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Soils and Plant Nutrition Department

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Introduction

Various administrative changes were made during the year, which flowed from the amalgamation of the two original departments described in *Rothamsted Report for 1977*. The most important was the re-structuring of the Department, with two organisational Senior Principal Scientific Officers within the Department to supervise defined groups of projects. One of these posts has been filled already. The planned redeployment of effort has progressed with the filling of one more vacancy with staff who will work on soil/root relationships, which is an ARC priority topic.

As in previous years, much of our total effort has been devoted to nitrogen in soils and fertilisers. Work to determine the efficiency and usefulness of nitrification inhibitors in practice has been extended, in collaboration with ADAS, to wetter areas of the country where leaching losses are more serious. More attention is being given to basic work, and several xanthates and their derivatives have been tested as inhibitors, because they release CS₂ more slowly than the trithiocarbonates, and are likely to be cheaper. It is interesting that these compounds also inhibit urea hydrolysis in soil. Because nitrification inhibitors give us a degree of control over the ratio of ammonium to nitrate N offered to crops, some work on the physiological responses of grass to these two forms of N has been started. These responses have often been shown to differ greatly in controlled conditions, but the differences have usually not been seen in field work.

Organic phosphorus is sometimes ignored in considering crop nutrition, but results from Rothamsted and Saxmundham show that mineralisation in long-term arable cropping can yield up to one-third of normal P offtake in crops. In a pot experiment, evidence has been found that part of the error in using soil analysis to predict P requirement could result from different levels of mycorrhizal inoculum in soil. These lines, with planned work on short-term cycling of P in the biomass, will give a stronger biological orientation to our phosphorus studies.

Work on drainage, leaching models and ion diffusion has been brought together as different aspects of the movement of solutes in soil. Our collaboration with the Water Research Centre, who have made test borings into the underlying chalk, has given us a better insight into subsoil conditions, and may provide a tool for determining long-term nitrate leaching losses from our fields. Ion diffusion work, which has just started, is aimed at understanding ion movement to plants in the field, whereas almost all previous work has been done in more or less artificial conditions.

The work reported on soil organic matter challenges the very widespread assumption that cultivation always leads to a major loss of organic matter from soil. Over periods of up to 8 years, little or no difference in total topsoil organic matter or biomass could be detected between ploughed and direct drilled soil in three separate experiments; the biomass measurements should be an especially sensitive indicator of relative accumulation or loss. An important factor in this work is that comparisons are between strictly equal weights, rather than depths, of soil. Similar work will be done on other relevant field experiments.

The fundamental mechanisms underlying structure formation are still not understood. Work done as part of the Rothamsted Soil Structure Working Group programme has given new evidence that the dimensional stability of pore size in the range 0.2–30 μm is correlated with the shrinkage and final structure of clay on drying. The new mercury porosimeter will be of great value for this work.

A variety of work on mineralogy is reported, including an interesting application of X-ray techniques to the effects of pre-treatment on the availability of magnesite for the sugar-beet crop. The observation that weak X-ray emissions occur at energies lower than that of the K_α line for a range of elements in the X-ray fluorescence spectrometer is potentially important. The mechanism of their production has been explained, and they

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appear to be unusually sensitive to the chemical environment of the emitting atoms, hence this may be a useful tool in structure determination. The structure of the synthetic clay minerals produced by Professor Velde in Paris have now been determined, and the effects of the different potassium abundances on structure have been explained.

Studies on the chalky boulder clay soils discussed here indicate some relationship between soil age and degree of weathering, and the capability of the soil for cropping. The relationship of soil profile and composition properties to yield variation is currently a matter of great interest, and several other lines of work, not reported here, are being developed.

Investigation on nitrogen

Nitrification inhibitors

Aqueous N fertilisers and nitrification inhibitors for grass. Work at Rothamsted and Woburn on injecting nitrification inhibitors with aqueous N for grass (*Rothamsted Report for 1977*, Part 1, 276) was extended to Liscombe EHF (West Somerset), which is in a region of high winter rainfall (with high risk of loss of N applied in autumn) and small summer soil-moisture deficit (allowing prolonged uptake of N injected in spring). Both winter 1977/78 and summer 1978 were wet (rainfall December–April, 660 mm; May–September, 375 mm).

Aqueous urea (375 kg N ha^{-1}) was injected in November 1977 or April 1978 into pasture on a silty clay loam (High Week series), in bands either 30 or 60 cm apart, alone or with 'N-Serve' (nitrapyrin) or with sodium trithiocarbonate (STC). About half the N injected in November had been nitrified by the end of February. On 25 April, when growth had just begun, 5% of the N injected at 30 cm spacing remained as $\text{NH}_4\text{-N}$ without inhibitors, but 10% with either inhibitor; at 60 cm spacing, these quantities were 10 and 25% respectively. Both inhibitors increased yields and N uptake when injected in November, and although they depressed early growth when injected in April, greater growth later partly compensated, which is a desirable effect if grass is to be grazed (Table 1). Increasing the band spacing to 60 cm tended to produce similar effects to adding inhibitors, probably because of the greater amounts of ammonia injected per unit length of slit. Greatest inhibition was therefore found with wide spacing combined with inhibitors. However, broadcasting 'Nitro-Chalk' in three equal applications for the three cuts gave appreciably more grass, though no greater N uptake, than one application of injected N. (Ashworth, Gibbs, Hewitt, Penny and Widdowson, with ADAS South-West Region)

Aqueous N fertiliser and nitrification inhibitors for direct-drilled winter wheat. Field experiments at Rothamsted and Hexton, Herts compared broadcasting all N as 'Nitro-Chalk' in spring with aqueous urea or aqueous ammonia injected either in October, before sowing, or in late March, without or with either sodium trithiocarbonate (STC) 'N-Serve' (nitrapyrin) as nitrification inhibitors. The experiments also tested injecting part of the N with either inhibitor in autumn and broadcasting the remainder as 'Nitro-Chalk' in spring. At Rothamsted each plot was split to test conventional sowing versus direct drilling; at Hexton, all the wheat was direct drilled.

Analyses of soil samples taken after autumn injection at Rothamsted showed that the injected band of N was smaller in cross-section, and much nearer the soil surface, on direct-drilled than on cultivated soil, presumably due to the effects of soil compaction on knife penetration and mobility of ammonia. $\text{NH}_4\text{-N}$ in the injected band persisted longer in direct-drilled soil, but the nitrification inhibitors were no more effective than in cultivated soil. STC was markedly more effective when applied with urea, rather than NH_3 , perhaps because NH_3 increases decomposition of STC to CS_2 , thereby impairing inhibi-

TABLE 1

Dry grass yield ($t\ ha^{-1}$) and N uptake ($kg\ ha^{-1}$) at Liscombe EHF

	375 kg urea N ha^{-1} in November				375 kg urea N ha^{-1} in April				SED	'Nitro-Chalk' N $kg\ ha^{-1}$			
	at 30 cm		at 60 cm		at 30 cm		at 60 cm			0	375	SED	
	alone	+ inhib*	alone	+ inhib*	alone	+ inhib†	alone	+ inhib†					
Dry weight ($t\ ha^{-1}$)	1st Cut	4.3	4.9	4.4	4.7	4.9	4.5	4.1	3.8	± 0.17	2.5	5.6	± 0.34
	Total of 3 cuts	8.3	9.1	8.5	9.1	10.0	9.9	9.7	9.5	± 0.24	4.7	11.3	± 0.27
N uptake‡ ($kg\ ha^{-1}$)		96	116	100	113	154	144	109	106	± 6.2	40	141	± 4.1

Rates of inhibitor ($kg\ ha^{-1}$) at 30 cm spacing

* Nitrapyrin, 1.5; STC, 30 } results with both inhibitors averaged.

† Nitrapyrin, 1.0; STC, 20 }
(at 60 cm spacing, rates were half the above).

‡ These data apply to first cut.

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tion, and perhaps also because STC slightly inhibits urea hydrolysis (see page 280). By the end of November all $\text{NH}_4\text{-N}$ was nitrified in the absence of inhibitor, and by mid-January only about 20% of the injected N remained as $\text{NH}_4\text{-N}$ with nitrapyrin, and none with STC. At Hexton, nitrification was faster and the inhibitors (particularly STC) even less effective than at Rothamsted.

At Rothamsted there was no consistent effect of the inhibitors on $\text{NO}_3\text{-N}$ or % total N in plants sampled in January and February, nor on % total N in plants taken in May and June from plots injected in spring.

Nitrapyrin increased the response to autumn-injected N by about 1 t ha^{-1} , but yield was still about 1 t ha^{-1} less than from spring injection without inhibitor; STC was much less effective (Table 2). Inhibitors did not improve the efficiency of spring-injected N, and at Rothamsted the effects of inhibitors did not differ consistently with method of sowing. Aqueous urea was slightly better (0.18 t ha^{-1}) than aqueous ammonia. Injecting part of the N dressing in autumn and then broadcasting the remainder in spring was much superior to injecting it all in autumn, but had no benefit over injecting it all in spring. On average, 100 kg N ha^{-1} injected in spring was equivalent to 85 kg N ha^{-1} broadcast, in contrast to 1977 when they were equally effective (*Rothamsted Report for 1971*, Part 1, 278-9). At Rothamsted, yields from direct drilling were larger than from conventional sowing, the two methods giving 5.98 and 5.70 t ha^{-1} respectively. (Widdowson, Ashworth, Penny, Hewitt and Gibbs)

TABLE 2

Mean yields of wheat grain from two experiments, t ha^{-1} , at 85% dry matter in 1978

(Averages with 80 and 120 kg N ha^{-1} , and with urea and ammonia)

Aqueous N injected	Inhibitor		
	None	STC	'N-Serve'
In autumn	4.40	4.63	5.44
In spring	6.50	6.49	6.45

Lysimeter experiments with nitrification inhibitors. Aqueous urea was injected by pipette in November 1977, either alone or with nitrapyrin or STC to pairs of outdoor lysimeters at Aberystwyth and Newcastle; and KNO_3 solution was applied to the surface of another pair of lysimeters, all at 400 kg N ha^{-1} . These tests attempted to simulate the effects of inhibitors normally injected in the field and similar concentrations would occur in treated soil in the lysimeter as in a band.

Mean amounts of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (corrected for native mineral N, and expressed

TABLE 3

Percentage applied N recovered in leachate or remaining in lysimeters

		Treatment			
		KNO_3	urea	urea + nitrapyrin	urea + STC
Aberystwyth (600 mm)*	Leachate in lysimeter	106 0	89 4	66 18	42 30
	Total	106	93	84	72
	Newcastle (370 mm)*	Leachate in lysimeter	81 0	65 51	37 38
	Total	81	116	75	93

* Rainfall between dates of treatment and dismantling

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as a percentage of the N applied) in the leachate during November 1977–May 1978, or remaining in soil when the lysimeters were dismantled in June 1978, are shown in Table 3. At both sites inhibitors suppressed leaching losses, but total recoveries varied. (Ashworth, with Dr. K. Shaw, ADAS, Newcastle, and Mr. E. Jones, ADAS, Aberystwyth)

Effects of NH_4 - and NO_3 -N on ryegrass yields. In grassland experiments, nitrification inhibitors injected with NH_3 or urea in spring have increased yields slightly in 4 successive years at Rothamsted, but have tended to depress yields at Woburn. These results seem unlikely to be due to inhibitors preventing leaching, because this is more likely on the sandy soil at Woburn. To test the direct effects of forms of N on growth, pots of soil from the fields used for the grassland trials were sown to ryegrass (S.23) after adding NH_4 -N, NO_3 -N, or a 2:1 combination of both, either alone or with CS_2 or a combination of CS_2 and nitrapyrin. Pots were kept in Saxcil cabinets under routine conditions and the grass cut after 3, 7 and 12 weeks.

Measurement of nitrate and ammonium in soil samples taken from similar pots without grass showed that nitrification of NH_4 -N was normally rapid, but completely inhibited where CS_2 and nitrapyrin was used; CS_2 alone was temporarily effective.

On both soils, yields at cut 1 from pots given NO_3 -N were less (due to a slight salt effect on germination), but after three cuts much more, than yields from pots given NH_4 -N or NH_4 - and NO_3 -N, which produced similar amounts. The inhibitors affected yields but not % N in grass from all forms of N supplied. On Woburn soil early detrimental effects were reversed by final harvest—this effect has been observed in the field, at Rothamsted, but not Woburn. The effects observed were unexpected and require further investigation. (Ashworth)

Xanthates as inhibitors of fertiliser N transformations. The most successful of the patented nitrification inhibitors, nitrapyrin, is still expensive and has found only modest commercial application. Although CS_2 is a cheaper alternative, it is flammable and toxic; and it also evaporates rapidly from injected soil. STC, which when applied to soil breaks down almost immediately to CS_2 , is safer to handle but is again expensive because of the high application rate needed.

Prolonged exposure of nitrifiers to low concentrations of CS_2 is much more inhibitory than brief exposure to high concentrations. Potassium ethyl xanthate (KEtX) breaks down in soil to CS_2 much more slowly than STC. Whereas 150 mg CS_2 kg^{-1} of Batcombe soil inhibited nitrification in glasshouse pots for less than a week, KEtX containing the same theoretical amount of CS_2 was completely effective for 6 weeks. STC normally inhibits nitrification for the same time as the equivalent quantity of CS_2 . Early ryegrass growth was retarded by KEtX, but mean ryegrass yields per pot after 7 weeks were not significantly different from those of pots without inhibitor.

The analytical procedure devised for STC (Ashworth, Briggs, Evans & Matula, *Journal of the Science of Food and Agriculture* (1977), **28**, 673) has been adapted to study the breakdown of xanthates. KEtX in Batcombe soil evolved only 20% of its theoretical CS_2 content after 4 days, and 30% after 40 days. In gas chromatography of soil air, sampled after adding KEtX, CS_2 (the major product), H_2S and an unidentified minor product were detected.

In incubation tests KEtX, cellulose xanthate and, to a lesser degree, STC were found also to inhibit urea hydrolysis. KEtX at 100 mg kg^{-1} soil was nearly as effective as 50 mg kg^{-1} hydroquinone, a powerful urease inhibitor. In separate tests CS_2 itself had no effect on urea hydrolysis. Preliminary results suggest, however, that under field conditions KEtX would only have a slight advantage over STC in urease inhibition.

In the solid state KEtX is much more stable than STC and could possibly be incor-

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porated in granular fertilisers. If injected with fertiliser N into soil, the phytotoxicity of KEtX is unlikely to be significant. Cellulose xanthate may be a cheaper alternative to KEtX, but its composition is variable and it is relatively unstable in solution. (Ashworth, Rodgers, Messer and Mitchell, with Briggs, Chemical Liaison Unit)

Neem oil, cake and kernel materials tested by the Plant Pathology Department were also tested for urease inhibition and nitrification inhibition, but were completely ineffective even at the rate of 1 g material kg⁻¹ soil; this conflicts with claims by workers in India. (Ashworth)

The effects of times and amounts of nitrogen and of fungicides on spring barley at Saxmundham. Part of the large variations in yield in 1967-71 were believed to be caused by changing incidence of leaf diseases, particularly brown rust (*Puccinia hordei*). Spring barley experiments begun in 1973, with the Plant Pathology Department, showed that the rust fungicide benodanil increased yields more with high than low rates, and more with late than with early applications of N (*Rothamsted Report for 1974*, Part 1, 79-80). Because we knew little of the interactions between N and barley mildew (*Erysiphe graminis*), the experiments were expanded to test both mildew and rust fungicides, together with late sprays of liquid N (ammonium nitrate/urea). Two barley varieties (Julia and Wing), with or without a mildew fungicide (ethirimol) seed dressing, were given seedbed or top-dressed N, at either 50 or 100 kg N ha⁻¹. Plots sown with ethirimol-treated seed were also sprayed with tridemorph. Sprays of liquid N and of benodanil were each applied on two occasions in June-July.

TABLE 4a

Mildew and brown rust (% area of 2nd youngest leaves at G.S. 73-85) on two spring barley cultivars grown at Saxmundham in 1975-78*

	Mildew†		Brown rust‡	
	Julia	Wing	Julia	Wing
1975	17.9	26.1	9.1	12.1
1976	12.8	13.2	8.7	7.2
1977	7.1	9.7	4.8	6.4
1978	3.9	5.9	2.2	3.8

* Zadoks, Chang and Konzak (1974) *Weed Research* 14, 415-421.

† Average amounts of mildew in plots without ethirimol and tridemorph.

‡ Average amounts of brown rust in plots without benodanil.

TABLE 4b

Mean yields, ranges and effects of variety and nitrogen (amount and timing) and mildew and rust fungicides at Saxmundham 1975-78 (t ha⁻¹ of grain at 85% dry matter)

Year	Average	Range	Variety (W-J)	SN Rate (100-50)	SN Time (E-L)	LN Rate (50-0)	Mildew fungicide (ET-O)	Rust fungicide (B-O)
1975	3.61	2.27-4.88	0.24	0.30	0.56	0.22	0.26	0.16
1976	3.43	2.34-5.17	0.16	0.03	0.06	0.28	-0.16	0.09
1977	4.46	3.26-5.91	0.03	0.77	0.74	0.13	0.25	0.23
1978	5.30	4.39-6.23	-0.04	-0.09	0.67	-0.20	0.14	0.37
Mean	4.20		0.10	0.25	0.51	0.11	0.12	0.21

SN = Solid N
 LN = Liquid N
 J = Julia
 W = Wing
 E = N to seedbed
 L = N top-dressed
 ET = Ethirimol dressing and tridemorph spray
 B = 2 sprays of benodanil
 50 } = kg N ha⁻¹
 100 }

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Both mildew and brown rust were usually more severe on Wing than on Julia and were more severe in 1975 and 1976 than in 1977 and 1978 (Table 4a). Table 4b shows that yields were small in the dry 1975 and 1976 summers but average in later years. Wing lost its superiority with time. Doubling the N given from 50 to 100 kg ha⁻¹ had different effects in different years, but it was always more beneficial when given at sowing instead of as a top-dressing. Late sprays of liquid N increased yields until 1978, when severe lodging occurred, but less than the same amount of seedbed N did. Mildew fungicides increased yields in 3 years, but diminished them under the drought conditions of 1976. By contrast benodanil always increased yields, and more in the moist 1977 and 1978 summers than in the two dry ones, even though rust in 1978 was apparently less severe than in any of the previous 3 years. Its mean benefit was almost double that of the mildew fungicides with a maximum yield response (in 1978) of 0.49 t ha⁻¹ with the variety Wing. An application of 100 kg N ha⁻¹ consistently gave a larger yield than 50 kg N ha⁻¹ only when (a) it was applied to the seedbed and (b) fungicides were also given. Mean increases from the fungicides were 0.14 t grain ha⁻¹ with 50 kg N ha⁻¹ and 0.19 t ha⁻¹ with 100 kg N ha⁻¹. (Widdowson and Penny, with Jenkyn, Plant Pathology Department)

Yield and grain composition in relation to fertilisers

Relationship of yield and % N in grain to fertiliser N rate. The shapes of fertiliser N response curves for winter-wheat yield and % N in grain in experiments done between 1955 and 1973 (*Rothamsted Reports for 1976*, Part 1, 85-86 and *for 1977*, Part 1, 282) were compared on 43 winter-wheat experiments with 4, 5 or 6 levels of fertiliser nitrogen. Just less than half the 163 yield response curves had a positive linear or curvilinear relationship with applied fertiliser N up to about 175 kg N ha⁻¹, without any decline in yield even at the highest rates of application. The rest of the curves had either a negative linear relationship throughout, or—the majority—showed a decline with the larger amounts of applied N. Almost all the response curves for %N in grain continued to rise—almost 75% linearly if 'dilution effects' at the lowest rate of N application are ignored. Percentage changes for responses between 100 and 150 kg N ha⁻¹ in Table 5 illustrate this contrast between %N in grain and yield. (Benzian, with Lane, Statistics Department)

TABLE 5
Differences in yield and % N of grain caused by increasing fertiliser nitrogen from 100 to 150 kg N ha⁻¹ in 129 response curves

Percentage changes between 100 and 150 kg N ha ⁻¹ of fertiliser nitrogen	Number of values	
	Yield	%N in grain
≥ 15.0	7	12
14.9 to 5.0	34	92
4.9 to -5.0	54	25
-5.1 to -15.0	32	0
≤ -15.0	2	0

Effect of manuring on the amino-acid composition of barley grain. Investigations of the effects of various manurial treatments on the protein content and amino-acid composition of barley grain (cv. Julia) were concluded using samples taken in 1977 from three plots of the Hoosfield Continuous Barley experiment, each of which had been subdivided to test four rates of nitrogen. The protein content of the grain was least on plots given PKNaMg fertilisers, intermediate on the unmanured plot and largest on the plot given farmyard manure (FYM) annually. On the unmanured soil and on the soil given fertilisers, protein in grain was slightly decreased by the smallest amount of N (48 kg N ha⁻¹) applied but was increased at the higher rates (96 and 144 kg N ha⁻¹) in agree-

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ment with the results summarised above. On the FYM treated soil, %N in grain increased with each addition of N fertiliser.

As in previous work (*Rothamsted Report for 1975*, Part 1, 90) the amino acid composition of Julia barley grain was little affected by either PKNaMg fertilisers or by FYM despite large differences in yield. The relative amounts of glutamic acid and proline were slightly smaller in grain grown without fertilisers or with PKNaMg fertilisers than with FYM and the lysine content was lowest in grain from FYM treated plots. (Lazarus and Johnston)

Investigations on phosphorus

Changes in soil organic phosphorus

Organic phosphorus in Rothamsted and Saxmundham soils. Long-term changes in total organic P, estimated as the mean of values by ignition and extraction methods of analysis (*Rothamsted Report for 1974*, Part 2, 61), were measured on stored samples from experiments at Rothamsted and Saxmundham as part of a programme to investigate the rate of release of non-labile P from soils. All samples were also analysed for total C and N.

Air-dry soil samples (0–22.5 cm), taken in 1961, 1967 and 1975/76, were used to compare the rates of mineralisation of organic P in an old Rothamsted arable soil (Sawyers) and in a soil (Great Field) ploughed out of permanent grass in 1956. Results where P was applied annually or every 6 years were very similar and values from the two treatments have been averaged (Table 6).

TABLE 6
Organic P contents of old arable (Sawyers) and grassland (Great Field) soils at Rothamsted, 1961–1975/76

Field	Treatment*	Organic P (mg P kg ⁻¹ soil)		
		1961	1967	1975/76
Sawyers (old arable)	No phosphate	226	218	206
	Added P	222	216	210
Great Field (ploughed from grass)	No phosphate	306	289	266
	Added P	306	281	273

* For details, see *Rothamsted Report for 1969*, Part 1, 53.

Organic P decreased by 12–20 mg P kg⁻¹ soil between 1961 and 1975/76 on the old arable soil and by 33–40 mg P kg⁻¹ soil on the old grassland soil. The C:N ratio did not decrease between 1961–1975/76 on the old arable soils and decreased only slightly (from 9.8 to 9.4) on the old grassland soils. The N:organic P ratio decreased more (from 8.5 to 7.2 on the old grassland soils and from 7.0 to 6.4 on arable soils), hence mineralisation of soil organic C and N was faster than that of soil organic P.

TABLE 7
Organic P contents of arable soils from Saxmundham (Rotation II)

Treatment	Manuring* 1899–1964	Amount of P applied, 1965–67 (kg P ha ⁻¹)	Organic P (mg P kg ⁻¹ soil)		
			1968	1973/74	1977/78
1	None	0	146	127	134
2	FYM	0	151	134	138
4	FYM + P	230	169	145	146
8	FYM + 2P	0	162	149	150

* For details, see *Rothamsted Report for 1969*, Part 2, 91.

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Organic P contents were measured on Saxmundham soil samples (0–25 cm) taken in 1968, 1973/74 and 1977/78 from four treatments tested in the Rotation II experiment at Saxmundham which has been in arable cropping (potatoes, sugar beet and barley) for the past 10 years. Results in Table 7 are means of sub-plots with and without fresh P, applied as superphosphate, since 1969.

Organic P decreased by 13–24 mg P kg⁻¹ soil during the first 5–6 years but changed negligibly during the following 3–4 years. The largest decrease was on treatment 4 which had received 230 kg P ha⁻¹ as farmyard manure (FYM) in 1965–66 and the smallest decrease was on treatment 8, last given FYM in 1952.

Annual rates of mineralisation of organic P. Weights of stone-free soil are about 3.0 Mkg ha⁻¹ for Rothamsted soils (0–22.5 cm) and 3.5 Mkg ha⁻¹ for Saxmundham (0–25 cm) soils. Using these figures, average annual rates of mineralisation of organic P (kg P ha⁻¹ year⁻¹) are Sawyers (arable) 3.2; Great Field (ploughed from grass in 1956) 7.8 and Saxmundham (arable; some FYM applied) 5.5. Rates of mineralisation are larger than those previously measured on arable soils at Woburn (*Rothamsted Report for 1974*, Part 2, 61) which ranged from 1.5–3.5 kg P ha⁻¹, and represent about one-third of average P removals by cropping. In preparing balance sheets to assess the amounts and forms of phosphate remaining as residues in soils the contribution of organic P appears greater, in some soils, than has previously been assumed. (Chater and Mattingly)

Mycorrhizal effects on the interpretation of soil analyses for phosphorus. Vesicular-arbuscular (V.A.) mycorrhiza can increase the efficiency with which their host plants take up soil phosphorus. This suggests that the extent and type of infection could influence the predictive value of chemical methods used to assess soil P available to plants.

This idea was tested in a glasshouse pot experiment in which the shoot yields of leek plants grown on eight Rothamsted soils ranging in initial NaHCO₃-soluble P from 2 mg kg⁻¹ to 93 mg kg⁻¹ were recorded after 10 weeks. Each soil had one of three treatments; (i) plants on untreated soil allowed to become mycorrhizal by natural infection; (ii) plants infected with spores of a yellow-vacuolate V.A. endophyte (*Glomus mosseae*) on gamma-irradiated soil (0.8 Mrad); (iii) non-mycorrhizal plants on irradiated soil. Response curves for P were obtained for each soil/treatment combination by adding five levels of phosphate from 25 mg P kg⁻¹ of soil to 125 mg kg⁻¹ together with a basal nutrient mixture. The NaHCO₃-soluble P in the soils was determined 5 days after P addition.

Inoculated and uninfected treatments each gave smooth response curves when yield data from all P levels on all soils were plotted against soil NaHCO₃-soluble P content. The same maximum yields and P uptakes were found with both uninfected and artificially infected plants, which occurred at 90 mg kg⁻¹ NaHCO₃-soluble P for the former, but at 50 mg kg⁻¹ for the latter. In contrast, naturally infected plants gave no clearly defined single response curve to soil P, and similar levels of NaHCO₃-soluble P gave widely different yields on different soils, particularly with the Barnfield soils.

These variations in the predictive value of NaHCO₃-soluble P were reflected by differences in the extent of mycorrhizal infections. Plants infected with *G. mosseae* showed a progressive decline in percentage root length infected from 80% at the lowest soil P to 22% at the highest. Levels of natural infection were generally more random and lower, and may have involved more than one species of endophyte. The Barnfield soil gave low infections, with few and degenerate arbuscules.

Future work will test these ideas in field experiments. (Stribley, Tinker and Snellgrove)

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Investigations on potassium

Potassium and calcium equilibria in Saxmundham soil. Potassium-calcium exchange equilibria were investigated on whole soils from the Nil and PK plots of the Saxmundham Rotation I experiment, and the Ca, Ca + K and K forms of fine and coarse clay and silt fractions of the Nil plot soil. Free energy values (Deist & Talibudeen, *Journal of Soil Science* (1967), **18**, 138–148) and enthalpy values (Talibudeen *et al.*, *Laboratory Practice* (1977), **26**, 952–955), showed that K was preferred to Ca by all the solids, but less so with increasing particle size and % K saturation of the CEC (Table 8). A comparison of the 'differential enthalpy of exchange: % K saturation' relationship for the whole soil with those of its particle size fractions (alone or in mixtures), suggested that sites with highest K selectivity are altered to give a lower selectivity for K by soil dispersion during particle size separation. We attribute this to the destruction of 'frayed' edges (where high K selectivity sites occur) and rearrangement of the spatial position of exchangeable cations. The mineralogical composition of the soil separates and the differential enthalpy data suggested that maximum selectivity for K was associated with a vermiculite/smectite component of interstratified minerals, and that the decrease in K selectivity on K treatment was an irreversible, or very slowly reversible, process occurring in the interlayer space in this component. These results from equilibrium studies confirm previous conclusions based on K release to ion-exchange resins (*Rothamsted Report for 1976*, Part 1, 95–96).

TABLE 8

Standard free energies and enthalpies of Ca→K exchange on soils from the Nil and PK treatments of the Saxmundham experiment, Rotation I, and their fractions

	<0.2 μm		0.2–2 μm		2–20 μm		whole soil	
	Ca	Ca + K	Ca	Ca + K	Ca	Ca + K	Nil	PK
ΔG_0 (kJ equiv. ⁻¹)	-10.40	-9.49	-8.24	-7.20	-7.62	-6.03	-9.65	-8.22
ΔH_0 (kJ equiv. ⁻¹)	-8.5	—	-6.0	—	-2.0	—	-7.0	—

The total isotopically exchangeable Ca, measured using ⁴⁵Ca before and after CaCO₃ removal by acid washing, showed that, in the untreated solids, most of the isotopically exchangeable Ca could be attributed to the CaCO₃ fraction. The high specific surface area thus calculated, in relation to the mean particle diameter, suggests that the CaCO₃ particles are extremely porous, more so in the coarser fractions. Also, isotopic exchange on the decalcified solids showed that, for the Ca + K forms of the fine and coarse clay fractions, exchange was instantaneous but that for the Ca forms the rate of exchange was measurable. We attribute this to traces of blocking materials (CaCO₃ or hydroxy-aluminium polymers) remaining in the Ca forms. These would be removed during treatment with the KCl solution, so that isotopic exchange with Ca was then much more rapid. (Goulding and Talibudeen)

Critical potassium potentials for crop growth. This work investigates the concept that the nature of the yield response of plants to the chemical potential of a nutrient in the growth medium in controlled environments is a characteristic of the crop.

Perennial ryegrass was grown on Delharding soil (Batcombe series), adjusted to 16 K levels, in controlled environment cabinets under two light intensities. Cuts were taken 4, 8 and 12 weeks after germination. Soil K potentials, $\Delta G_{K, Ca} = RT \ln(a_K/a_{Ca+Mg})$, were determined for each treatment before germination and after each cut. Curves were fitted to the cumulative yield and mean K potential data using the Mitscherlich equation. From these, K potential values were derived which (a) gave 99% of the maximum yield

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predicted by the curve ($\Delta G_{\text{optimum}}$), and (b) would give zero yield ($\Delta G_{\text{exhaustion}}$) (Talibudeen & Page, *FAO Bulletin* No. 37 (1977), 88–99). The critical potentials thus obtained were ΔG_{opt} -2080 and -2430 ; ΔG_{exh} -5200 and -5090 cal mol⁻¹ under 800 and 1600 lumens respectively.

Potassium uptake at each cut was linearly related to soil exchangeable K and sigmoidally to $\Delta G_{\text{K, Ca}}$. For the same 'quantity' or 'potential' level of soil K, uptake under the two light intensities was the same.

Potassium potentials were determined in three soils (Batcombe, Newport and Andover series) before, during and after cropping with spring wheat (variety Highbury) in the glasshouse. ΔG_{exh} values for grain yield derived from the curves were -5600 , -5230 and -4850 , and ΔG_{opt} , -4080 , -3321 and -3510 cal mol⁻¹ for the Andover, Batcombe and Newport soils respectively. The exhaustion and optimum potentials corresponded approximately to 0.55 and 2.2 % K saturation of the CEC respectively on the three soils. (Page, Talibudeen and Parker)

Potassium release. A visiting Romanian worker started an investigation of the cation exchange properties of a zeolite being used in Romania as an amendment for sandy soils. X-ray examination showed the material to consist mainly of a zeolite closely similar to the clinoptilolite-heulandite zeolites identified in certain soils in southern England and implicated in potassium release, and it proved possible by density and size separations to concentrate an almost monomineralic zeolite component. The framework composition is $\text{Si}_{28.8}\text{Al}_{7.2}\text{O}_{72}$ and the channel cations are $\text{Ca}_{1.7}\text{Mg}_{0.4}\text{Na}_{0.15}\text{K}_{1.56}$; unit cell dimensions, based on 16 reflections resolved in the X-ray powder pattern are, $a = 1.769$ nm, $b = 1.794$ nm, $c = 0.741$ nm, $\beta = 116.28^\circ$. This zeolite can be described as a Si-poor clinoptilolite-Ca.

The purity of this sample allowed an accurate study of its cation exchange properties, which are difficult to determine with certainty in the mixed samples usually concentrated from soils, and these proved to be peculiar, though not untypical of zeolites. Early experiments showed that the amount of K exchanged by CaCl_2 was comparable with that obtained from a hydrobiotite or a reactive biotite, and about 100 times the level from most soil clays. However, these experiments were not done at equilibrium, and rate experiments have shown that equilibrium is difficult to achieve. Potassium concentration in CaCl_2 suspension increased steadily with time up to at least 20 days; in NaCl solution, however, the initial release of K was faster, reaching a maximum in 2 h, but the concentration then declined as K was reabsorbed by the zeolite, until at 20 days it was less than in the CaCl_2 . This is almost certainly due to redistribution of cations within the zeolite. After treatment with NaCl, K is released more slowly to CaCl_2 and it appears that K release depends on Na content.

The clinoptilolite structure has channels bounded by 8 and 10 membered (Si, Al) O_2 rings, two parallel to the c axis, and one parallel to a . Within these channels there are four different cation sites, but concurrent occupancy of M(3) sites by K and M(1) sites by Na, Ca is not possible due to charge proximity. In structures like this intersite influences can occur, and may explain the unusual exchange reactions in this clinoptilolite. (Chiriac, Branson and Newman)

Investigations on trace elements

Complexing of copper by constituents of the soil solution. We have further investigated the influences of the ionic strength and pH of the solution, and of the concentrations of copper, calcium, inorganic anions and organic matter on the complexing of copper by colloidal and non-colloidal organic matter. Dialysable and colloidal fractions of humified

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organic matter were separated from extracts of plant material that had been incubated aerobically in the presence or absence of excess subsoil, of Rothamsted topsoil, and of peat. Cupric and calcium salts were added, and the effects of sodium or potassium phosphate, sulphate, bicarbonate or nitrate on the ratios of complexed to ionic Cu^{2+} determined with a cupric ion-sensitive electrode.

The strength of copper complexing by alkali extracts was greater than by the corresponding water extracts, but there was no consistent difference between the strengths of complexing by the colloidal and dialysable fractions. The strength of complexing increased with decreasing ionic strength, with increasing pH and with decreasing concentrations of copper. The pH-dependence of copper complexing was much greater with colloidal than with the non-colloidal fractions.

Calcium competed with copper for the organic matter; except for bicarbonate, inorganic anions did not compete significantly for copper, and except for phosphate, did not affect the complexing of copper by organic matter. Phosphate slightly enhanced copper complexing, presumably because of the formation of copper-organic matter-phosphate complexes. The concentration of copper in natural soil solutions and drainage waters ($10^{-7} - 5 \times 10^{-7}\text{M}$) is too small to be determined accurately by the electrode, but extrapolation of the results obtained at greater copper concentrations indicates that 10^{-7}M copper is overwhelmingly (>98%) present as organic complexes.

As with the colloidal and non-colloidal fractions, there is no great difference between the strength of copper complexing by the conventional humic and fulvic fractions. It has been claimed that fulvic acid is the agent mainly responsible for the mobilisation and transport of heavy metals in the soil, and in this context we studied the sorption of organic matter by clay from Rothamsted subsoil. Between pH 4-7.7, treating the organic extract with clay caused a nearly two-fold absolute increase in the fulvic acid which remained unsorbed, compared with the original extract. The most probable explanation of this anomaly is that much fulvic acid is normally coprecipitated with humic acid when the extract is acidified; humic acid is sorbed preferentially by clay so that coprecipitation is less extensive when a clay-treated extract is acidified. This observation reinforces our view that the traditional distinction between humic and fulvic acid has no real relevance, and that to distinguish between colloidal and non-colloidal soil organic matter is more realistic. (Bloomfield, Sanders and Pruden)

Ion movement and drainage

Composition of water in unsaturated and saturated chalk at Rothamsted and Woburn. During November 1977 three boreholes drilled to depths varying from 25 to 30 m were made by the Water Research Centre, Medmenham, on the permanent bare fallow on Highfield and a fourth in the south-west corner of Knott Wood, to determine the concentrations of ions in the interstitial water of the unsaturated zone.

On Highfield, the boreholes first entered the Chalk at depths of 4-12 m. Concentrations of nitrate N up to 40 mg litre^{-1} were detected in the interstitial waters of the unsaturated zone at 10 m, which decreased to less than 20 mg litre^{-1} at 15 m. These concentrations were more variable and decreased more rapidly with depth when the overburden of clay was greater. Chloride concentrations showed less variability. Nitrate concentrations at this site, fallowed for 17 years after permanent grass, were similar to those found under arable land elsewhere by the Water Research Centre. At the Knott Wood site under old woodland they were similar to the low values found elsewhere under grassland. The cores on this site also contained remarkably large concentrations of chloride ($>1000 \text{ mg litre}^{-1}$), sulphate S ($380 \text{ mg litre}^{-1}$) and sodium ($340 \text{ mg litre}^{-1}$) at a depth of 1-2 m, which decreased to $<100 \text{ mg litre}^{-1}$ at 3 m. The borehole in Knott

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Wood, which entered the Chalk at 0.8 m and the water table at 23 m, was lined and used for sampling groundwater for comparison with the other two sources measured at Rothamsted. The composition from all three Rothamsted sources is fairly similar, and the concentration of nitrate N remained below 9.6 mg litre⁻¹ during the period reported here. (Williams)

TABLE 9
Chemical composition of groundwaters
(7 December 1977 to 30 September 1978)

Element	Mean concentration (mg litre ⁻¹)			
	Rothamsted			Woburn Mains supply
	Mains supply	Farm borehole (100 m)	Knott Wood borehole (23 m)	
Na	11.9	7.9	7.7	9.5
K	1.2	1.1	1.3	3.4
Ca	124	115	89	42
Mg	2.2	1.9	1.6	3.9
NH ₄ -N	<0.05	<0.05	<0.05	0.02
NO ₃ -N	8.3	6.8	7.6	7.1
PO ₄ -P	<0.01	<0.01	<0.01	0.21
Cl	20.7	13.6	13.3	21.2
SO ₄ -S	6.1	3.0	4.3	11.6
Si	8.0	8.0	5.8	9.1
Conductivity (μ mhos cm ⁻¹ (25°C))	572	529	310	272
pH	7.7	7.8	7.6	7.4

Modelling of leaching in structured soils. A simple computer model, which assumes the soil to be divided into mobile and non-mobile phases (*Rothamsted Report for 1976, Part 1, 87*), was used successfully to predict winter leaching. A version adaptable to winter or summer conditions has now been developed and is being tested in the field. A further adaptation of the model, using diffusion kinetics, has been made to deal with slow solute equilibration, as may occur in soils with large aggregates.

The initial models assumed equilibration between the phases to occur only when movement in the mobile phase ceased. An additional program has been written to deal with soils in which leaching is slow enough for continuous equilibration to occur during movement.

Mineralisation of soil organic N during leaching can now be included in the models. To provide rate constants, soils from Broadbalk (farmyard manure plot), Highfield permanent fallow and Long Hoos VI (an arable site) have been incubated at 5, 10, 15, 20 or 25°C and the amount of N mineralised measured. This has provided empirical relationships between mineralisation, time and temperature for use in simulation of leaching. (Addiscott)

Ion diffusion in structured soil. The rate at which nutrients can move through the soil may be as important in some cases as the nutrient content of the soil, but relevant information for field soils is lacking because almost all previous work has been done on sieved soils in the laboratory. Such studies need methods for measuring diffusion coefficients and tortuosity factors in natural field soils. A technique used for determining such parameters in sieved soil has been modified for cores of field soil. This involves placing an ion-exchange membrane on the surface of the soil core to act as a 'sink' for ions diffusing out of the soil (Vaidyanathan & Nye, *Journal of Soil Science* (1966), 17, 175-183). Several practical problems have been encountered, particularly the difficulty

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of equilibrating a structured soil core with a given solute, and unexpectedly low tortuosity factors have been found in preliminary work. (Barraclough and Tinker)

Soil organic matter

Measurement of ATP in soil. Two methods for measuring adenosine 5'-triphosphate (ATP) in soil were compared, one based on extraction with $\text{NaHCO}_3\text{-CHCl}_3$ (Paul & Johnson, *Applied and Environmental Microbiology* (1977), **34**, 263–269), and the other on extraction by a trichloroacetic acid-phosphate-paraquat reagent (Jenkinson & Oades, *Soil Biology and Biochemistry* (1979), **11**, 193–199). Recoveries of added ATP were greater with the $\text{NaHCO}_3\text{-CHCl}_3$ reagent but the extraction of 'native' soil ATP by $\text{NaHCO}_3\text{-CHCl}_3$ was only about a third of that by TCA-phosphate-paraquat.

Microbial biomass C and ATP were measured in six contrasting English soils, using the fumigation method to measure biomass C and the TCA-phosphate-paraquat method to measure ATP. Similar measurements had earlier been made on a range of 11 grassland and arable soils from Australia (Oades & Jenkinson, *Soil Biology and Biochemistry* (1979), **11**, 201–204). Taking the English and Australian measurements together, there was a close ($r = 0.975$) linear relationship between ATP and microbial biomass C:

$$\text{Biomass C in soil} = 124.3 (\text{ATP content of soil})$$

However, an acid woodland soil from Geescroft Wilderness (pH 3.9) contained much less biomass C, as measured by the fumigation method, than would have been expected from this relationship. This and other evidence suggests that the fumigation method for measuring biomass breaks down in soils with pHs below 4.5.

The ATP content of the soil biomass did not depend on the P status of the soil, as indicated by NaHCO_3 extractable P. (Jenkinson, Davidson and Powlson)

Cultivation effects

The effect of direct drilling on the amount of organic matter in soil. Soils that have been direct drilled for a number of years contain more organic matter on or near the surface than ploughed soils. However, it is not clear whether this is entirely a result of the different distribution of organic matter in direct drilled soil, or whether there are also differences in the total amounts present in the profile, as would be suggested by the common belief that cultivation increases organic matter breakdown. To investigate this, soils were taken from ploughed and direct drilled plots of three long-term experiments set up to test cultivation systems for continuous cereals. These were the NIAE trials at Rothamsted and Boxworth EHF and an experiment at Leeds University Farm at Headley Hall, Yorkshire, which had run for 5, 6 and 8 years respectively. The direct drilled soils were more compacted (Table 10); soil cores were therefore taken to a depth of 25 cm in the ploughed plots and to a depth that contained the same weight of soil in the direct drilled plots, to allow valid comparisons to be made.

Table 10 shows that the ploughed and direct drilled soils at Rothamsted and Headley Hall contained very similar total amounts of topsoil organic C and N. At Boxworth the direct drilled soil contained slightly more C and N, though not significantly so. A change in management from ploughing to direct drilling would indeed be unlikely to have an appreciable effect on *total* C or N within 5 to 8 years. However, previous work has shown that the soil microbial biomass responds more quickly to management changes that alter either the input of organic matter into the soil or its rate of decomposition. Biomass measurements can therefore give early warning of changes long before changes in total C or N become measurable. Soil ATP content, which is highly correlated with biomass (Jenkinson & Oades, *Soil Biology and Biochemistry* (1979), **11**, 193–199), will presumably

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respond similarly. Table 10 shows that at Rothamsted and Headley Hall there were no differences in biomass or ATP content between ploughed and direct drilled soil, but at Boxworth the direct drilled soil contained 20% more biomass C and 16% more ATP than the ploughed soil. Thus, even these very sensitive methods gave little clear evidence of a net accumulation of organic matter in direct drilled soil, with a barely significant effect at one site only. At all sites, including Boxworth, the ploughed and direct drilled soil mineralised almost equal amounts of N when incubated in the laboratory.

The results on these sites do not support the belief that organic matter decomposition is retarded in direct drilled soil, and that this leads to an overall accumulation of organic matter compared with ploughed soil. (Powlson and Jenkinson)

TABLE 10
Some properties of ploughed and direct drilled soils

Site	Management	Sampling depth cm	Bulk density g cm ⁻³	Organic C %	Total N %	Biomass C ATP	
						$\mu\text{g g}^{-1}$	oven-dry soil
Rothamsted	Ploughed	25.0	0.88	2.14	0.195	435	2.32
	Direct drilled	21.1	1.03	2.12	0.187	408	2.33
Boxworth	Ploughed	25.0	0.94	2.19	0.237	567	3.04
	Direct drilled	20.5	1.20	2.32	0.256	667	3.50
Headley Hall	Ploughed	25.0	1.44	1.57	0.167	368	1.94
	Direct drilled	23.7	1.49	1.63	0.172	414	2.00
SED within sites			± 0.079	± 0.127	± 0.0151	± 34.1	± 0.138

The effect of cultivation on the mineralisation of nitrogen in soil. The experiment done in autumn 1977 (*Rothamsted Report for 1977*, Part 1, 284), in which nitrate was measured in cultivated and uncultivated soil, was repeated. Each of the uncultivated plots of the previous experiment, which had been kept bare since October 1977, were split: one half was cultivated (ploughed and then rotavated) in June 1978 and the other half was left undisturbed. As before, leaching losses were prevented by covering with shelters.

Two weeks after cultivation the soil that had grown wheat in 1977 contained 4 kg ha⁻¹ more mineral N in the plough layer than the corresponding uncultivated soil. Six weeks after cultivation the difference was 6 kg N ha⁻¹. The corresponding amounts of extra mineral N in the cultivated soil that had grown grass in 1977 were 4 and 3 kg N ha⁻¹. Thus, a very drastic cultivation caused only a small increase in the mineralisation of soil nitrogen. Conventional ploughing and seedbed preparation presumably would have an even smaller effect. (Powlson)

Soil structure

Physical behaviour of clay soils. The measurements of pore structure on Hanslope, Ragdale, Evesham, Denchworth, Flint and Salop series soils, which is part of collaborative work on soil structure at Rothamsted, were completed during the year. Aggregates from the heavy textured horizons of these soils showed some region of normal shrinkage during drying from the water content at 0.05 bar pore water tension. As all the soils contained some air-filled pores at this tension (equivalent to 60 μm diameter) such pores appeared to be unchanged by drying. However, they are greatly influenced by management practices or weather, as was shown by resampling the Hanslope site after an interval of 2 years. The transition from normal to residual shrinkage occurred at water contents in the range 0.16–0.20 g g⁻¹ for all the soils, but the pore water tension at this transition varied widely from about 2 bar in deep subsoil of the Hanslope to over 500 bar in the Denchworth. This transition is clearly an important property of a soil, is influenced by its

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organic matter content, and may be one reason why soils develop different field structures.

Water release data do not necessarily measure the pore size distribution ('p.s.d.') in soils that shrink, and the further aim of this work was to determine p.s.d. by mercury porosimeter on soils dried directly from the moist state, and also on samples of the same soils in which the pore water was replaced by methanol and liquid CO₂ in succession, the latter being removed by evaporation above its critical point ('CP drying'). It was confirmed that much of the shrinkage on direct drying can be prevented by CP drying, and the mercury porosimeter p.s.d. measurements showed that the pore structure was often greatly influenced by the method of drying.

In general, two types of behaviour were found. The first type occurred when soils apparently contained rather little stable pore volume in the size range 200 nm to 30 μ m equivalent plate separation (e.p.s.), for example, the Denchworth soil. The main volume of pores in this soil is smaller than 1 μ m, with a maximum in the distribution at 30 nm, and on drying, the whole distribution moves to smaller sizes with a maximum near 8 nm. As the displacement in size is proportional to the decrease in volume, these pores are probably slit- or wedge-shaped, and under the increasing pore water tension of direct drying, the slits narrow so that shrinkage can occur without air entry. For this reason, the size of these pores is expressed in terms of the e.p.s. Soils with predominant porosity of this type show a large region of normal shrinkage and air-entry is delayed to high pore water tensions; they dry to dense intractable aggregates and have coarse blocky or prismatic subsoil structures. In the second type of behaviour, soils having stable porosity in the range 200 nm to 30 μ m e.p.s. show a shorter range of normal shrinkage and the transition to residual shrinkage occurs at lower tensions. Such pores act as planes of weakness for crack initiation as the soil dries, so that the soils have a friable structure that can regenerate after drainage.

In each of the pairs of contrasting soils examined there was evidence of some difference in stability of pores in the range 200 nm to 30 μ m e.p.s. The differences were most marked in comparisons of the Evesham and the Denchworth soils, the well-structured Evesham containing stable pores throughout, and of the Hanslope and Ragdale subsoils, the latter containing little stable pore volume sized 200 nm to 30 μ m e.p.s.; however, the Ragdale topsoil appeared to be quite stable, possibly because of its organic C level. The Flint and Salop soils showed relatively little contrast though, below 60 cm in the Salope profile, the heavy-textured horizon was distinctly less structurally stable and had fewer stable pores, than the corresponding horizon in the Flint profile. (Newman)

The conclusions from the work reported above should be tested on a wider range of soils, and work was started on an Althorne series soil on London Clay. This stagnogleyic pelosol was chosen because field evidence suggested that it was more favourable for root penetration than the related and more widely distributed Windsor series soil. An attempt was made to determine the variation of water content and volume as a function of pore water tension, simultaneously on the same samples. In previous work, these were measured in separate experiments on different samples of the same soil, but natural variations within soils make this procedure less accurate. In addition, higher tensions were used than previously so that the conditions at the beginning of air-entry could be estimated more precisely than before. Critical point dried aggregates have been prepared from replicates used in the moisture characteristic determinations and p.s.d. will be determined on these. Currently, p.s.d. measurements are being made on further replicates by organic liquid retention.

It has been suggested that soil aggregate size could be determined by measuring bulk density as a function of sample size, the inference being that as the soil volume exceeds that of the aggregate, the air-filled pore space (V_a) should increase. Using the Althorne soil and the Saran resin technique, we have increased the sample size from 6 to 35 cm³

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but not found evidence of any significant increase in V_a ; the experiment will be continued with still larger volumes. (Newman)

Soil and clay mineralogy

X-ray spectra and chemical structure. Although the wavelengths of X-ray emission lines and bands of an element are to a first approximation independent of its state of chemical combination, small changes in wavelength occur that are related to the immediate chemical and electronic environment of the emitting atom. For the geochemically abundant third row elements, variations in wavelength of the $K\alpha$ lines and the $K\beta$ band have been used to obtain information on chemical state (e.g. White & Gibbs, *American Mineralogist* (1969), **54**, 931–935) by comparing wavelength shifts for materials of known crystal structure, oxidation state, etc. with wavelength shifts observed in unknown materials. These methods are particularly useful in poorly crystalline and non-crystalline materials such as gels and glasses.

To investigate the environment of the Al atoms in the pale-buff allophane-like material described previously (*Rothamsted Report for 1977*, Part 1, 287), the Al K spectral region of some oxides, hydroxides and aluminosilicates was examined using spectra generated by Cr anode radiation in a Philips PW 1540 flat crystal X-ray fluorescence spectrometer designed for elemental analysis. The region 0.834 nm (1486.6 eV) to 0.75 nm (1653.1 eV), which encompasses the standard published entire Al K spectrum was scanned, and differences between the spectra of the oxides/hydroxides and the aluminosilicates in the region 0.785–0.767 nm (1579–1616 eV) were noted. Further studies in the region from Al $K\alpha$ to Si $K\beta$ for the metals, a range of compounds of Al and Si, and materials containing neither Si nor Al, showed that the differences noted were due to radiation in the wavelength range 0.772–0.779 nm (1606–1592 eV) emitted by silicon atoms, and hence was a part of the Si K spectrum having energy less than that of the Si $K\alpha_{1\alpha_2}$ doublet (1739.8 eV). According to the generally accepted rules governing X-ray emission spectra, no such band should have been found, because K spectra of energy less than the $K\alpha_{1\alpha_2}$ doublet are forbidden. The intensity of this Si radiation was about the same as that of the high energy Al K satellites in this region for equal proportions of Si and Al.

To confirm the effect of the K spectral region of a range of compounds of Na, Mg, Al, Si, P, S, Cl and K was examined, using two different dispersing crystals for some elements to eliminate the possibility of spurious experimental effects. Similar spectral bands were found from all the elements at energies that were systematically related to atomic number. X-ray satellites of greater energy than the characteristic $K\alpha$ and $K\beta$ emissions have been long known. Literature search revealed three well-documented instances of K spectra of energy less than the $K\alpha_{1\alpha_2}$ doublet: Das Gupta (*Physical Review Letters* (1959), **3**, 38–40), Åberg and Utriainen (*Physical Review Letters* (1969), **22**, 1346–1348) and Sparks (*Physical Review Letters* (1974), **33**, 262–265). The irradiated elements were C, Be, Mg, Cu, Fe, Al, Si, S, Ni, Zn, Ge and Ta. Sparks gave the most convincing general explanation as being inelastic resonance scattering when monochromatic $CuK\alpha$ X-rays were incident on various target elements, and when the absorption edge energy of the target was greater than the energy of the incident X-rays.

In the present work two distinct bands have been observed for most of the elements examined. The stronger lower-energy band corresponds in shape and energy to the bands shown by Åberg and Utriainen and by Sparks, and can be accounted for, as suggested by Sparks, as radiation generated by the large amount of fluorescent $K\alpha$ radiation produced within the sample which is in near resonance with its own K absorption edge. Preliminary experiments suggest that the second and weaker band observed in this work from Al, Si, P, S, Cl and K, very close to the $K\alpha$ line on the low energy side, may be

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explained by the same mechanism generated, in this case, by the fluorescent $K\beta$ radiation. This second weaker band was difficult to observe from K and impossible from Na and Mg because of insufficient separation from the very intense $K\alpha$ line with the Ge and T1AP analysing crystals used for these elements.

Experiments with Si- and Al-containing materials have shown that the energy corresponding to the band head and the structure within the stronger band are very sensitive to the chemical state of the emitting element. For example, the Si bands from elemental silicon, silicon carbide and silicon dioxide are quite different in shape, whereas those from two forms of silicon dioxide (precipitated silica and quartz) are the same. The sharp high energy edge of the stronger band for Al_2O_3 shifts about +5 to +6 eV compared to Al metal, which is almost twice as large as the shift reported for the $AlK\beta$ band and almost ten times the shift of the $AlK\alpha$ line. Preliminary measurements indicate that the shift between $AlPO_4$ and Al_2O_3 , in which aluminium is 4- and 6-coordinated respectively, is about six times greater than the corresponding $K\alpha$ shift.

The experiments outlined above show that two K satellite bands of lower energy than the $K\alpha_{1,2}$ doublet are readily observable for most of the elements, Na to K, using unmodified X-ray fluorescence analysis spectrometers, and they lend support to the mechanism suggested by Sparks. The variation in the energy of the band head and of the fine structure within the bands between different compounds of the same element, merit further detailed study with equipment of greater resolving power than the conventional X-ray fluorescence analysis spectrometer because of their related importance in providing information about chemical bonding. (Brown)

Crystal form and crop availability of magnesite. Experiments at Broom's Barn have shown that calcined magnesite may be more suitable than kieserite as a maintenance dressing for supplying magnesium to sugar beet, and that the availability of magnesium in the soil may be decreased by long times and high temperatures in the calcining process.

To understand the effects of the firing procedures, samples of calcined magnesite prepared by heating magnesite from Spain for $\frac{1}{2}$ h at 750, 850, 950 and 1050°C and at 1050°C for 12 h were compared with two commercial calcined magnesites by X-ray powder diffraction methods. The samples were supplied by Hutchinson, Broom's Barn. All the materials apart from those prepared at 1050°C showed measurable line broadening, which decreased with increasing firing temperature, indicating that the MgO crystals were larger in the materials prepared at higher temperatures. The approximate mean crystal diameters range from 30 nm for material prepared at 750°C to >200 nm for material prepared at 1050°C.

Some preliminary experiments were made to produce even smaller MgO crystals in the calcined product which would presumably have greater availability to crops. It was found that by introducing magnesite into a furnace preheated to 640–650°C for $\frac{1}{2}$ h the MgO formed had a mean crystal size of about 15 nm. (Brown)

The nature of illite. The work reported in *Rothamsted Report for 1975*, Part 1, 214–215 has been completed. Minerals synthesised at 300°C and 2Kb in the composition range $KAl_2(Si_3Al)O_{10}(OH)_2$ (muscovite) to $K_{0.8}Al_2(Si_{3.2}Al_{0.8}O_{10})(OH)_2$ (illite) are micaceous with a partially disordered stacking sequence of layers giving a polytype that is intermediate between 1M and 1Md. They have a small cation exchange capacity of about 10 me/100 g, water in excess of their structural requirements, but no interlamellar swelling or collapse. Decreasing K contents cause a small decrease in the unit cell *b*-dimension and a change in habit from tabular to platy. Thus the minerals in this range of composition form a solid solution series.

The term illite (I) used in the above sense has a special meaning because in addition

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to being the K-poor end-member of the muscovite-illite series, it also represents the composition of the non-expanding micaceous component of interstratifications with beidellite (B). These occur at K contents smaller than 0.8 K/(Si, Al)₄O₁₀ and have both high-charge (0.8 K) illite layers and low-charge K-beidellite layers. With decreasing K contents and consequently increasing proportions of B layers the amount of exchangeable K ions and interlamellar water increases, the habit of the particles becomes lath-shaped, but there is little change in the cell *b*-dimension. Illite and beidellite layers are randomly interstratified when the proportion of B layers is large, but as the proportion of illite increases I and B layers alternate with segregation of unpaired I layers.

We think that these forms occur because the energy of formation of illite with dehydrated K ions is lower than that of beidellite of high or intermediate charge density and hydrated K ions, and thus illite and low-charge beidellite are the stable phases. Further, the unit cell *b*-dimensions of illite and low charge K-beidellite are sufficiently similar to permit either to form the termination of a 2:1 silicate layer without gross distortion of the layer, thus permitting different types of interstratification of I and B layers to occur. (Weir, Rayner and Brown, with Professor Velde, University of Paris)

Soil forming processes

Soil development on chalky tills. The different soil types that occur on the chalky boulder clays of eastern England and the east Midlands have a range of agricultural capability apparently dependent upon their different developmental histories. The better soils, such as the Hanslope series (class 2), show little profile development, and probably occur where older soils were removed by extensive erosion during the last (Devensian) cold stage of the Quaternary, about 70 000–10 000 years ago. The poorer (generally class 3) soils have undergone more extensive alteration, and show a considerable range of decalcification depth, clay translocation and mineral weathering. In some Essex soils on chalky till (Oak and Essendon series), this alteration resulted from a fairly complex period of soil development during warm and probably also cold periods before the Devensian (*Rothamsted Report for 1977*, Part 1, 256–258). In soils mapped as Winchester and Carstens series, which occur on extremely chalky till on the Lincolnshire Wolds and have some field characteristics in common with the Oak and Essendon series (e.g. reddish mottles and strong subsoil clay enrichment), we have now traced a similarly complex pre-Devensian history of development, though the extent of mineral weathering is difficult to estimate because of the variability of the till.

The poorer class soils on chalky till in the east Midlands (Ragdale and Faulkbourne series) do not seem from their field properties to have undergone such complex pre-Devensian histories, probably because the till there was deposited more recently than at least that in Essex. Future work will attempt to clarify the origin of Ragdale soils; in particular, it is hoped that knowledge of how the subsurface horizons became clay-enriched may help explain the weak structural development and imperfect drainage, which contribute to their poor performance under arable cultivation. (Catt, with Bullock, Soil Survey)

Leaf protein extraction

During the winter a new juice extractor was made, which is similar to the one already described, but slightly larger. It uses less power than the IBP pulper and press combination, it is simpler and works on crops as harvested without the need of chaff-cutting, but it does not extract quite as much juice. In late summer, as crops became more fibrous, minor defects became apparent in the trip mechanism that disconnects the auger feed, but the general design seems to be satisfactory.

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As the crops matured, laboratory scale measurements were made of the polyphenol in, and the extractability of protein from, the leaves of four varieties of sunflower, winter oilseed rape, winter wheat, field beans, *Atriplex hortensis* and barley. The extractability of protein from rape and winter wheat was measured using the IBP pulper and press. No water was added to the pulp to compensate for changes in DM as the crop aged. Extractability from winter wheat decreased with age, while polyphenols g^{-1} DM remained constant. Both remained constant with rape. The other crops were studied with water added to the pulp to compensate for the increased DM of the leaves as they matured. Protein extractability decreased with age in *Atriplex* but not with the others. Contrary to experience with many other species, especially peas, the amount of polyphenol g^{-1} DM tended to decrease with age. It seems probable that, with these other species, the diminution in extractability that has been found to accompany maturity is caused more by an increase in the proportion of fibre in the DM than by increased polyphenol content.

Except for elder, the tree leaves that have been tested extract badly. Attempts to improve extraction by various pretreatments had the opposite effect. Some of the pretreatments have therefore been tried on leaves (*Atriplex*, broad bean, elder, runner bean and sunflower) that extract well. Exposing the intact leaves to ether vapour for 1–4 h diminished the extraction of chloroplast but not cytoplasm protein and hence produced a paler material. This effect is particularly striking with broad bean. With some species chloroplasts seem to become entrained in the fibre if this is centrifuged at low speed out of pulp suspended in 2–5 times its weight of water. Both these methods may be simpler than those now advocated for making pale fractions of leaf protein. (Butler and Pirie)

Methods, apparatus and techniques

Elemental analysis of individual insects. The Entomology Department are interested in the possible application of 'chemoprints' to the study of insect populations and migration (see p. 90 of this Report). 'Chemoprints' are the elemental compositions of individuals over a range of elements that may be specific to location, environment, or genetic composition.

The analytical technique used in most of the previous chemoprint studies is energy dispersive X-ray fluorescence analysis, which allows the simultaneous detection of a wide range of elements but which has been used in a largely qualitative way (e.g. McLean & Bennett, *Environmental Entomology* (1978), 7, 93–96). X-ray fluorescence analysis is the most convenient method for chemoprint studies, and we have tested the use of our sequential wavelength-dispersive spectrometer for quantitative analysis of single insects.

We aimed to determine a wide range of elements and concentrations in single insects, with acceptable rates of work, and of accuracy, and without having to modify the spectrometer in any way that would limit its use for normal X-ray fluorescence analyses. We have mainly used the relatively large moth *Noctua pronuba* (150–250 mg dry weight), but we have also made some preliminary studies using the aphid, *Sitobion avenae* (100–200 μg dry weight). So far we have only analysed the more abundant elements Al, Si, P, S, Cl, K, Ca, Ti, Fe, Cu and Zn; but these well represent the analytical problems that would occur with a wider range of elements. The practical problems are concerned with the presentation of small specimens to allow determination of elements present in widely different amounts and with the effects of absorption within the sample.

Quantitative X-ray fluorescence analysis is easiest if the specimens are so thick ('infinitely thick') that little or no measurable increase in intensity would be obtained if a thicker specimen were used, or so thin that absorption within the specimen can be neglected. For different elements the mass per cm^2 required for these two conditions varies widely.

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The moths can be regarded as infinitely thick specimens by pelleting into 13 mm diameter discs which are placed on a sheet of uniformly thin polycarbonate film, or between two such sheets, held in the specimen holders normally used for liquids. Aluminium or plastic specimen holders were found to be almost equally suitable for the heavier elements if a thin brass liner was used to screen the walls of the sample holders when K, Cl, S, P, Si and Al were determined. To give homogeneous and sufficiently thick coherent sample discs representative of the insect, single moths are prepared by oven-drying, weighing, adding an equal weight of a 50/50 mixture of pure boric acid and glucose, grinding for 8 min in a Tema disc mill and pressing all the resulting powder to produce the 13 mm diameter disc. A Cr tube was used for excitation.

Intensities of the various radiations from moths and the NBS orchard leaves reference standard are punched on paper tape, from which the concentrations are computed. Corrections for matrix effects are made for Ca, K, Cl, P, S, Si and Al by the method of Norrish and Hutton (*X-ray Spectrometry* (1977), 6, 7–11) and for the heavier elements by using mass absorption coefficients calculated from the major element composition, or by using mass absorption coefficients measured for each sample (Hutton & Norrish, *X-ray Spectrometry* (1977), 6, 12–17). In our preliminary work the calculated mass absorption coefficients agree well with those measured directly and are obtained much more easily. The total instrument time required to analyse one moth for Zn, Cu, Fe, Ti, Ca, K, P and S is about 10–15 min.

Individual aphid specimens were made by squashing as flat as possible between two sheets of polycarbonate film. Very small insects may be treated as infinitely thin for penetrating radiation emitted by heavy metals, but these are present in small amounts and are difficult to detect. Difficulties are experienced with a group of elements (Ca, K, Cl, S and P) whose radiations are strongly absorbed, but not so much that the sample can be treated as infinitely thick. (Brown and Stride)

Correcting for seed P effects in L-value determinations. In very low P soils, measurement of the L-value requires correction for P in plant seeds by subtracting this from P uptake. However, if only top growth of ryegrass is harvested, this simple correction is not possible. Experiments to determine the partition of seed P between tops and roots were therefore made.

Ryegrass seed was sown in pots of sand given different rates of labelled P. Seed P in the tops was determined from the measured ^{31}P and ^{32}P in the plant tops, the total seed P and the specific activity of the applied P. At the same time, L-values were obtained from soils with initial NaHCO_3 -soluble P values of 4, 14 and 39 mg P kg^{-1} soil by cropping with ryegrass.

Dry matter yields from the sand-culture pots ranged from 0.2 to 1.4 g and the seed P in the tops increased from 0.14 mg P per pot at the lowest yield, to a maximum of 0.21 mg P per pot at about 0.6 g yield. The relationship of dry matter yield and seed P content of tops was used to correct the L-values obtained from the soils experiment, the top-root ratios of plants grown in sand and soil being comparable.

The correction reduced L-values by up to five-fold in the first soil, and by 21 and 10% in the two others. (Brookes and Everett)

Effects of Fe (III) on ^{32}P estimated by Cerenkov counting. We now use Cerenkov counting exclusively for ^{32}P determinations in aqueous media. Recent measurements on acid digests (0.06N-HCl) of roots and tops of ryegrass grown in ^{32}P labelled soils showed that the specific activity of the 'root' digests was invariably, and unexpectedly, lower than that of the 'tops' digests, by up to 50% in the third harvest.

The Fe (III) content of the root digests ranged from 20 to 250 mg Fe litre $^{-1}$, possibly

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due to soil contamination and/or Fe adsorption. Subsequently, Fe (III) at 10 and 100 mg litre⁻¹ was found to decrease the cpm in Cerenkov assay by about 10 and 30%, respectively, in 0.06N-HCl. The effect was even greater in more acid solutions. The relationship of Fe (III) concentration and count rate was very similar to that between transmittance at 200 nm and Fe (III) concentration, suggesting that 'colour' quench is responsible for this effect because the Cerenkov emission occurs around this wavelength. These levels of Fe are not visible, hence results published in the literature on plant and soil digests based on Cerenkov assay of ³²P may need careful scrutiny. (Brookes and Smith)

Isotopes section

Radioactivity in soil. Preliminary investigations using a 256 channel gamma spectrometer were done aimed at estimating fertiliser residues in soils from the amounts of radionuclides contained in the rock phosphate and potassium fertilisers applied. The activities of naturally occurring radionuclides in 1 kg soil samples taken from the Classical experiments were measured (Talibudeen, *Soils and Fertilizers* (1964), **27**, 347-359 and Talibudeen & Yamada, *Journal of Soil Science* (1966), **17**, 107-120). Initially, work has concentrated on the measurement of ⁴⁰K but each analysis also provides data for the estimation of members of the naturally occurring uranium/radium and uranium/thorium decay series. (Smith and Talibudeen)

Routine analyses. Approximately 8900 samples—26% more than the previous year—were assayed for radioactivity using the Beckman liquid scintillation spectrometer; 69% of these samples originated in other departments. (Smith)

Analytical section

Routine analyses. Over 100 000 digestions and analyses were done this year—27.5% more than last year—and included: Digestions, 14 520; Kjeldahl, 3407; NH₄-N, 22 540; NO₃-N, 8863; P, 11 846; K, 11 826; Ca, 10 528; Mg, 10 206; Na, 2612; Mn, 492; Zn, 72; Cu, 45; Fe, 90; Cl, 2525; S, 1143; Si, 970; Urea-N, 272; Allantoin, 809. Of the total 13.3% were for other departments. The second edition of our *Manual for the Analysis of Crops, Soils and Fertilizers* has been completed and is now available. (Avery, Cosimini, Jasko, Messer and Roberts)

New methods. Allantoin analysis was set up for routine work on the 'Technicon AutoAnalyzer' with J. M. Day, Soil Microbiology Department (Pentz, *Technicon International Congress, Advances in Automated Analysis* (1969), **1**, 111-116). Analytical methods for total amino nitrogen (Mor, Zimmerli & Fiechter, *Analytical Biochemistry* (1973), **52-53**, 614-624) and iodine (van Vliet, Basson & Böhmer, *Analyst* (1975), **100**, 405-407) are currently being tested, by coupling the 'Technicon AutoAnalyzer' to a Hitachi spectrophotometer and recorder. (Messer)

Staff and Visiting Workers

M. Roberts retired in December after 33 years on the staff. J. Bolton left in July to take up an appointment with the International Agricultural Development Service. Other staff leaving the Department were K. Perrins, Carolyn Wilkins and A. J. Gibbs. A. R. Bromfield continued his work in Kenya for the Ministry of Overseas Development. P. B. Barraclough was appointed in March to work on ion transport in soil.

In February P. B. Tinker visited Brazil, at the invitation of the Brazilian Science Research Council, to advise research centres in Brazil on the use of rock phosphates for fertilisers and to identify areas for joint research. He gave invited papers at a mycorrhiza symposium in February at the Pierre and Marie Curie University, Paris; at a meeting

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on Mineral Nutrition of Forest Trees Species in October at Louvain-la-Neuve, Belgium; and at a symposium on potassium in November in New Delhi, organised by the Potash Research Institute of India and the International Potash Institute. In India, Tinker also visited and lectured at the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) in Hyderabad. N. W. Pirie was invited by the Trilateral Commission to Paris in February. In April he visited Singapore to take part in a Bioscience Education Seminar; Kuala Lumpur, Malaysia to attend the annual meeting of The Coordinating Organisation of Science and Technology in Development (COSTED), and to present a paper at the S.E. Asia Regional Conference on Technology for Rural Development; and Madras and Bangalore for discussions on COSTED and UNCSTD. These visits were at the invitation of COSTED and the Commonwealth Foundation. In May, Pirie was invited by the Centro de Citological Experimental U.P. to take part in a Congress at Oporto, Portugal; and in June he attended a symposium at New York on 'The origins of modern biochemistry' at the invitation of the New York Academy of Sciences. Later in June he attended an International Council of Scientific Unions (ICSU) *ad hoc* Group on Agriculture at the invitation of ICSU. F. V. Widdowson visited France in June, with R. D. Prew of the Plant Pathology Department. This was at the invitation of the Institut Technique des Cereales et des Fourrages, and Widdowson and Prew saw cereal experiments at experimental stations and private farms. In June P. B. Tinker, G. E. G. Mattingly, J. H. Rayner and Blanche Benizian attended the 11th Congress of the International Society of Soil Science in Edmonton, Canada, where they each presented a paper. Tinker also visited the Institute of Pedology in Saskatoon and, on his way to Canada, Rayner visited laboratories in the Washington D.C. area—Smithsonian Institution, Soil Conservation Service of USDA, US Geological Survey and the National Institutes of Health. A. E. Johnston was invited to attend the 11th Congress of the International Potash Institute on 'Potassium research—review and trends', held in September in Bern on the 25th anniversary of the Scientific Board of IPI. A. H. Weir visited Århus and Copenhagen, Denmark for a week in October/November at the invitation of the University of Århus, The Royal Veterinary and Agricultural University of Copenhagen and the Danish Soil Science Society, to lecture on interstratified clay minerals in soils and sediments.

Z. Karim and K. N. Wickramasinghe were awarded Ph.D. degrees by Reading and London Universities respectively.

The following were visiting scientists in the Department: Mr. A. Ali, Jute Research Institute, Bangladesh; Mr. D. Balland, Institut Technique des Cereales et des Fourrages, France; Dr. P. Nørnberg, Århus University, Denmark; and Mr. Hok-Lap Yeung, University of Hong Kong. Dr. I. S. Webb spent several months in the Department, writing up pedological work undertaken in the Solomon Islands for ODM, and Mr. J. F. Osborne spent a month in the department acquiring experience in analytical techniques before going to Thailand to participate in an acid sulphate soil project sponsored by ODM. Mr. Mohd. Zahari bin Abu Bakar arrived in February from Malaya to work on acid sulphate soils, and Dr. H. Imai arrived in September from Japan. The department's visiting students were Z. Karim, K. N. Wickramasinghe, A. Gildon and A. J. Moffat; sandwich course students were S. A. Davidson, Elizabeth A. Everett, R. E. Leverton and Jacqueline Parker.

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