
Without autumn N	20	3.10	3.98	4.72	—
With 50 kg N ha ⁻¹ in autumn	13	—	3.81	4.83	5.51

* At Rothamsted amounts were 48, 96, 144 and 192 kg ha⁻¹

the longest. At Saxmundham, failure to control blackgrass (*Alopecurus myosuroides*) satisfactorily in 1975 and 1976 has decided us to grow barley on the site of this experiment in 1977. (Widdowson, Johnston and Penny)

Liquid NPK fertilisers for potatoes and winter wheat

Potatoes. Experiments during 1963-65 compared several methods of applying granular NPK fertiliser (containing 13% N, 13% P₂O₅, 20% K₂O, abbreviated here to 13-13-20) for maincrop potatoes. The smallest amount tested (625 kg ha⁻¹) was best placed in a band on each side of the seed, but the largest (1875 kg ha⁻¹) was best broadcast and worked into the seedbed because, when placed, it checked early growth and gave much smaller yields (*Rothamsted Report for 1965*, 50-51). During 1971-72 we confirmed that up to 2510 kg ha⁻¹ of the 13-13-20 fertiliser significantly increased yields at Rothamsted and Woburn provided it was thoroughly incorporated into the soil (*Rothamsted Report for 1973*, Part 1, 46).

In 1974 and 1975 several methods of applying liquids for main-crop potatoes were tested at Rothamsted and Woburn to establish whether placing a liquid fertiliser to the side of seed potatoes increased fertiliser efficiency and yield. In 1974 liquid and granular NPK fertilisers having N:K₂O ratios either of 1:1 or 1:1.5 were compared to assess the need for extra K for potatoes on our soils. The liquids (7-7-10 and 9-9-9) were either (i) sprayed over the seedbed and rotavated in, (ii) partly sprayed (two-thirds of the total amount given) and partly placed in a band on each side of the seed, or (iii) placed on each side of the seed; the bands were 18 cm apart (9 cm from centre of seed potato). Granular fertilisers (13-13-20 and 15-15-15), which were used as a standard treatment, were broadcast and rotavated in. All fertilisers were applied to give 188, 282 and 376 kg N ha⁻¹. In 1975 only one liquid fertiliser (7-7-10) was compared with one granular (13-13-20) fertiliser. The liquid was either (i) sprayed over the seedbed and worked in, (ii) half sprayed and half placed on each side of the seed, or (iii) placed on each side of the seed. Both fertilisers were applied to give 125, 188, 250 or 314 kg N ha⁻¹ to seed spaced either 36 or 48 cm apart. The liquid fertilisers were based on urea, diammonium phosphate and potassium chloride.

Table 7 shows that in 1974 yields from broadcasting the granular fertilisers exceeded those from the liquids on both farms. At Rothamsted placing more than 188 kg N ha⁻¹ as either of the liquid fertilisers in bands checked growth until mid-July. Leaf analyses, made at this stage of growth, showed that % P and % K were largest where the liquid fertiliser had all been placed, indicating that these nutrients had been taken up later than on plots given other treatments. This was probably because the pH in the fertiliser band increased greatly as the urea hydrolysed and so diminished initially the availability of the

ROTHAMSTED REPORT FOR 1976, PART 1

TABLE 7

Yields of main-crop potatoes grown at Rothamsted and Woburn with liquid and granular NPK fertilisers, 1974-5

Fertiliser treatment	1974		1975	
	Rothamsted*	Woburn*	Rothamsted**	Woburn*
	Yield of total tubers (t ha ⁻¹)			
Granules				
Broadcast	64.1	72.4	36.3	41.5
Liquids				
All sprayed	60.8	67.8	34.3	40.9
Part sprayed, part placed	62.0	70.6	36.4	42.4
All placed	58.1	71.2	34.5	43.6
SE of difference	±1.46	±1.52	±1.40	±0.75

* Pentland Crown

** King Edward potatoes

water-soluble phosphorus (Matzel, *Archiv für Acker und Pflanzenbau und Bodenkunde* (1974), **18**, 489-502). Temporary shortage of P would greatly limit early growth on this soil, which contains little bicarbonate-soluble P.

At Woburn, where the soil contains more soluble P, placing the liquids in bands did not check early growth and yields from placement were larger than from sprays and only a little smaller than from the granular fertilisers. At Rothamsted yields were increased by each increment of the granular fertilisers, but not by the liquids. At Woburn, however, total yields were increased by each increment of each fertiliser and averaged 66.8 t ha⁻¹ with 188 kg N ha⁻¹ and 74.0 t ha⁻¹ with 376 kg N ha⁻¹. Changing the ratio of N to K₂O from 1:1 to 1:1.5 increased yield by 2 t ha⁻¹ at Rothamsted and by 3 t ha⁻¹ at Woburn.

In 1975, the very wet spring delayed planting until early May but afterwards the summer was dry and yields were smaller than in 1974. Placing the liquid fertiliser in bands did not check growth in either experiment, but yields from placing all the fertiliser were larger than from broadcasting the granules only at Woburn (Table 7). Yields were smallest at both farms where all the liquid fertiliser was sprayed on the soil surface before planting.

Winter wheat. Residual effects of fertilisers given to potatoes were measured with winter wheat. In 1975 nitrogen was applied at 0, 30 or 60 kg N ha⁻¹ at Rothamsted and 30, 60 or 90 kg N ha⁻¹ at Woburn in all combinations with fertiliser given for the potatoes. Even after a very wet winter and spring, when October-March rainfall was 147 mm above average at Rothamsted and 145 mm at Woburn, there were large residual effects. At Rothamsted these ranged from 0.86 t ha⁻¹ (yield with 376 minus yield with 188 kg N ha⁻¹ to potatoes) without fresh N, to 0.47 t ha⁻¹ with 60 kg ha⁻¹ of fresh N. The corresponding residual effects at Woburn ranged from 1.23 t ha⁻¹ with 30 kg ha⁻¹ of fresh N to 0.15 t ha⁻¹ with 90 kg ha⁻¹ of fresh N.

In 1976 the wheat was given 0, 30, 60 or 90 kg N ha⁻¹ in both experiments. In contrast to 1974-75, October-March rainfall was much less than average at Rothamsted (-183 mm) and at Woburn (-160 mm) but the residual effects of the fertilisers applied for potatoes were no larger than in 1975. At Rothamsted they ranged from 0.90 t ha⁻¹ (314 minus 126 kg N ha⁻¹ to potatoes) without fresh N, to 0.05 t ha⁻¹ where the wheat was given 90 kg N ha⁻¹, and at Woburn from 0.54 t ha⁻¹ without fresh N to 0.08 t ha⁻¹ with 90 kg N ha⁻¹. The size of the responses to fresh N depended more in 1976 than in 1975 on the amount of fertiliser applied for the potatoes. At Rothamsted the wheat responded to no more than 60 kg N ha⁻¹ after potatoes given 126, 188 or 231 kg N ha⁻¹ and to no more than 30 kg N ha⁻¹ after potatoes given 314 kg N ha⁻¹. At Woburn, the wheat re-

CHEMISTRY DEPARTMENT

sponded to 60 kg ha⁻¹ of fresh N after potatoes given 126 kg N ha⁻¹, to 30 kg N ha⁻¹ after potatoes given 188 or 231 kg N ha⁻¹, but not at all to N after potatoes given 314 kg N ha⁻¹. (Widdowson, Penny and Hewitt)

Potassium in Saxmundham soils

Potassium-calcium exchange. Isotherms for K-Ca exchange at 20°C were obtained for Saxmundham soil (taken in 1966 from Rotation I, Nil and PK treatments) and its clay and silt-size fractions. Standard free energy values, $(\Delta G_0)_{Ca \rightarrow K}$, showed that K selectivity decreased in the order Nil > PK for the whole soil, and Ca > (Ca + K) and (<0.2 μm) > (0.2-2 μm) > (2-20 μm) for the size fractions.

$(\Delta G_0)_{Ca \rightarrow K}$ values showed that K selectivity increased with increasing surface area and decreasing surface charge density. Application of potassium fertilisers since 1899 and K treatment in the laboratory both decreased K selectivity. The resulting decrease in surface area implies that sites of high K selectivity are situated between clay platelets. The calculated surface charge density (SCD) is a mean value for groups of sites of various SCDs. High SCDs favour Ca sorption and so when groups of K selective sites with a low SCD are filled, the mean SCD increases. Increases in the SCDs of the (Ca + K) saturated (<0.2 μm) and (0.2-2 μm) fractions of 100 and 20% respectively, compared with the Ca fractions, were attributed to the comminution of the high SCD CaCO₃ particles (17 μe m⁻²) to about half their mean equivalent spherical diameter during K saturation. No significant increases in SCD on K saturation were observed for the (2-20 μm) fraction and for the whole soil. (Goulding and Talibudeen)

Extraction of potassium by ion-exchange resins

Particle-size fractions. The rates of K removal by Ca-saturated resin from the various particle-size fractions, saturated with Ca, Ca + K and K, and from soils of the Nil and K plots from Rotation I at Saxmundham, were measured. (Partial K saturation of the Ca forms was attained by equilibrating soils with a 0.9 N-Ca + 0.1 N-K chloride solution.)

The cumulative extraction of K with time was analysed (*Rothamsted Report for 1975*, Part 1, 91-92) on the basis of simultaneous fast and slow rate processes, yielding rate constants D_1/l^2 and D_2/a^2 and associated amounts of potassium, M_1 and M_2 , where D is the appropriate diffusion coefficient, l the diffusion layer thickness for the rapid process and a the radius of the equivalent spherical particle.

This analysis showed that:

(i) for the rapid process, the rate function D_1/l^2 increased much more in going from the Ca to Ca + K forms, when small amounts of K were sorbed, than from the Ca + K to K forms when much larger amounts of K were sorbed. This difference between the increments of D_1/l^2 was more pronounced in the coarser fractions; e.g. in changing from Ca → Ca + K → K forms for the fine clay and fine sand fractions, the function D_1/l^2 was 2 → 8 → 13 × 10⁻⁵ sec⁻¹ and 1 → 18 → 25 × 10⁻⁵ sec⁻¹ respectively;

(ii) for the slow process, which accounted for much smaller amounts of added K, differences in the increase of the rate function D_2/a^2 in going from the Ca to Ca + K and from the Ca + K to K forms were less, but they were more pronounced for the finer fractions, e.g. for the same forms and fractions as in the example above, D_2/a^2 was 0.5 → 8 → 69 × 10⁻⁹ sec⁻¹ and 0.4 → 0.4 → 0.4 × 10⁻⁹ sec⁻¹ respectively.

These observations suggest that the sorption of added K attributed to the rapid and slow processes is associated with mineralogically distinct phases in the various fractions. X-ray diffraction and surface area measurements (by ethylene glycol vapour sorption) show that sorption of added K reduces the interlayer expansion of the interstratified

ROTHAMSTED REPORT FOR 1976, PART 1

minerals. K-exchange by Ca during resin cropping restores and even increases the expanded clay surface. In 200 h this reaction removes nearly all the added K from the K forms of the fractions coarser than the fine clay, but only 64% from the fine clay, indicating greater K selectivity in the finer fractions. Smaller proportions of added K were removed from the Ca + K forms than from the K forms because the more K-retentive sites were filled first.

Comparison of size fractions with whole soils. Using the particle size distribution in these soils (see p. 224), weighted mean averages for D_1/l^2 , D_2/a^2 , M_1 , M_2 and M_t (the total K) were calculated on a 'whole' soil basis for the Ca, Ca + K and K forms. Table 8 shows that values for the unfractionated soils are intermediate between those for the Ca and Ca + K forms. The Ca form represents a very K-deficient soil and the Ca + K form a soil in which exchangeable K is adequate for most crops.

TABLE 8

Rate functions and amounts of K calculated for Ca, Ca+K and K forms of the whole soil from particle-size fraction data, and values observed for soils from the nil and K-treated plots of the Saxmundham experiment, Rotation I

Soil	D_1/l^2	D_2/a^2	M_1	M_2^*	M_t^{**}
		(s^{-1})		($\mu e g^{-1}$)	
From particle-size fraction data					
Ca	1.6×10^{-5}	0.4×10^{-9}	1.4	276	331
Ca + K	13.9	2.6	9.4	319	345
K	20.9	19.9	93.4	362	481
Soils					
Nil	9.8	0.9	3.3	330	333
K	12.1	0.8	5.0	—	—

* These values, multiplied by 39.1, give $mg kg^{-1}$

** Total K determined by X-ray fluorescence spectrometry

It can be predicted from the resin exchange results for the Ca and Ca + K forms of the whole soil that 55% of the native K and 70% of the added K would be extracted from the fine clay in 200 h. However, although this fraction would, in the long term, still provide 70% of the added K, its 'native K' contribution would progressively decrease to a minimum value of about 30% whilst that of the micaceous minerals identified in the coarser fractions, particularly those in the fine sand, would increase. (Talibudeen, with Weir, Pedology Department)

Denitrification in soils

We have calculated from available free-energy data (Chao & Kroontje, *Soil Science Society America Proceedings* (1963), 27, 44-47, and Van Cleemput & Baert, *Overdruk UIT: Mededelingen Fakulteit Landbouwwetenschappen, Gent* (1974), 39, No. 1) that NH_4-N in solution could be transformed chemically under acid (pH 4), aerobic conditions to 51% NO_3^- , 22% NO_2 and 27% N_2O , and under anaerobic conditions to nearly 100% N_2O . The corresponding values under alkaline conditions (pH 9) would be 59% NO_3^- , 18% NO_2 and 23% N_2O , or nearly 100% N_2O respectively. In soils, however, nitrifying and denitrifying processes would be superimposed on values calculated for these transformations. We have developed a 'dynamic equilibrium' apparatus to investigate these reactions.

A new soil reaction cell for studying soil nitrogen transformations. A continuous gas flow-through system was developed to estimate quantitatively in the laboratory the rate and

CHEMISTRY DEPARTMENT

amount of nitrogen loss (as NH_3 , N_2 , N_2O , NO_2) from soil under 'steady state' conditions. The design of the cell enables 200 g soil to be used at various oxygen and water tensions and temperatures. Various amounts and kinds of N fertilisers, with or without inhibitors, can be incorporated in the soil and their losses compared. The apparatus has been specially designed to estimate N losses by denitrification in soils containing large amounts of organic matter and given large amounts of N fertilisers under heavy rainfall and high temperature regimes. (Wickramasinghe and Talibudeen, with Berneye, Instrument Workshops)

Sampling and assay. A continuous and quantitative gas sampling technique was developed to monitor gases from the soil reaction cell which was coupled to a twin column Becker 409 Gas Chromatograph for estimating N_2 , N_2O , CO_2 and O_2 . The column packings were molecular sieve 5A for N_2 and O_2 analysis and Porapak Q for N_2O and CO_2 . Helium was used as the carrier gas. The lower limits of measurement on the gas chromatographic system are 50 v.p.m. N_2 , 75 v.p.m. N_2O and 50 v.p.m. CO_2 . Gaseous NH_3 and NO_2 were estimated by absorption in a $\text{N-K}_2\text{SO}_4 + 2\text{N-H}_2\text{SO}_4$ mixture (Bremner and Shaw, *Journal of Agricultural Science, Cambridge* (1955), 46, 320) followed by steam distillation (Bremner, *Rothamsted Report for 1959*, 59). (Wickramasinghe and Talibudeen, with Witty and Day, Soil Microbiology Department, and Berneye, Instrument Workshops)

Liming experiments

Changes in soil composition. Soil samples, taken in autumn, were analysed from each plot of two long-term liming experiments (*Rothamsted Report for 1970*, Part 2, 98–112) where ground chalk was applied in 1962–63 at rates equivalent to 0, 5, 10 and 20 t ha^{-1} CaCO_3 . Soil pH (in water) was increased after one year by the 5 t ha^{-1} rate to values predicted by the standard ADAS lime-requirement method. The two larger rates increased pH proportionally less. Soil pH decreased after the first year at the 5 t ha^{-1} rate but increased at the 20 t ha^{-1} rate for six years in the sandy-clay loam at Rothamsted and for three years in the loamy-sand at Woburn before starting to decline. Calcium soluble in N ammonium acetate decreased from 1963 to 1974 at approximately linear rates in all plots of both experiments. The rate of decrease was smaller at lower than at higher rates of liming and depended primarily on the average pH. Annual rates of loss of CaCO_3 from the surface 23 cm of soil ranged from 225 to 823 kg ha^{-1} at Rothamsted and from 307 to 752 kg ha^{-1} at Woburn; 91% of the variation of these rates with average soil pH was accounted for by the equation

$$\text{CaCO}_3 \text{ kg ha}^{-1} \text{ year}^{-1} = -702.3 \text{ pH} + 74.03 (\text{pH})^2 + 1920$$

A model of the Ca leaching processes, which takes account of all anions, particularly bicarbonate, and cations, predicted a relationship between pH and annual losses of CaCO_3 different in form from the above equation but there was a reasonable fit with the experimental data. (Bolton)

Extraction of Al from standard clay minerals

A method was developed for saturating various clay minerals with Al^{3+} ions reproducibly and then determining exchangeable and non-exchangeable Al (by extraction with $\text{M-NH}_4\text{NO}_3$ at pH 3) without altering initially the equilibrium with 0.1 N- Al^{3+} at pH 3. Various modifications of the 'leaching' method for extracting Al with $\text{M-NH}_4\text{NO}_3$ at pH 3, used successfully with soils earlier (*Rothamsted Report for 1975*, Part 1, 94), were found to be unsatisfactory for the clay minerals. A 'centrifugation' method was finally developed

ROTHAMSTED REPORT FOR 1976, PART 1

and used. Kinetic curves for the extraction of Al were corrected iteratively for entrained Al and analysed graphically as before to give exchangeable and non-exchangeable Al. After several successive extractions (different for each mineral) the supernatant solution pH remained unchanged and the Al extracted became approximately constant. However, for the mica the final constant pH was 3.3 whereas, for the other minerals, it was not significantly different from pH 3.0, the initial pH of the extracting $m\text{-NH}_4\text{NO}_3$ solution. Values of exchangeable Al agreed with those expected for the CEC of these minerals. The rates of extraction of non-exchangeable Al were different for each mineral and followed the order: Illite ($<1 \mu\text{m}$) $>$ Biotite ($<50 \mu\text{m}$) $>$ Mica ($<1 \mu\text{m}$) $>$ Kaolinite ($0.5\text{--}0.25 \mu\text{m}$) $>$ Kaolinite ($2.5\text{--}1.5 \mu\text{m}$) $>$ Montmorillonite ($0.2\text{--}1 \mu\text{m}$), suggesting that these values indicate the relative magnitudes of the edge-faced surfaces of these minerals from which non-exchangeable Al dissolves at a constant rate. (Cabrera and Talibudeen)

Leaf protein extraction

Fodder fractionation. The dry summer made quantitative work on protein extraction difficult. Effort was therefore concentrated on improving our leaf protein extraction unit. Several changes have been made in the design of the barrel and rotor of the unit to ensure a smooth flow of pulp. We have made an arrangement that stops the feed auger when there is an incipient overload, without stopping the process of disintegration and pressing. We are working on an arrangement that will permit the feed auger and disintegration section to run at different speeds without complicating the unit unduly. A larger unit is being designed. (Butler and Pirie)

Methods, apparatus and technique

Chemical analysis

Organic carbon in soils. A dry combustion method for determining organic carbon in soils was adapted from one described by Rickson (*Analyst* (1948), **73**, 268–274). Organic matter in soil samples is oxidised in a silica combustion tube with an oxygen flow rate of 80 ml min^{-1} . The tube is placed in an electric furnace maintained at 800°C in the half in which oxygen enters and at 700°C in the exit half of the tube. The latter end is filled with catalysts to complete the oxidation of $\text{CO} \rightarrow \text{CO}_2$ and to remove gaseous forms of the halogens, sulphur and phosphorus. The carbon dioxide is absorbed in excess baryta solution and determined by titration with standard HCl. A combustion-titration run takes on average 30 min. Analyses of glucose and standard soil samples gave 98–101% recovery of carbon. (Jasko)

Trithiocarbonate solutions. CS_2 itself, or CS_2 in aqueous emulsions, can be analysed by conversion to potassium ethyl xanthate by treatment with an excess of alcoholic KOH. The reaction product is titrated with iodine solution after neutralising excess KOH with acetic acid. This well known method has been applied to the analysis of CS_3^{2-} solutions using Conway diffusion units of the type described by Bremner and Shaw (*Journal of Agricultural Science, Cambridge* (1955), **46**, 320–328). An aliquot (1 ml) of solution is added to air-dry soil (5 g) in the central compartment of the unit and the CS_2 generated is trapped in KOH/EtOH in the outer compartment, where it can be titrated. The H_2S simultaneously produced apparently remains in the soil and does not interfere during the titration. Evolution of CS_2 was complete within 2 h using silty clay loam, pH 7.5 (Batcombe series) and within 24 h using coarse sand, pH 5.0 (Cottenham series). Differences in permeability of the air-dry soils may partly account for the different rates of decomposition. With both soils, the presence of NH_3 in Na_2CS_3 solution unexpectedly

CHEMISTRY DEPARTMENT

accelerated decomposition, which we expect will be a general finding since the two soil series differ markedly. Autoclaving or γ -irradiating Batcombe soil had little effect on the rate of Na_2CS_3 decomposition, which suggests that only chemical catalysis is involved.

Using the technique described above it was apparent that solutions of CS_3^{2-} in water, or even in concentrated aqueous NH_3 , decompose only slowly on standing. Stability apparently increases when an excess of hydroxide ion is present after preparing CS_3^{2-} solutions. This suggests the important practical implication that aqueous NH_3 and CS_3^{2-} solutions can be mixed before injection, without the risk of serious loss of effectiveness in the event of delay in their application. (Ashworth, with Macdonald and Spokes, Soil Microbiology Department)

Errors in the estimation of nitrate N. Nitrate N in extracts of soil is measured routinely in this department by an automated technique in which the sample, mixed with sodium acetate solution, is passed through a column of zinc shot. A proportion of the $\text{NO}_3\text{-N}$ in the sample is reduced to $\text{NO}_2\text{-N}$ which is determined complexometrically. The $\text{NO}_3\text{-N}$ in the sample is estimated by comparing optical absorbance after complexing, with that of standard solutions of pure $\text{NO}_3\text{-N}$. This method is in general use in other analytical laboratories. The estimate is erroneously large if samples already contain some $\text{NO}_2\text{-N}$, which is often present in extracts of soil taken from injection slits where NH_3 has been applied. The error becomes more serious as the efficiency of the Zn column declines, and 2 ppm $\text{NO}_2\text{-N}$ can cause $\text{NO}_3\text{-N}$ to be overestimated by 10 ppm, in the concentration range 5–30 ppm. The $\text{NO}_3\text{-N}$ concentrations of soil extracts containing appreciable amounts of $\text{NO}_2\text{-N}$ are therefore best obtained by using standard curves for $\text{NO}_3\text{-N}$ containing appropriate amounts of $\text{NO}_2\text{-N}$. (Ashworth and Messer, with Briggs, Chemical Liaison Unit)

Estimation of small amounts of nitrate in soil extracts. Our present attempts to produce more accurate nitrogen balance sheets (N added *minus* N removed) for experiments on wheat and barley at Woburn require the determination of small, but important, amounts of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in surface and subsoils. Recently, our standard procedure has been to extract soil with acidified $\text{N-K}_2\text{SO}_4$ (pH 1) and determine the nitrate and ammonia by distillation from the extract. There is, however, often less than 1 mg N litre⁻¹ in the extract and such small quantities cannot be determined accurately after steam distillation because the amount of acid used in the titration is very small. When the Technicon AutoAnalyzer was used it consistently underestimated $\text{NO}_3\text{-N}$ in acidified K_2SO_4 by as much as 40%. The determination was improved if the pH of the extract was adjusted to about 7 with 2M-KOH. Small amounts of nitrate N are best determined quantitatively on the Technicon AutoAnalyzer using 2M-KCl, although results do not differ appreciably with M-KCl or N- K_2SO_4 solutions. (Igbokwe and Johnston)

Radiochemical analysis

Liquid scintillation spectrometer performance. Previous work (Rothamsted Report for 1975, Part 1, 98) indicated an apparent increase in the counting efficiency of low activity samples containing <0.500 g of ^{14}C and ^3H -hexadecane standards. This was caused by evaporation of the toluene-based scintillation cocktail during sample preparation by weight, and was eliminated by first diluting the labelled standards with unlabelled hexadecane and then preparing samples for counting by volume. (Smith and Talibudeen)

Gamma spectrometer. A Canberra 256 channel multichannel analyser has been installed, coupled to a NaI (Tl) detector in an existing automatic sample changer with a

ROTHAMSTED REPORT FOR 1976, PART 1

50 planchet capacity; samples labelled with gamma emitters can now be assayed. The system is being calibrated for efficiency as a function of photon energy. The detector-analyser combination can be used for all γ -emitters and is being used routinely to check the thyroid of Rothamsted workers who use Iodine-125. (Smith)

Apparatus and technique

The LKB microcalorimeter. The microcalorimeter has been standardised to measure reaction heats in the range 0.5 to 15 000 mJ with a sensitivity range of 0.01–400 mJ per division and with linear response. A device for delivering five μ l volumes of reactant solutions simultaneously to the reaction and reference cells has been designed, constructed and installed in the microcalorimeter using Hamilton syringes. The apparatus is designed for manual or automatic operations and will deliver consecutive volumes at predetermined intervals after the heat evolved at each reaction step has been recorded. This enables experiments to determine the heat of adsorption of a soil or clay over a wide range of K saturation to be completed within 2–3 days without handling the calorimeter chamber. Preliminary runs with Saxmundham soil have given good results. (Talibudeen and Goulding, with Edwards, Minter and Woodcock, Instrument Workshops)

Staff and visiting workers

The present Chemistry and Pedology Departments will be amalgamated in 1977. Professor P. B. Tinker (University of Leeds) has been appointed Head of the joint Department from 1 March 1977. Blanche Benzian retired in March after 35 years on the staff. She will continue to work half-time for a further two years on factors affecting the nitrogen content of cereal grains, supported by a grant from the Home Grown Cereals Authority. A. R. Bromfield continued his work on sulphur cycles in East African agriculture for the Ministry of Overseas Development. J. Bolton was seconded to the Ministry of Overseas Development in December to work in Indonesia on the Trans-Sumatra Highway Development Project. G. A. Rodgers (nitrogen chemistry) and P. C. Brookes (phosphate residues in soils) were appointed and J. B. Butler (leaf protein extraction) was awarded a Wolfson Foundation grant.

The following visitors worked in the department: Dr. F. Cabrera (Spain), Mr. C. T. Figueiredo (Kenya), Mr. A. T. Halm (Ghana), Mr. M. C. Igbokwe (Nigeria), Professor R. N. Joshi (India), Dr. R. Llorca Llorca (Spain), Dr. J. Matula (Czechoslovakia), Professor M. Miyaguchi (Japan), Dr. S. R. Poonia (India), Mr. K. N. Wickramasinghe (Sri Lanka) and Mr. R. Yeadon (Centre for Overseas Pest Research, London). J. E. N. Goggin, Jean Smalley, Jean Sutcliffe and A. Davidson were sandwich course students.

N. W. Pirie was invited by the Organising Committee to take part in an International Cycle of Conferences 'Food: a right of the people' in Madrid and twice visited India, at the invitation of the Indian National Science Academy, to attend the Science Congress in Vizagapatnam, a Nutrition Congress in Patna and visit leaf protein research centres. His attendance at a meeting of the International Union of Biological Sciences in Bangalore was sponsored by the Royal Society. Pirie also attended a meeting of the International Council of Scientific Unions in Washington and, on behalf of ICSU, the meeting of the Advisory Committee on the Application of Science and Technology to Development, in Geneva. In March T. M. Addiscott was invited by Deutsche Forschungsgemeinschaft to give a paper at their workshop on 'Regulation of storage processes in crop plants' at the University of Hohenheim (Stuttgart). J. Bolton visited Telemark, Norway, as UK delegate to an International Conference on 'The effects of acid precipitation' sponsored by the Department of the Environment. G. E. G. Mattingly and A. E. Johnston gave papers at the International Conference on 'Very long-term fertiliser experiments and their

CHEMISTRY DEPARTMENT

results' held in Paris-Grignon in July; the Agricultural Research Council sponsored their visit. G. A. Rodgers attended the Surtsey Biology Group Symposium in Iceland at the invitation of the Swedish Academy of Sciences. In November O. Talibudeen gave a lecture in Buteweg, Hanover, West Germany, at the invitation of Kali und Salz AG. O. Talibudeen, J. Bolton and A. E. Johnston attended the autumn meeting of the British Society of Soil Science in Dublin.

P. C. Brookes was awarded a PhD degree by the National Council for Academic Awards.

Publications

BOOK

- 1 PIRIE, N. W. (1976) *Food resources: conventional and novel*. 2nd Edition. Harmondsworth: Pelican Books, 256 pp.

GENERAL PAPERS

- 2 BENZIAN, B. (1977) Nitrogen in cereal grain (and straw). *Home-Grown Cereals Authority. Progress Reports on Research and Development, 1975-76*, 41-42.
- 3 COOKE, G. W. (1975) Sources of protein for people and livestock; the amount now available and future prospects. *Proceedings of the 11th Colloquium of the International Potash Institute, Bornholm/Denmark, 1975*, pp. 29-51.
- 4 JOHNSTON, A. E. & MATTINGLY, G. E. G. (1977) Experiments on the continuous growth of arable crops at Rothamsted and Woburn Experimental Stations: effects of treatments on crop yields and soil analyses and recent modifications in purpose and design. *Annales Agronomique*, A6, Hors-serie, 117-144.
- 5 MATTINGLY, G. E. G. & JOHNSTON, A. E. (1977) Long-term rotation experiments at Rothamsted and Saxmundham Experimental Stations: the effects of treatments on crop yields and soil analyses and recent modifications in purpose and design. *Annales Agronomique*, A6, Hors-serie, 91-116.
- 6 PIRIE, N. W. (1976) The production, quality and use of leaf protein. *Proceedings of the All India Seminar on Nutrition*. Rajendra Memorial Research Institute, Patna, pp. 19-26.
- 7 PIRIE, N. W. (1977) Physical limitations on the food supply. *Proceedings of the British Nutrition Foundation Conference, April 1976*, 157-165.
- 8 PIRIE, N. W. (1977) Restoring esteem for leafy vegetables. *Appropriate Technology* 3, 24-25.
- 9 PIRIE, N. W. (1976) New foods. *Medicine* 17, 826-828.
- 10 PIRIE, N. W. (1976) Food protein sources. *Philosophical Transactions of the Royal Society (B)* 274, 489-498.
- 11 THURSTON, J. M., WILLIAMS, E. D. & JOHNSTON, A. E. (1977) Modern developments in an experiment on permanent grassland started in 1856: effects of fertilisers and lime on botanical composition and crop and soil analyses. *Annales Agronomique*, A6, Hors-serie, 13-46.

PAPERS IN ROTHAMSTED REPORT, PART 2

- 12 JENKINSON, D. S. & JOHNSTON, A. E. (1977) Soil organic matter in the Hoosfield Continuous Barley experiment. *Rothamsted Experimental Station. Report for 1976, Part 2*, 87-101.

ROTHAMSTED REPORT FOR 1976, PART 1

- 13 JOHNSTON, A. E. & POULTON, P. R. (1977) Yields on the Exhaustion Land and changes in the NPK content of the soils due to cropping and manuring, 1852-1975. *Rothamsted Experimental Station. Report for 1976, Part 2*, 53-85.

RESEARCH PAPERS

- 14 ADDISCOTT, T. M. & COX, D. (1976) Winter leaching of nitrate from autumn-applied calcium nitrate, ammonium sulphate, urea and sulphur-coated urea in bare soil. *Journal of Agricultural Science, Cambridge* **87**, 381-389.
- 15 BOLTON, J., NOWAKOWSKI, T. Z. & LAZARUS, W. (1976) Sulphur-nitrogen interaction effects on the yield and composition of the protein-N, non-protein-N and soluble carbohydrates in perennial ryegrass. *Journal of the Science of Food and Agriculture* **27**, 553-560.
- 16 CABRERA, F. & TALIBUDEEN, P. (1977) Effect of soil pH and organic matter on labile aluminium in soils under permanent grass. *Journal of Soil Sciences* **28**, 259-270.
- 17 CARRUTHERS, I. B. & PIRIE, N. W. (1976) Mechanical dehydration of potato tubers. *Experimental Agriculture* **12**, 329-335.
- 18 COX, D. & ADDISCOTT, T. M. (1976) Sulphur-coated urea as a fertiliser for potatoes. *Journal of the Science of Food and Agriculture* **27**, 1015-1020.
- 19 GASSER, J. K. R. & KALEMBASA, S. J. (1976) Soil nitrogen. IX. The effect of leys and organic manures on the available-N in clay and sandy soils. *Journal of Soil Science* **27**, 237-249.
- 20 HOLFORD, I. C. R. (1976) Effects of phosphate buffer capacity of soil on the phosphate requirements of plants. *Plant and Soil* **45**, 433-444.
- 21 HOLFORD, I. C. R. & MATTINGLY, G. E. G. (1976) A model for the behaviour of labile phosphate in soil. *Plant and Soil* **44**, 219-229.
- 22 HOLFORD, I. C. R. & MATTINGLY, G. E. G. (1976) Phosphate adsorption and plant availability of phosphate. *Plant and Soil* **44**, 377-389.
- 23 LACEY, J. & PIRIE, N. W. (1976) Chemical preservation of partially dried potato pulp. *Experimental Agriculture* **12**, 337-340.
- 24 LIM, T. S. & TALIBUDEEN, O. (1977) Effect of aluminium on the growth and mineral composition of some tropical legumes in a glasshouse investigation. *Proceedings of the 3rd ASEAN Soil Conference, Kuala Lumpur 1975, Session IV—Soil Fertility (Annual Crops) Paper 6*.
- 25 PENNY, A., WIDDOWSON, F. V. & ASHWORTH, J. (1977) Results from an experiment on permanent grass evaluating aqueous ammonia and aqueous urea injected in bands either 30 or 60 cm apart. *Journal of Agricultural Science, Cambridge* **88**, 319-331.
- 26 PIRIE, N. W. (1977) A simple unit for extracting leaf protein in bulk. *Experimental Agriculture* **13**, 113-118.
- 27 POONIA, S. R. & TALIBUDEEN, O. (1977) Sodium-calcium exchange equilibria in salt-affected and normal soils. *Journal of Soil Science* **28**, 276-288.
- 28 TALIBUDEEN, O., PAGE, M. B. & MITCHELL, J. D. D. (1976) The interaction of nitrogen and potassium nutrition on dry matter and nitrogen yields of the graminiae: perennial ryegrass (*Lolium perenne*). *Journal of the Science of Food and Agriculture* **27**, 999-1004.
- 29 TALIBUDEEN, O., PAGE, M. B. & NAIR, P. K. R. (1977) The interaction of N and K nutrition on dry matter and N yields of the graminiae: spring wheat. *Journal of the Science of Food and Agriculture* **27**, 1179-1189.

CHEMISTRY DEPARTMENT

- 30 WIDDOWSON, F. V. & PENNY, A. (1977) Results from two sets of experiments with spring barley, the first comparing injected with broadcast nitrogen granules, the second comparing injected and combine-drilled NPK solutions with broadcast NPK granules. *Journal of Agricultural Science, Cambridge* **88**, 35-45.