Report for 1962

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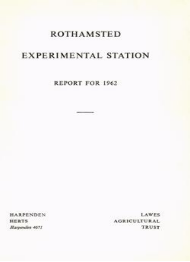

Chemistry

Rothamsted Research

Rothamsted Research (1963) *Chemistry ;* Report For 1962, pp 40 - 70 **- DOI: https://doi.org/10.23637/ERADOC-1-95**

CHEMISTRY DEPARTMENT

G. W. COOKE

The Department was saddened by the death in May after a long illness of J. R. Wilkinson. He had been with us for 16 years, and we valued his range of skills and good humour in all our field work.

S. G. Heintze retired after more than 30 years at Rothamsted. P. W. Arnold left to become Professor of Soil Science at King's College, Newcastle, and Marie Blakemore to take a post in New Zealand. Margaret Chater and P. D. Salt were appointed to the staff.

Blanche Benzian attended the 4th International Colloquium on Plant Analysis and Fertiliser Problems at Brussels in September. G. W. Cooke attended a meeting of Commissions IV and V of the International Society of Soil Science in New Zealand in November; he visited Research Institutes and Experimental Farms there and in Australia. He also attended the 7th Congress of the International Potash Institute held in Athens in May, as a guest of the Institute, and the Technical Conference of the International Superphosphate Manufacturers' Association in Avignon in September, as guest of the Association.

J. K. R. Gasser and R. C. Salmon were awarded the Ph.D. Degree of London University.

The following visitors joined the Department: Mr. W. D. Chona (Nyasaland), Mr. I. S. Cornforth (A.R.C. Scholar), Mr. P. B. Hoyt (Canada), Dr. K. F. Nielsen (Canada), Dr. N. E. Nissim (Israel) and Mr. G. N. Ngoka (Nigeria).

Organic Manures and Soil Organic Matter

Farmyard and other manures. The results of 113 field experiments with organic manures, done between 1939 and 1947, were prepared for publication by Dr. A. H. Bunting (now Professor of Agricultural Botany at Reading University). The effects on crop growth of farmyard manure (FYM), sewage sludge and composts of straw with sewage sludge and with inorganic N were compared on 56 sites. FYM contained three to six times as much K as the other organic materials tested; it and the other strawy manures supplied K to crops, but sewage sludges did not, for the K they contained was unavailable and may have been derived from the clinkers used for the drying beds or from soil in sewage. Sewage sludges are mainly sources of N and P. All materials supplied N, and all except the straw composts made with only inorganic N supplied P. At the rates used (8 and 16 tons/acre of strawy manures, and 5 and 10 tons of sludge dry matter) FYM increased yields of farm crops more than did the other organics. Fertiliser dressings (most of which were too little for maximum yields) greatly lessened the effects of all the organic manures on yield, except with red beet which responded particularly well to strawy manures. Only in 10 of the experiments (on nine sites) did the results suggest that organic manures had an effect not ascribable simply to the total plant

https://doi.org/10.23637/ERADOC-1-95

nutrients they supplied to the crops. The nine sites were all light soils, some of which compacted in dry weather. The experiments gave no evidence of a special need for organic manuring on heavy soils or on shallow soils over limestone. All the materials that had effects not simply explicable in terms of nutrient supplies contained rotted straw or involved the rotting of straw.

Amount of organic matter *as such* was not important—sewage sludges supplied about twice as much *organic matter* but were far less effective than FYM. Though the manures containing rotted or rotting straw had important effects on crops, the benefits are difficult to interpret because these manures all supplied much K; straw composts made with inorganic N, and also ploughed-in straw, were much less effective than FYM or composts of sewage sludge and straw. Even where organic manures sometimes had effects other than expected from their nutrient content, organic manuring had no obvious cumulative effects.

Seventy-three other experiments tested bulky organic manures in simple "micro-plot" layouts between 1940 and 1949 (Garner, H. V., *Emp. J. exp. Agric.* (1962), **30**, 295–304). The experiments also tested NPK fertilisers, but usually at rates not more than half those now known to be (economic) "optima"; simple nutrient effects therefore could not be separated from possible "complex" effects from organic matter as such. All the organic manures at 16 tons/acre increased yields of main crop potatoes more than did fertiliser dressings, usually 0·6 cwt N, 0·6 cwt P_2O_5 and 0·9 cwt K_2O/acre. FYM was better than raw or digested sewage sludges, treated town refuses and screened refuse dust. Sewage sludges of domestic and industrial origins supplying 10 tons dry matter/acre usually gave one-third to one-half of the increase given by 16 tons of FYM. Fermented town refuses and composts of sewage sludge and town refuse at 16 tons/acre had from one-third to two-thirds of the effect of 16 tons of FYM. Screened dust from town wastes was more variable and generally inferior to other wastes. The main value of sludges for potatoes was to supply N and P. Screened dusts and fermented refuses supplied little N or K. For most vegetables FYM was much superior to all other organic manures, but sludge was effective for savoys and kale.

These older experiments failed to show exactly how organic manures and fertilisers affect crop yields because the nutrients applied by organic and inorganic materials were rarely equalised; also fertilisers were usually tested at only one rate, the form of the response curve was not established, and the nutrients supplied by manures were not quantitatively assessed. Our recent work in field experiments at Rothamsted and Woburn has been planned to value the nutrients supplied by organic manures and also to search for other physical or biological effects that are not connected with the supply of crop nutrients. Wherever differences in performance of farmyard manure and fertilisers have occurred in long-term experiments the crops, soils and manures are being examined to see whether differences in amounts of nutrients can account for effects on yields. Many of the principles involved are now being clarified.

FYM given regularly for nearly 120 years in the Broadbalk Wheat Experiment has had no effects not achieved by fertilisers. The effects of residues of long-continued dressings of FYM in the Hoosfield Exhaustion Land and Permanent Barley Experiments seem to result solely from the N, P and K left in the soil. Many of the differences between yields of test crops in the Ley–Arable Experiments at Rothamsted and Woburn reflect differences in supplies of K. Crops (particularly grass) take much K from the soil; organic manures usually supply large amounts. In experiments in Forestry Commission Nurseries, K, Mg and Cu supplied by "organics" have accounted for their better performance than inorganic NPK fertilisers.

There are, however, instances of beneficial effects of unidentified nature (perhaps physical or biological or both). Work on the Woburn Market Garden Experiment (discussed in previous Reports) has continued. Organic manuring has had effects on red beet not matched by fertilisers; in particular, the better germination of the beet on the FYM plots seems unlikely to be from differences in nutrient supplies. Also at Woburn E. J. Russell and J. A. Voelcker stated that yields of continuously grown cereals deteriorated slower on FYM plots than on those with fertilisers. It was not possible to account completely for this difference.

Barnfield. At Rothamsted the Barnfield Continuous Mangold Experiment was modified in 1962; potatoes were grown on half of each plot and the fertiliser dressings were altered by including a full scale of nitrogen. Yields of potatoes on the FYM strips were consistently larger than on strips with N, P, K, Na and Mg fertilisers. The N response curves on FYM plots and on fertiliser plots were almost parallel, but FYM plots gave 5 tons/acre more potatoes when no N was given, and 3½ tons more at the high rate (1·8 cwt N/acre). (Warren and Johnston)

FYM for sugar beet at Woburn. Experiments at Woburn with sugar beet, begun in 1961 (*Rep. Rothamst. exp. Sta.* for 1961, p. 42) to compare NK fertilisers and FYM on an equal K basis, were repeated in 1962 on a new site. As in 1961, the best fertiliser treatment and the highest rate of FYM gave almost identical yields of sugar, but again NK fertiliser produced 4 tons/acre more tops than the manure; all plots received a dressing of superphosphate. The yields in the two years were:

	Sugar (cwt/acre)		Tops (tons/acre)	
	1961	1962	1961	1962
Farmyard manure	70	81	10	18
NK fertiliser	69	80	14	22
None	51	56	7	9

In both years the manures were dug in in March and the beet was sown in April. Applying less fertiliser N in 1961 to decrease the growth of tops lessened the yield of sugar. In a further attempt to produce the same top/sugar ratio with NK fertiliser as with FYM, part of the N of the NK fertiliser was delayed in 1962, two-thirds of the N was dug in and the remainder applied as top-dressing 2 weeks after singling the beet. The yield of tops was the same (22 tons) as when all the N was dug in, but the yield of sugar (75 cwt) was 5 cwt less. When fertiliser N equal to one-third of the N in the NK fertiliser was dug in with FYM the yield of tops was 22 tons (4 tons more than with FYM), but the yield of sugar was the same (81 cwt); this combination of fertiliser N and FYM had the same effect as NK fertiliser alone.

In 1961 500 lb/acre of $MgSO_4.7H_2O$ was applied to the whole of the experiment, but in 1962 this dressing was tested on half-plots. Although the dressing increased % Mg in the sugar beet tops, it did not affect yields of sugar or tops. (Johnston and Warren)

Experiments on ley and arable rotations. In the Rothamsted experiments on Highfield and Fosters Field, wheat grown after 3 years of lucerne has yielded more than after 3 years of grazed ley, cut grass or arable. In 1961 % N in the wheat grain on both fields, grown without fertiliser N, was more after lucerne than after the other 3-year cropping systems. The values after arable were larger than those after grazed ley or cut grass. Previous cropping did not affect the % N in the wheat straw except that it was less after arable on Fosters Field. The wheat after lucerne contained more N (20–25 lb/acre on Highfield and 35–40 lb on Fosters Field) than wheat after other crops. The larger yields of wheat after lucerne came in part from the extra N in the soil after lucerne; this is supported by the results of test applications of fertiliser N to the wheat. Where 0·9 cwt/acre of fertiliser N was given to wheat after arable on Fosters Field the yield was nearly equal to that of the crop after lucerne which also received 0·9 cwt N as fertiliser. The yields after grazed ley and after cut grass were much increased by N, but were still below the yield after lucerne. On Highfield loss of grain by lodging and birds was most on the lucerne plots; judging by the wheat straw yields, however, 0·9 cwt N as fertiliser removed the differences from previous cropping, except after cut grass, where the wheat crop was still a little smaller.

Previous cropping did not affect the Ca, Mg and K contents of the grain and straw. Manganese content was also unaffected on Fosters, but on Highfield it was increased as follows by lucerne:

	ppm Mn in dry matter	
	Grain	Straw
After lucerne	54	42
After other cropping	42	23

Grazed ley increased the Na content of the straw, but not the grain, on both fields.

	Fosters	Highfield
	% Na in straw	
After grazed ley	0·022	0·025
After other crops	0·008	0·009

It is not known whether these differences in Mn and Na contents had any effect on yield.

The values for mineralisable N in the soil after the four cropping systems, measured by incubation tests, did not agree with the uptakes of N by the wheat. Soils from the grazed ley plots on both fields contained more mineralisable N than the other plots; there was least after arable cropping. (Warren, d'Arifat and Smith)

Fractionating soil organic matter. Chemical and biological fractionation of labelled carbon in soils which had been incubated in the field with labelled plant material continued. Labelled carbon in the biomass decreased rapidly as incubation proceeded and confirmed the earlier finding that the half life of the biomass is about two years. However, the *total* biomass in the soils (which had not received any organic matter after adding the labelled plant material) was little changed in three years, presumably because the autochthonous population was maintained by slow decomposition of unlabelled "humus" in soil.

The decomposition of micro-organisms in soil was studied by adding *Nitrosomonas europaea* uniformly labelled with carbon-14 (grown by N. Walker) to unlabelled calcareous soil; samples of the soil were then treated with chloroform vapour, or oven dried, or given no treatment. After being moistened and incubated for 10 days, the oven-dried soil evolved 37% of the microbial carbon as CO_2, the chloroform-treated soil evolved 28% and the untreated 20%. This sequence is the same as that obtained when similarly treated labelled soil (pre-incubated with labelled plant material for one year in the field) was incubated (*Rep. Rothamst. exp. Sta.* for 1961, p. 44), and confirms the theory that the biomass is the fraction of soil organic matter influenced by these treatments.

A fraction of the soil organic matter, tentatively identified as the biomass, had a specific activity very much larger than soil carbon as a whole. Attempts were made to extract material having the same specific activity as the biomass. Hot water, cold *N*-hydrochloric acid, cold barium hydroxide solution and cold 10% trichloracetic acid all extracted material of specific activity three to five times that of the whole organic matter from soil incubated for 1 year in the field. More drastic reagents which dissolve material from the "humus" carbon gave smaller specific activities: cold *N*-HCl extracted 1·1% of the organic carbon from a soil, and of this 4·7% was labelled, whereas treatment with *boiling* *N*-HCl for 30 minutes dissolved 6·3% of the carbon, of which 3·4% was labelled. Shaking with cold 0·1*N*-barium hydroxide for 30 minutes extracted organic matter of greatest specific activity, but the actual amount dissolved was small. Table 1 shows that, as incubation proceeds, the amount of labelled material extracted by barium hydroxide diminishes more quickly than does total labelled carbon, the fall being roughly similar to that of the fractions rendered decomposable by oven drying or treating with chloroform vapour. (The incubation tests were done for 10 days at 25°.) (Jenkinson)

Leaching of soil organic matter. Long-term experiments on the leaching of organic matter from various soils were started as part of an investigation on the decomposition of plant material. From April to October 1962, 8·5 in. of drainage were collected from two soils, one with 18% and the other with 8% of clay, both given labelled plant material in April. The leachate from the heavier soil contained 1·3% of the added plant carbon in organic form and from the lighter soil 2·3%. (Jenkinson)

TABLE 1

Loss of labelled carbon from different fractions of soil organic matter as decomposition proceeds in the field

The labelled material remaining in a fraction is expressed as a percentage of the corresponding amount remaining after 1 year in the field.

Fraction	After 2 years	After 3 years
Whole soil organic matter	85	71
C dissolved by cold 0·1*N*-$Ba(OH)_2$	61	46
C released on incubating soil that had been oven dried at 80°, then reinoculated and remoistened	67	47
C released on incubating moist soil exposed to $CHCl_3$ vapour for 24 hours, then reinoculated	61	41

Decomposition of chlorophyll-type compounds in soil. Chlorophyll derivatives have been found by others in woodland soils and in lake mud, but little is known of the decomposition of chlorophyll and related substances in cultivated soils. The rate at which chlorophyll and its degradation products break down is being studied in laboratory and field experiments; quantities are estimated by spectrophotometry and the path of degradation is being followed by paper chromatography. These convenient methods make it much easier to follow this decomposition than that of most other substances present in plant material. The work has the secondary object of seeing whether the presence of chlorophyll, or materials derived from it, can indicate recently added and active plant residues in soil. Chlorophyll has been found in a range of cultivated soils as well as in forest soils. The amounts of the compounds investigated were highest in bog soils that have recently been cultivated.

In soils incubated in the laboratory chlorophyll-type compounds decomposed rapidly for the first 20–30 days and afterwards more slowly. All plant materials used (grass, lucerne and spinach) behaved in the same way and broke down at similar rates in different kinds of soils. In field experiments on Rothamsted and Woburn soils chlorophyll decomposed more slowly than in the laboratory. Chlorophyll in fresh grass and lucerne broke down more quickly than chlorophyll in dried samples of these plants. Paper chromatography showed that no chlorophyll A or B was left in the soil after fresh plant material had decomposed for 18 days in the field; but with the dried material both substances were still present after 72 days. Recent laboratory work has investigated the effects of aeration, soil reaction and enzymes on breakdown of the chlorophyll in fresh grass. No decomposition occurred in water-logged soil. In acid soil chlorophyll was rapidly converted to pheophytin, but further breakdown was slower than in neutral soil. The presence of the natural plant enzymes accelerated the breakdown of chlorophyll. When incubating farmyard manure with soil, the absorption peaks of chlorophyll-type compounds increased for the first 12 days; afterwards they decreased normally. (Hoyt and Cooke)

The effects of cropping systems on soil stability. A way of assessing the stability of soil aggregates, by measuring the loss in pore space when soil crumbs slaked in water, was developed two years ago (*Soil Sci.* (1961), **92**, 33). The method was developed further and made more sensitive to distinguish finer differences in soil stability. The principle is that the amount of water present between soil particles after slaking is compared with the amount held by the same volume of artificially stabilised soil crumbs. One sample of aggregates is stabilised by a dilute solution of "Perspex" in chloroform; another sample is untreated. The two samples are set up in shallow beds and are treated with water on a tension plate. "Free" water is allowed to drain away and then the interparticle water is extracted by a tension sufficient to remove all the water that would be held *between* the aggregates used if these did not slake at all. (If slaking occurs, interparticle space becomes smaller and less water can be removed at the tension used. The appropriate tension using 4–6-mm aggregates was 4·5 cm of water.) The volume of water removed from slaked soil, expressed as a percentage of the volume removed from stabilised soil, is an empirical "stability index". The method showed the increase in soil stability of a sandy loam caused by 1, 2 or 3 years under grass and the slight degradation of structure that followed ploughing of grassland on a clay soil. Table 2 shows some results from the Ley–Arable Experiments on Highfield at Rothamsted, and on Stackyard Field at Woburn. (Williams)

TABLE 2

The effects of grass and of ploughing on the stability of soil aggregates

		Approximate and empirical stability indices	
Highfield (*Rothamsted*)			
Permanent grass stabilised		100	
Permanent grass		93	
Four years of continuous fallow		34	
		Sampled	
	Before ploughing	26 days after	54 days after
Ley rotations			
12-year-old ley grazed	91	89	67
3-year-old ley used for cutting	82	77	49
Stackyard Field (*Woburn*)			
3-year-old ley stabilised		100	
Four years of bare fallow		33	
Samples taken from unploughed leys aged			
1 year		56	
2 years		71	
3 years		75	

Stabilising soil with rubber latex. Two unstable soils (a heavy clay loam from the headland of Barnfield at Rothamsted and a sandy loam from Stackyard Field at Woburn) were treated with rubber latex emulsion and then tested in laboratory and greenhouse experiments. Both treated soils were completely stable in a test with simulated rain that slaked the untreated soils completely. In the greenhouse kale germinated much better in the stabilised soils than in the untreated ones. The latex stabilised only the surface layers of the soil aggregates, and when the thin outer skin of a crumb was removed the residue was as unstable as untreated soil. Stabilisation achieved in this way with latex is therefore unlikely to persist through ordinary cultivations, but the technique may be useful in assisting the germination of sensitive crops in soils that are liable to surface capping after rain. (Williams)

Field and Laboratory Experiments with Fertilisers

Alternative nitrogen fertilisers for spring barley. In 1962 six experiments compared yields from urea or sodium nitrate with yields from ammonium sulphate. Each fertiliser was tested at two rates (0·35 and 0·70 cwt N/acre), when broadcast over the seedbed, when combine-drilled (i.e., in contact with seed) or when placed 1 in. to the side of the seed. Five of the experiments were on calcareous soils and one on Clay-with-Flints. This concludes 3 years' work with urea. Table 3 shows mean yields from the sixteen experiments made from 1960 to 1962 and compares alternative methods of applying urea and ammonium sulphate. Calcium nitrate and sodium nitrate were tested in the later experiments. Eleven experiments were made on calcareous soils, where losses of ammonia, from the ammonification of urea, were most likely. In 1960, however, urea and ammonium sulphate, broadcast over three very calcareous soils, yielded similarly, so in 1961 calcium nitrate was tested to compare yields from nitrate and from ammonium. Broadcast urea and ammonium sulphate gave similar yields, but less than calcium nitrate. In the 1962 experiments sodium nitrate replaced calcium nitrate; broadcast urea and ammonium sulphate gave similar yields again, but on five soils which contained much $CaCO_3$ sodium nitrate consistently gave more, particularly at the high rate of dressing, where the nitrate gave about 4 cwt more grain/acre than the ammonium salt.

TABLE 3

Mean yields of barley given by different forms of nitrogen fertilisers in experiments in 1960–62

(cwt of grain/acre at 15% moisture content)

		0·35 cwt N/acre			0·70 cwt N/acre		
	Without nitrogen	Broad-cast	Drilled	Placed	Broad-cast	Drilled	Placed
Yields from 16 experiments 1960–62							
Ammonium sulphate	19·4	25·0	26·8	26·9	29·0	29·3	29·0
Urea		25·3	26·6	26·7	29·4	28·2	30·5
Yields from 7 experiments 1960–61							
Ammonium sulphate	21·7	26·9	28·2	29·1	30·9	31·0	30·4
Calcium nitrate		28·0	28·5	28·1	32·1	31·4	32·4
Yields from 6 experiments in 1962							
Ammonium sulphate	16·2	21·7	24·1	23·0	25·4	25·4	24·7
Sodium nitrate		24·0	24·3	24·4	28·4	29·2	29·1

Results from methods of application differed with the fertiliser tested. Combine-drilled ammonium sulphate (at either 0·35 or 0·70 cwt N/acre) usually gave more grain than did an equivalent broadcast dressing; this fertiliser delayed germination least. Combine-drilled urea checked early growth, especially of crops sown late, and when 0·70 cwt N/acre was given many plants died and yields were less than from equivalent broadcast dressings. Combine-drilled calcium nitrate also severely checked growth when dry weather followed sowing, but subsequently most plants grew. Yields from combine-drilling and broadcasting were similar.

Placing the dressings beside the seed checked early growth less than did combine-drilling. With ammonium sulphate, yields from placing were better than from broadcasting, but not better than from combine-drilling; with calcium nitrate, placing was worse than broadcasting, but for urea placing was better than broadcasting and much better than combine-drilling. Consistently high yields from urea were obtained only by side-placing, presumably because this technique limited both damage to the germinating seeds and losses of ammonia to the atmosphere. Placing and combine-drilling sodium nitrate both similarly outyielded broadcasting.

As similar yields of barley are given by broadcasting urea and ammonium sulphate, even on soils containing very much calcium carbonate, losses of ammonia from these two fertilisers are probably similar. The work confirms that combine-drilled ammonium sulphate usually gives more grain than broadcasting, but that combine-drilling has less advantage with calcium nitrate because it checks early growth more, the salt is mobile and does not suffer loss of NH_3 on chalky soils. Combine-drilling of urea is dangerous, but placed dressings are safe and give good yields. Fertilisers containing some or all of their nitrogen as nitrate are unlikely to give better yields when combine-drilled than when broadcast, particularly as germination is harmed more by nitrate than by ammonium–nitrogen. Other experimenters have not agreed with our conclusions about the advantages of combine-drilling nitrogen fertilisers; they have usually used fertilisers containing ammonium nitrate. Our recent work shows that gains from combine-drilling N are restricted to fertilisers containing most or all of their N as ammonium. (Widdowson and Penny)

Timing of nitrogen dressings for winter wheat on light soil. In experiments made from 1958 to 1960 (*J. agric. Sci.* (1961), **57**, 329), May was the best time on average for top-dressing wheat grown on medium and heavy-textured soils. This work has now been extended to light land at Woburn. October-sown Cappelle was treated with four rates of "Nitro-Chalk" in March, April and May. The yield of grain without N was only 13·3 cwt/acre, which was raised (averaging the times of application) to 29·9 cwt with only 0·5 cwt N/acre, to 36·6 cwt with 1 cwt N, and the maximum average yield (37·6 cwt) was from 1·5 cwt N/acre. When 0·5 cwt N was used, 1 March was the best time; largest yields (over 40 cwt/acre) with both 1·0 and 2·0 cwt N/acre came from April dressings. When the four rates of application were averaged dressings on 9 April gave 2·3 cwt/acre more grain than dressings on 1 March or 9 May. Splitting the 1·0-cwt and 2·0-cwt N dressings between March and April, and also between March, April and May, gave less yield than applying the same amount of N wholly in April. (Cooke)

Concentrated fertilisers and forms of nitrogen. An experiment started at Rothamsted in 1960 to compare a concentrated fertiliser containing 20% N, 10% P_2O_5 and 10% K_2O with a mixture of ammonium sulphate, superphosphate and muriate of potash for kale, Italian ryegrass and barley, ended in 1962. The rates used supplied 1·0 or 2·0 cwt N/acre to grass and kale and 0·3 or 0·6 cwt N/acre to barley; all the fertilisers were broadcast over the seedbed. Although differences were small, higher yields of barley grain and straw, ryegrass and kale were obtained each year with 20 : 10 : 10 than with the "dilute" mixture.

The experiment also compared ammonium sulphate with ammonium nitrate, calcium nitrate and urea on the same crops and at the same rates of N. Superphosphate and potassium bicarbonate, at rates of P and K equivalent to those supplied by the double rates of 20 : 10 : 10, were applied to all plots testing these N fertilisers. All four nitrogen fertilisers when used to supply 2·0 cwt N/acre checked the establishment of spring-sown Italian ryegrass more than did equivalent 20 : 10 : 10. Initial damage was greatest with urea and the "dilute" mixture, but later in the spring urea and calcium nitrate delayed growth most. 2·0 cwt N/acre in any form checked early growth of kale, but calcium nitrate did so most. With 1·0 cwt N/acre, there was little damage, and early growth was best with ammonium nitrate. Barley was not checked by any fertiliser, because the rates used were much less. Table 4 gives average yields over the three years. For barley, ammonium and calcium nitrates were best when 0·3 cwt N/acre was given, but at twice this rate ammonium nitrate was best. Ammonium sulphate and urea behaved similarly, giving smaller yields. For grass, ammonium nitrate was best when 1·0 cwt N/acre was given, but with 2·0 cwt N/acre ammonium sulphate gave slightly better total yields, because each year it yielded best at the second cutting. Urea gave least grass at the first cutting and had the least residual value at the second cutting. For kale, calcium nitrate was best at each N level. Ammonium nitrate was better than ammonium sulphate or urea. (Widdowson and Penny)

TABLE 4

Mean yields of barley, Italian ryegrass and kale from four nitrogen fertilisers in 1960–62

	Barley		Italian ryegrass		
	Grain	Straw	First cut	Second cut	Kale
N fertiliser given	(cwt/acre at 15% moisture content)		(cwt dry matter/acre)		(tons/acre)
None	17·9	9·4	8·9	5·8	13·6
Ammonium sulphate					
Low rate	29·4	19·1	23·5	10·8	20·2
High rate	37·1	25·8	28·1	21·0	23·3
Ammonium nitrate					
Low rate	30·8	20·9	28·2	12·8	20·7
High rate	38·3	26·4	29·6	18·5	23·9
Calcium nitrate					
Low rate	30·9	20·5	26·1	11·7	22·0
High rate	37·3	25·3	28·2	18·4	24·8
Urea					
Low rate	29·4	18·9	23·7	11·1	20·7
High rate	37·5	27·0	27·3	16·7	23·3

Comparisons of liquid and solid fertilisers. Experiments comparing liquid and solid N, and NPK fertilisers for grass and kale respectively, were continued. For grass, a liquid fertiliser containing 20% N (as urea and ammonium nitrate) was compared with solid urea at rates up to 1·0 cwt N/acre for each of two cuts. Some "scorch" occurred when more than 0·4 cwt N/acre per cut was applied as a liquid to leaves 4–6 in. high. At each of two cuts, and independent of rate, solid N gave more grass than did liquid N; but the mean differences between the solid and liquid forms were only 1·2 and 0·2 cwt of dry matter/acre at the first and second cuttings respectively.

For kale a liquid fertiliser containing 14% N, 6% P_2O_5 and 8% K_2O was compared with its equivalent as solid urea, superphosphate and muriate of potash. Both fertilisers were applied at rates supplying 1·0 or 2·0 cwt N/acre, either to the seedbed in April or to the leaves in July. The July-applied liquid scorched the leaves badly, whereas the solids did not. Solid NPK gave more kale than did liquid NPK at each rate and at each date of application; the mean difference of 1·3 tons/acre was independent of time of application. April dressings gave larger yields than the July dressings. (Widdowson and Penny)

Residues of nitrogen fertilisers given to wheat and potatoes. An experiment made from 1960 to 1962 measured effects on yields of potatoes and wheat by the residues from ammonium sulphate applied to the preceding wheat and potato crops. For each test crop residual effects were compared with the response to fresh dressings of ammonium sulphate. The autumn of 1960 was unusually wet, potato harvest was delayed and spring wheat had to be sown; the 1961 autumn was drier and winter wheat was sown.

In both years ammonium sulphate given to potatoes increased yields of following wheat. Where no nitrogen was given, the residues of 1·5 cwt N/acre to the previous potatoes increased yields of the 1961 spring wheat by 7 cwt/acre, and the 1962 winter wheat by 9 cwt/acre. Even where the wheat received 1 cwt of fresh N/acre, the residues of earlier dressings increased yields by 1·3 and 6·2 cwt/acre in 1961 and 1962 respectively. The residues of 1·5 cwt N/acre given to potatoes had roughly the same effect on following wheat as a *fresh* dressing of 0·5 cwt N/acre. In 1961 potatoes grown without fresh N yielded slightly more where they followed wheat receiving 1 cwt N/acre, but the 1962 potato yields were not affected by residues of N given to previous wheat. (Widdowson and Penny)

One-year leys for winter wheat. The effects of three kinds of one-year ley on the yield of following winter wheat were compared. Ryegrass (S.22), clover (Dorset marl) or mixed ryegrass–clover leys were cut three times for silage and then ploughed before sowing wheat. Grass was grown without N and with 1·0 or 2·0 cwt N/acre (as "Nitro-Chalk"); the grass–clover ley was grown without N and with 1·0 cwt N/acre; the clover leys were grown without fertiliser N. Three levels of N and three levels of K manuring were tested on the following wheat, and Table 5 shows some of the yields obtained. Without N in 1962 the wheat after clover yielded 16 cwt/acre more grain than the wheat after ryegrass grown without N. When N was given to the wheat it still yielded most at each N level after clover. The residual value of the N left in the soil after clover, in terms of a fresh dressing of "Nitro-Chalk" applied to the wheat, was rather more than 0·5 cwt N/acre.

A previous experiment (*Rep. Rothamst. exp. Sta.* for 1960, p. 53) showed that wheat heavily manured with N yielded less after ryegrass dressed with

1·5 cwt N/acre than after ryegrass grown without N. Table 5 shows that this also happened in the 1962 experiment, but that when 2·4 cwt K_2O/acre was given to the wheat (half was ploughed down and half was combine-drilled) all wheat after pure ryegrass leys yielded similarly. These experiments show, on Rothamsted soils at least, that one-year leys heavily manured with N can remove so much K that yields of following wheat crops are diminished unless much K fertiliser is given. The best way of replacing the K withdrawn by the ley was not examined in this experiment, but the dressing of 2·4 cwt K_2O/acre needed by the wheat after ryegrass cannot be applied to the seedbed without risking effects on germination. (Widdowson and Penny)

TABLE 5

Yields of leys grown in 1961 and of the wheat that followed in 1962

	Clover	Clover–ryegrass		Ryegrass		
N to ley, cwt/acre	0·0	0·0	1·0	0·0	1·0	2·0
	1961 yields of dry herbage in cwt/acre					
	80·4	86·2	96·8	54·3	94·3	102·9
	1962 yields of wheat grain in cwt/acre (15% moisture content)					
From nitrogen (averaged over K levels)						
No nitrogen	47·3	38·4	35·8	31·2	33·3	33·6
1·0 cwt N/acre	57·6	54·3	55·0	56·0	53·8	51·7
From potash (averaged over N levels)						
No potash	53·5	45·0	44·8	42·5	43·0	39·1
2·4 cwt K_2O/acre	54·3	47·8	47·4	44·8	44·5	45·0

Soil samples were taken from the 1961/62 experiment just before the wheat was sown in October 1961, and in March 1962. With the October but not the March samples, more N was mineralised on incubating rewetted air-dried soil when the leys had contained clover than when they had not. (Gasser)

Green manures, straw and nitrogen for barley. A 3-year barley experiment was made from 1960 to 1962 to measure the effect on yield in 1962 of under-sowing barley with ryegrass in 1960 and in 1961, with and without returning the combined straw after harvest. The treatment crops were ploughed-under in December each year. Each of these treatments was compared at three levels of N (0·0, 0·3 and 0·6 cwt/acre), which were also given as a third factor to the 1962 barley; mean yields in 1962 are in Table 6. The fresh dressings of N given in 1962 had large effects on yield. Ploughing in ryegrass or ryegrass plus straw had no residual effect, but ploughing in the ryegrass alone in 1961 diminished barley yield by 4·0 cwt and ploughing in ryegrass plus straw did so by 2·0 cwt/acre. "Nitro-Chalk" applied at 0·6 cwt N/acre in 1960 and in 1961 did leave small residues for the 1962 barley, particularly when straw was ploughed in. This confirms results obtained with wheat and grass at Rothamsted; clearly the heavy N fertiliser dressings now commonly used leave residues that benefit subsequent crops on many soils. (Widdowson and Penny)

TABLE 6

Mean yields of barley grown in 1962 after pretreatments in 1960 and 1961

(cwt of grain/acre containing 15% moisture)

Effect of ploughing in ryegrass and straw in 1960 and 1961			
None	Ryegrass	Ryegrass + straw	S.E.
30·8	31·0	30·8	±0·33
Residual effect of nitrogen broadcast in 1960 and in 1961			
None	0·3 cwt N/acre	0·6 cwt N/acre	
30·4	30·6	31·6	±0·33
Effect of nitrogen broadcast in 1962			
None	0·3 cwt N/acre	0·6 cwt N/acre	
22·2	32·3	38·1	±0·33

Rates of action of phosphate fertilisers. Micro-plot experiments using ryegrass to measure the rates of action of several phosphate fertilisers were described earlier (*Rep. Rothamst. exp. Sta.* for 1960, p. 56). These same fertilisers were tested on barley in three micro-plot field experiments at Rothamsted in 1961–62. The fertilisers were broadcast before sowing at 0·45 cwt P_2O_5/acre and their efficiencies in terms of superphosphate as standard are shown in Table 7 for *yields* of crops harvested in early July when ears were forming. Corresponding figures from the 1959–60 ryegrass experiments are also given, but these were derived from P uptakes because the yield response curves were not very steep:

TABLE 7

Comparisons of phosphate fertilisers for promoting early growth

	Percentage superphosphate equivalents	
Fertiliser	1961–62 Barley (from yields)	1959–60 Ryegrass (from P uptakes)
Dicalcium phosphate dihydrate	60	118
Gafsa rock phosphate	7	96
Basic slag	22	93
Nitrophosphates with following % of total P soluble in water:		
5%	1	107
26%	25	111
50%	53	93
Potassium metaphosphate	23	130

Both at an early sampling in May and at ear-formation, all the fertilisers tested gave much lower yields of barley than equivalent P as superphosphate. Results with the granulated nitrophosphates show the value of increasing the percentage of the total P that is soluble in water.

In contrast to the earlier results with ryegrass, the nitrophosphates having 5% and 26% water solubilities, and also the potassium metaphosphate, acted too slowly to establish barley well in adverse growing conditions. In 1961 the seedbed was very bad after the wet winter.

In 1962, when seedbeds were excellent, the crop was sown in February in one experiment and in March in the other; but early growth was very slow during the exceptionally cold and dry spring. (Mattingly and Penny)

Residual effects of phosphates. The experiments, started in September 1959 (*Rep. Rothamst. exp. Sta.* for 1960, p. 56) to compare residues of the fertilisers tested for early action in the micro-plot experiments described above, have now been cropped for one complete rotation of potatoes, barley and swedes. Mean yields (for the 3 years 1960–62) without phosphate, the increases from cumulative dressings of superphosphate applied every year and the increases from residues of fertilisers applied at 3·0 cwt P_2O_5/acre in September 1959 are in Table 8. (Results for nitrophosphates on barley are omitted because the crop lodged badly in 1960.) Residues from the heavy dose of all forms of phosphate have given higher mean yields over the first 3 years than the cumulative annual dressings of superphosphate supplying 0·5 cwt P_2O_5/acre. The only clear difference was that rock phosphate residues on this acid soil (pH 5·3–5·8) were significantly worse for potatoes (but not for barley or swedes) than residues of the other phosphates. (Mattingly)

Effects of nitrogen fertilisers on the forms of soluble nitrogen and carbohydrates in grass. The NO_3-N content of grass is usually most when growth begins, and decreases later. Recent experiments at Rothamsted with Italian ryegrass show that the pattern of changes in NO_3-N content is not always the same, but depends greatly on weather. In 1960 ryegrass contained most nitrate 10 days after N-fertiliser was applied; this was because only 2 of the first 10 days of growth were without rain and altogether 1·6 in. fell in this time. In 1961 grass cut 14 days after applying N-fertiliser contained very little NO_3-N because of very dry weather; during the next 14 days, when 1·5 in. of rain fell, NO_3-N in the grass increased rapidly.

TABLE 8

Effects of phosphate fertilisers over 3 years

	Rate (cwt P_2O_5/acre)	Mean yields/acre in 1960–62		
		Potatoes (tons)	Barley (cwt)*	Swedes (tons)
Yields without P	0·0	10·40	33·1	7·62
		Increases in yield		
Annual dressings of superphosphate	0·25	0·86	2·0	8·03
	0·5	1·88	1·8	10·21
Single dressing of	3·0			
Gafsa rock phosphate		1·64	5·7	12·92
Basic slag		2·49	5·9	12·64
Nitrophosphates with				
5		2·47	—	14·09
26 % of total P soluble in water		2·81	—	13·10
50		2·63	—	13·23
Potassium metaphosphate		2·51	5·1	13·16
Superphosphate		2·71	4·9	13·70
S.E. of increase		0·379	1·21	0·978

* Grain at 15% moisture content.

The work started in 1960 (*Rep. Rothamst. exp. Sta.* for 1961, p. 51) on the effect of N-fertiliser on the soluble carbohydrate content of grass continued and recent results confirmed those reported earlier. Estimating the nutritional value of grass by chemical analysis is handicapped because we lack precise information about the amount of the carbon of soluble carbohydrates converted into microbial tissue by rumen micro-organisms. Nevertheless, we suggest that the total soluble carbohydrate carbon/soluble nitrogen ratio may be a better criterion than the conventional ratio of total soluble carbohydrate/crude protein. If 20% of the carbon of soluble carbohydrate is converted into microbial tissue there will be no excess of NH_3 in the rumen when the soluble carbohydrate carbon/soluble nitrogen ratio is about 25. (Nowakowski)

Interactions of water, nitrogen and potassium in glasshouse experiments on ryegrass. The effects of water supply on N–K relationships in perennial ryegrass were investigated in a glasshouse experiment using Woburn sand and Rothamsted clay soils. Three levels of water, two levels of N, and four levels of K were tested. The crops on the two soils behaved similarly. Decreasing the water supply decreased dry matter yields and also the percentage of total water-soluble carbohydrates, but it increased % total-N, % NO_3-N and % K in the grass at all N and K levels. These effects of water were greatest with most N.

Potassium fertilisation had no effect on the percentage of water-soluble carbohydrate at either of the N levels, nor any effect on the dry matter yield at the lower N level. However, K increased yield greatly at the higher N level. Increasing the K level increased % NO_3-N in grass receiving intermediate and small amounts of water; nitrate accumulation seemed unrelated to the cation–anion balance in the grass, because the total N taken up was the same at the different levels of applied K, whereas K uptake increased with the amount given.

The larger dressings of N increased yield and decreased the percentage of total water-soluble carbohydrate in the grass.

In general, lessening available water seems to affect ion absorption less than the growth and metabolism of the plant. (Shapiro, Nowakowski and Arnold)

Comparison of Sitka Spruce and Norway Spruce in Forest Nurseries

Between 1945 and 1958 Sitka spruce (*Picea sitchensis*) was grown in many experiments on nutritional problems in forest nurseries. In later experiments Norway spruce (*Picea abies*) were included because the transplants often showed a reddish-brown discoloration (a colour symptom different from any seen in Sitka transplants), and because in some production nurseries they developed a severe, often fatal, scorch, while the Sitka alongside remained healthy. In 1959 plots in two existing experiments on seedbeds (at Bagley (Oxford) and Wareham (Dorset) nurseries) and two on transplants (at Wareham) were split to compare the two species.

Seedlings. In the four years (1959–62) results for Sitka and Norway spruces were closely comparable, except that there were slight differences in colour symptoms, particularly those caused by K-deficiency. Both species showed large and consistent height responses to N and P at both Bagley and Wareham nurseries and also to K at Wareham; well-defined deficiency symptoms were caused by lack of N, K and Mg.

Transplants. From 1959 to 1961 both species responded similarly: there were moderate height increases from N, small or no increases from P and large increases from K. The reddish-brown discoloration previously observed in non-experimental beds was found to be a K-deficiency symptom (under these conditions Sitka spruce show purple colours).

Spring 1962 was very cold and windy, and June was dry; in July Norway spruce suddenly developed a severe rusty red "scorch" on many plots, and many plants subsequently died; on the same plots Sitka spruce remained normal and green. The P, K and Mg fertilisers had been dug in during the second half of February and the plants lined out in mid-April. This interval of seven to eight weeks between the two operations is normal. "Nitro-Chalk" and ammonium sulphate were applied as top-dressings in mid-May, end of June and end of July. The damage was associated with dressings of KCl and of superphosphate, but $MgSO_4$ caused no harm. "Scorch" was particularly severe on plots long treated with ammonium sulphate which had become very acid; "Nitro-Chalk" greatly lessened the "scorch" in one experiment, but had little effect in the other. Again in 1962 characteristic K-deficiency symptoms developed in both species on the "no K" plots; where bracken–hopwaste composts had been given, no "scorch" occurred.

Damage resembling that in these experiments was reported from production nurseries over a wide area of England and Scotland in 1962. Severe fertiliser "scorch" of Norway spruce transplants described by Němec (*Bodenk. u. PflErnähr.* (1939), **13**, 35–72) was attributed to chloride injury on very acid soils. The trouble was aggravated by drought and by too short an interval between applying fertiliser and lining out; the number of dead trees increased rapidly as the interval decreased from 42 days to none. (Benzian)

Investigations of Crop Failures on Shallow Soils

Much field and laboratory work has been done to find the exact causes of poor crops growing on some shallow soils in the recent series of years with dry springs. Although the effects are associated with water shortage, it seemed possible that there were also nutritional effects which, if corrected, would have improved the crops. Two soils were investigated in Lincolnshire; one was a shallow stony soil developed on Cornbrash, the other a light-textured alluvium over calcareous gravel. The second site was in Hertfordshire, where light gravelly soils overly glacial sands and gravels. All the non-irrigated crops observed were affected, but the field work was only with cereals. On all three sites early establishment and growth was good, but in dry springs the crops stopped growing in May or June, and later they withered. Soil examinations (including detailed mapping of the Lincolnshire areas by C. A. H. Hodge and R. S. Seale) showed that crop growth varied with depth of soil and that the worst failures were where massive limestone or coarse gravel were nearest to the surface. In the work described briefly below staff of Chemistry and Pedology Departments and the Soil Survey were mainly involved, but D. Slope (Plant Pathology Department) and Mary Franklin and Audrey Shepherd (Nematology Department) also examined the crops. Take-all was found in 1960 on wheat and barley from the Lincolnshire sites, but was eliminated by changes in the rotations used. Although cereal-root eelworm were present, they were not numerous enough to have caused any serious damage.

Composition of soils and crops. The only unusual feature of a spectrographic examination of the soils was that both the Lincolnshire and Hertfordshire soils had detectable levels of beryllium soluble in 0·5*N*-acetic acid; this element is not normally detected in soils. (Le Riche) As very little is known of the effect of beryllium on plants, a pot experiment testing various levels of Be is being done. (Williams)

Analyses of samples of ryegrass and cereals from Lincolnshire for major nutrients and micronutrients, and for heavy metals, gave values within the ranges regarded as normal except that % Cu was small in some of the crops and % Mg in all. (Le Riche, Arnold, Cunningham and Williams) Nitrate–nitrogen was large in all the stunted crops that were sampled, but especially oats (nearly 800 ppm) and spring wheat (1,100 ppm). Two samples of spring wheat that were examined in detail showed that the crop that was failing ("unhealthy") had very abnormal metabolism. A "satisfactory" sample had a normal distribution of the fractions of N determined, but the "unhealthy" sample had unusually much total soluble-N, NH_3-N and amide-N (especially glutamine-N). Large total N values are usually associated with small values for soluble carbohydrates, but with these samples the reverse was true. (Nowakowski)

Equilibrium studies on the soils suspended in 0·01*M*-$CaCl_2$ solution showed that those from Lincolnshire contained very little K or Mg and that dressings of K fertilisers were likely to depress uptake of soil Mg even further. (Arnold)

With this background information, obtained mostly in 1961, several field experiments were done in 1962, and detailed observations were made on crops and soils. One experiment done by Mr. L. H. Manning (Imperial Chemical Industries Ltd.) tested 15 tons/acre of farmyard manure and heavy dressings of kieserite, basic slag and ordinary superphosphate for barley on shallow soil overlying Corallian limestone in Lincolnshire. The crop "scorched" and withered in June, and none of the treatments had any effect. Each of the micro-nutrients B, Cu, Mn, Mo and Zn was tested (by Widdowson and Penny) in microplot experiments superimposed on the large main plots of the experiment; none of the micro-nutrients had any effect on growth.

Nitrogen and copper experiments. One experiment on spring barley in Lincolnshire, and one on barley and one on winter wheat in Hertfordshire, measured the effects on yield of foliar applications of copper oxychloride (3 lb in 20 gallons of water/acre) at increasing N levels. The copper spray severely scorched the moist leaves of wheat and barley at two centres, but not dry barley leaves at the other centre. The copper spray decreased the yields of "scorched" wheat and barley in Hertfordshire by 2·6 and 1·1 cwt/acre respectively. The experiments were not sufficiently precise to determine whether nitrogen and copper interacted.

These barley experiments also measured the responses to several nitrogen fertilisers. In Lincolnshire ammonium sulphate, urea and sodium nitrate were compared broadcast, combine-drilled or side-placed. Yields without N were exceptionally small (Table 9) and 0·70 cwt N/acre increased yields only to levels normally associated with barley grown without any N fertiliser on local Chalk soils low in soil N. Sodium nitrate gave rather more grain than did ammonium sulphate. In Hertfordshire yields without N were also small (Table 9), but more than double those in Lincolnshire; 0·3 cwt N/acre slightly increased yield, but with 0·9 cwt N/acre yields were decreased and were less than those on plots without N. (Widdowson and Penny)

TABLE 9

The effects of N fertilisers on yields of barley grown on two shallow soils in 1962

(in cwt/acre of grain at 15% moisture content)

N applied, cwt/acre	0·0	0·35	0·7	
Lincolnshire (alluvial sands and limestone)	4·1	10·8	13·3	
N applied, cwt/acre	0·0	0·3	0·6	0·9
Hertfordshire (glacial sands and gravels)	10·1	12·0	11·4	9·0

Measurements of mineral-N in fresh Lincolnshire soil taken in spring, when the experiments were laid down, and of mineralisable-N in the same soil after air-drying, showed very little available-N. Further soil samples, and barley plant samples, were taken in mid-June from plots with and without fertiliser-N. The soil analyses showed that all the fertiliser-N applied in the spring had been lost from the surface soil; plant analyses showed that, on the plots sampled, only 15–26% of the high rate of N applied in the spring had been recovered in the above-ground parts of the barley. Measurements of mineral-N down to 25 in. in fertilised but *uncropped* soil gave no indication that fertiliser-N had been leached down the profile. (Spring rainfall was less than average.) Not only is the Lincolnshire soil very poor in available-N but it also appears that fertiliser-N is inefficient and is easily lost by some process that has not yet been identified. (Gasser)

Tests of potassium and magnesium for barley. Tests were made in Lincolnshire of heavy dressings of potassium and/or magnesium sulphates broadcast over the ploughed land and then rotary cultivated; 4 and 8 cwt/acre of potassium sulphate and chemically equivalent amounts of kieserite were tried. The young plants growing on plots dressed with magnesium sulphate had dark-green leaves; on other plots they were pale green. Symptoms associated with Mg deficiency were made worse by K dressings. Dry weather limited yield, but at harvest yields of grain and straw (Table 10) were increased by Mg and decreased by broadcast K. Combine-drilling potash also decreased yields. (Widdowson and Penny)

Samples taken in May 1962 showed that the % K : % Mg ratio was large (14) in barley receiving heavy K manuring without Mg; when Mg was

https://doi.org/10.23637/ERADOC-1-95

given as well as K the ratio fell to 12, and where Mg alone was applied it was 8. (Williams)

TABLE 10

The effects of potassium and magnesium fertilisers on barley yields

(grain and straw in cwt/acre containing 15% moisture)

	Grain yields			Straw yields		
Magnesium rate applied	None	Low	High	None	Low	High
Potassium rate applied:						
None	20·5	22·9	22·0	9·1	10·5	10·4
Low	19·6	19·9	22·2	6·8	9·9	10·1
High	16·3	21·9	21·4	7·2	9·5	10·9

Physical conditions. The experiments showed that although there were nutritional problems on these soils (such as acute N deficiency, Mg deficiency and Mg/K antagonism in Lincolnshire), correcting these deficiencies gave only small improvements in yields. As the 1962 crops appeared to have no obvious pests or infectious diseases, the major reason for the spectacular failures observed seems to be shortage of available water in the shallow soils. Local meteorological records for South Lincolnshire show that potential evapotranspiration had seriously exceeded rainfall at the end of May in each of the years 1959, 1960 and 1961, when it is known that crops on the shallow soils yielded badly. Deficiencies at the end of May ranged from 2 to 4 in. and at the end of June from 5 to 7 in. of water; for satisfactory growth these deficits must be supplied from reserves in the soil. In 1962 the typical symptoms associated with previous failures had appeared by 5 June; at this time accumulated evapotranspiration for April and May already exceeded rainfall for these 2 months by 1·3 in. By 28 June most of the crops on the affected areas had deteriorated seriously. Cereals did not wilt, but they showed symptoms which we now recognise as characteristic of drought. Wheat had rigid and upright leaves, bluish but "scorched" at the tips; barley was stunted and leaves became yellow and withered from the tips downwards, the ears failed to emerge. Symptoms on some of the barley leaves could be mistaken for those of early copper deficiency. But P. J. G. Mann (Biochemistry Department) found that the level of ascorbic acid oxidase, a copper-containing enzyme, was of the same order as that in normal barley crops growing at Rothamsted. At the end of June the excess of potential evapotranspiration over rainfall for the preceding 3 months was 5·3 in.

To have satisfactory crops, soil must supply enough water to allow transpiration to proceed normally. Estimates of the water-holding capacities of the soil profiles were made and are given below, together with mechanical analyses of the two gravelly soils under affected crops:

(sizes in mm)	Lincolnshire	Hertfordshire
Stones, >6	13	34
Gravel, 2–6	7	4
Coarse sand, 0·2–2	50	39
Fine sand, 0·02–0·2	13	10
Silt, 0·002–0·02	3	4
Clay, <0·002	5	5
Water-holding capacity (w/w)	33	18

https://doi.org/10.23637/ERADOC-1-95

Both soils were very coarse, 83% of the Lincolnshire soil and 87% of the Hertfordshire soil being in particles of fine sand size and larger. Water-holding capacities were small; no good field capacity measurements were obtained, but sampling before and after sowing suggested that the Lincolnshire soils over gravel never had more than 10% water (on oven-dry basis), while uncropped areas of the heavier soil over Corallian limestone contained only 16% water in spring.

Top-soil compositions above are for the first 20–24 in. Immediately below, the subsoil under the area examined varied from interlocked fragments of limestone to coarse calcareous sand. Measurements in June showed that top-soils under poor crops had only about 5% of water, while under the better crops on deeper soils there was about 8% water. At this time the poor gravelly subsoil contained less than 2% of water (oven-dry basis). The pore space of the unsieved subsoil (from density measurements) was 39%, but at 60 cm of water suction it contained only 5·6% water. Most of the pores had equivalent diameter >0·05 mm, and more than 90% of the maximum water the subsoil could hold at full saturation was removed by this very moderate suction (60 cm). Taking average soil depth as 18 in. above the coarse subsoils, it is difficult to see that more than 3 in. of water could be available to crops in the soil at sowing. As evapotranspiration exceeded rainfall for the spring months by more than 3 in. at the end of May in some years, and during June in all of the last four years, it is clear that this was the main cause of the crop failures. The gravelly Lincolnshire soils showed signs of gleying, indicating that drainage had been impeded in the past (C. A. H. Hodge); drainage has recently been improved by deepening ditches, and over most of the area the water table in summer is below 9 ft. As the subsoil is so coarse, drainage is rapid and, with the large head above the water table, most of the topsoil water is removed. (An unsatisfactory feature of both soils is that they hold very little water at high tension.) The open subsoil and good drainage also prevent any rise of water from subsoil to surface soil. Local tradition on the Lincolnshire soils that overly gravel was that the soils were never ploughed deeply, but they were well rolled after sowing cereals. These measures to conserve water, together with higher water tables before the land was drained deeply, may have led to better crops in the past in dry years than have been obtained recently (but probably the high water tables made the land unworkable in winter).

At both centres the cereal failures were patchy. On the limestone soil in Lincolnshire narrow ridges of a normal good crop often ran irregularly through areas of stunted crop in "basins" up to 10 yards across. C. A. H. Hodge showed that these followed cracks where the underlying limestone was shattered. Under the withered areas the limestone pavement was continuous 12 in. below the surface, and it could be shattered only with a pick; where growth was normal limestone fragments in a clay matrix could be brought up from 20 in. by auger. Elsewhere on areas with gravel subsoil normal growth often occurred in strips running east and west. C. A. H. Hodge excavated one of these and found 26 in. of loamy soil overlying sand under the normal barley, but only 14 in. of comparable topsoil beneath the poor crop; he considers that these strips result from the "lands" of old ploughing systems. On this kind of soil there was one area where excellent crops formed a series of vertical "walls" above the usual withered areas. This was excavated (by Williams); under the area where the crop failed, massive limestone was 12 in. deep. This changed abruptly to a loamy soil made of limestone fragments and clay at least 42 in. deep. Fragments of coal and burnt limestone suggested that the area had been used as a limestone pit and kiln for lime-burning; the depressions seem to have been filled in after lime-working ended long ago.

Pot experiments on barley using unsieved field soil done in large containers showed that the Lincolnshire gravel soil restricted rooting much more than the Hertfordshire soil, particularly when the pots were kept dry. Lincolnshire soil had good physical properties in the field, but in pots it was slow to wet. When adequate water was given, magnesium dressings increased root growth in both soils; there were no crown roots on barley grown on Lincolnshire soil unless Mg was given. (Williams and Widdowson)

Soil Structure and Nutrient Uptake

Nutrient uptake by crops is affected by physical properties of soil, and a start has been made with examining some of the factors involved. Two soils from Barnfield, treated continuously with NPK fertilisers and with FYM respectively, were used in "good" and "bad" physical conditions. Good structure was that of the soil from the field, and "bad" structure was obtained artificially by puddling; both samples were then frozen and thawed to prepare aggregates for laboratory and greenhouse work. The effects of structure on rate of nutrient release were examined by repeated leaching with 0·01M-$CaCl_2$ solution. For most of the aggregate sizes chosen the rate of leaching of NO_3-N was not affected by differences in structure. The amounts of P released were not consistently related to differences between good- and bad-structured soils. With all the aggregate sizes used, and with both soils, most K was released from the bad-structured soil; more K was usually extracted from small than from large aggregates. Differences in the nutrients removed by ryegrass from these two soils are now being examined in a pot experiment. (Cornforth and Cooke)

Nitrogen in Soils

"Fixed" ammonium. Results from further experiments on isotopic exchange reactions between 0·01M-$^{15}NH_4Cl$ and NH_4-hydrobiotite showed that the presence of $^{15}NH_4$ in the fixed fraction was from adsorption and not isotopic exchange as at first thought. It is difficult to saturate hydrobiotite completely with NH_4, for the lattice contracts to the smaller layer spacing characteristic of NH_4-hydrobiotite before all the outgoing cations have been desorbed, so that the movement of cations between the layers is restricted. Our tracer experiments showed that a slow movement was still possible and the amount of $^{15}NH_4$ adsorbed was proportional to the logarithm of the reaction time when this exceeded 2 hours. Only part of the KCl-exchangeable NH_4 was exchangeable with $^{15}NH_4$, and this

https://doi.org/10.23637/ERADOC-1-95

difference was almost independent of the concentration of the KCl extractant. The effect may therefore be attributed to a difference in the affinities of K and NH_4 for hydrobiotite.

Other experiments studied the conditions necessary to desorb "fixed" NH_4. K was removed from hydrobiotite by extracting with sodium tetraphenylboron ($NaBPh_4$), and replaced by NH_4. Ammonium in the mineral was desorbed by shaking with NaCl–$NaBPh_4$ solution, which precipitates insoluble NH_4BPh_4. After 24 hours almost all the NH_4 was removed, but no rate-determining step could be identified. This suggests either that the exchange surface was heterogeneous or that more than one kinetic process was occurring. When $CaCl_2$ or NaCl was used as the extracting solution an equilibrium NH_4 concentration was established after 3 days. With 0·1*M*-NaCl all the NH_4 was desorbed after four extractions, but with 0·01*M*-NaCl 60% of the NH_4 was removed after six extractions. Mass action quotients for the reaction

$$Na^+ + NH_4\text{-hydrobiotite} \rightleftharpoons NH_4^+ + Na\text{-hydrobiotite}$$

were calculated for each extraction, and they increased from 0·001 at 5% exchange to 0·006 at 50% exchange, but fell sharply to 0·002 at 60% exchange. This behaviour again suggests that the exchange surface is heterogeneous.

NaCl solution removes K from hydrobiotite and also NH_4 from hydrobiotite in which K has been replaced by NH_4. NH_4-natural hydrobiotite, still containing its original K, released NH_4 but not K when treated with NaCl. This inhibition of K release by NH_4 merits further investigation. (Newman)

Some effects of sterilants on soil nitrogen. Sterilants applied to soils for controlling parasitic nematodes retard nitrification of NH_4-N whether this is formed by mineralisation of soil organic-N or added. The effects of several sterilants on the mineralisation of soil-N and its nitrification were measured. Dazomet, D-D, metham-sodium and methyl isothiocyanate were applied to seven glasshouse and four field soils; methyl bromide was applied to two of the field soils only. In both the glasshouse and field all sterilants retarded nitrification of ammonium-N, and in some soils increased the mineralisation of soil organic-N; dazomet had most effect and metham-sodium least. In field soils methyl bromide increased the mineralisation of soil organic-N more than twice as much as the other sterilants. (Gasser and Peachey)

Extraction of easily mineralised nitrogen. The value of a short extraction with cold barium hydroxide solution for detecting an active fraction of soil nitrogen was tested. If mineralisation of organic N occurs throughout the biomass in amounts proportional to the size of the biomass, and if $Ba(OH)_2$ extracts a constant fraction from the biomasses of different soils (the non-nitrate-N extracted being proportional to the C extracted), then a linear relationship between N extracted by $Ba(OH)_2$ and amounts of N mineralised in incubation tests may be expected. Forty-two different soils used by J. K. R. Gasser (*J. Sci. Fd Agric.* (1961), **8**, 562) which had been stored air-dry were examined. There were very high correlations ($r = 0{\cdot}97$, 0·95 and 0·99 for soils sampled from field experiments done in 1957, 1958 and 1959 respectively) between non-nitrate-N dissolved by $Ba(OH)_2$ and the mineral N released by incubating air-dried soils in Gasser's work. (A few soils with pH of 6·3 and below were excluded.) There were also good correlations between the N extracted by $Ba(OH)_2$ and the uptake of N by ryegrass in pot experiments done by Gasser ($r = 0{\cdot}84$, 0·83 and 0·99 for the soils sampled in the 3 years). Barium hydroxide extracts more N from a soil with a pH below 6·3 than from a soil with the same capacity for releasing N but with a pH above 6·3. pH 6–6·5 is the critical range above which the N mineralised in incubation tests is not increased by liming; it may be that qualitative changes in the biomass are reflected in the amounts of nitrogen extracted by $Ba(OH)_2$. (Jenkinson)

Phosphorus in Soils

Methods of analysing calcareous soils for soluble P. Work on the availability of the phosphorus present in highly calcareous soils in S.W. England, done in collaboration with Mr R. D. Russell, National Agricultural Advisory Service, Bristol (*Rep. Rothamst. exp. Sta.* for 1958, p. 51), was completed. The soils used came from eight field experiments on Jurassic Limestone (Sherborne series) where no superphosphate had been applied for 7 years to some plots, and 0·4 and 0·8 cwt P_2O_5/acre had been applied to others, and also from 10 plots of an experiment on Carboniferous Limestone (Lulsgate series) receiving differential P manuring for 7 years.

For the Sherborne soils best correlations between P uptake by ryegrass in the greenhouse, 40 days after sowing, and soil analysis were with $0{\cdot}5M$-$NaHCO_3$ ($r^2 = 0{\cdot}920$) and the worst with 1% citric acid ($r^2 = 0{\cdot}486$). Other methods ($0{\cdot}5N$-acetic acid, $0{\cdot}01M$-$CaCl_2$, $0{\cdot}5N$-acetic acid–sodium acetate and isotopically exchangeable P) accounted for between 63 and 81% of the variation in P uptake at the first cut of grass. For the Lulsgate soils (from a single site) all correlations between P uptake and soil analysis were higher ($r^2 > 0{\cdot}88$) except with 1% citric acid ($r^2 = 0{\cdot}68$). For both groups of soils $NaHCO_3$-soluble P was the most reliable laboratory test, Morgan's reagent the second best and 1% citric acid the worst.

An unusual feature of results with the Sherborne soils was that neither the intensity measurements in $0{\cdot}01M$-$CaCl_2$ nor isotopically exchangeable P were as closely correlated with P uptake at the first cut as some of the conventional methods of analysis. When the P concentration in $0{\cdot}01M$-$CaCl_2$ (on a logarithmic scale) was plotted against isotopically exchangeable P, separate and nearly linear relationships were obtained for the soils from each experiment. The slopes of these lines measure "P absorption capacity" for each soil. The Lulsgate soil had the least "capacity" (or steepest slope) and the heavier Sherborne soils generally had larger capacities.

The very small solubility of P in some of the Sherborne soils, rather than any acute P deficiency, seems to be their main characteristic. The concentration of P in $CaCl_2$ on soils from several sites was still only $0{\cdot}8$–$1{\cdot}2 \times 10^{-6}$ moles P/litre, even where 0·8 cwt P_2O_5/acre/year had been given for 7 years.

Correlations between isotopically exchangeable P were much closer for the total P uptake by ryegrass in three cuts than at the first cut of grass. The correlation coefficients for eight Sherborne soils were:

P uptake	$CaCl_2$ solution	Isotopically exchangeable P
First cut	0·796	0·861
Total for 3 cuts	0·560	0·979

When soils were used from a single field experiment for which there was a simple and nearly linear relationship between measurements of P concentration and of the "labile pool" of P either measurement is closely related to P uptake at *any stage of growth of grass*. This is illustrated by correlation coefficients below for the 10 Lulsgate soils (Mattingly and Jephcott):

P uptake	$CaCl_2$ solution	Isotopically exchangeable P
First cut	0·938	0·996
Total for 4 cuts	0·938	0·989

Potassium in Soils

The use of Rb–K exchange studies in determining K status of soils. The kinetics of the release of K from K-bearing minerals in soils was explored, assuming that the Ratio Law governs the composition of the soil solution after "instantaneous" surface exchange has occurred. The subsequent slow changes in Rb–K ratio of the soil solution as exchange diffusion brings new internal surfaces into play were assumed to be similarly controlled. The radioactive ^{86}Rb isotope was used for tracing changes in Rb concentrations. Early difficulties were caused by small concentrations of Rb being strongly adsorbed on glassware. The kinetics of Rb–K exchange in 12 soils selected from earlier work (*Rep. Rothamst. exp. Sta.* for 1961, p. 57) were examined; rapid exchange was completed in less than 15 minutes. The subsequent behaviour of the exchange process was specific to each of the soils, but generally increases in "exchangeable" K were small after 2½ days of reaction time. With soils where crops do not respond to K fertilisation, or which release more K than is predicted by "free energy change" values, there are large increases between the 15 minutes and the 60 hours "exchangeable" K values. These methods may be useful in extending our information on the K-supplying power of soils. (Talibudeen)

Magnesium in Soils

Forty-one English and Welsh soils were exhaustively cropped with perennial ryegrass and some with white clover in a glasshouse. Releases of non-exchangeable Mg were small compared with the amounts of exchangeable Mg initially present. The residual exchangeable Mg of some "exhausted" soils increased after wetting and drying, suggesting that exhausted field soils may recover Mg status by a similar process. Crops obtained nearly all their Mg from exchangeable and water-soluble forms, and the equilibria between these two fractions were studied. Variations in the activity ratio

$$\frac{a_{\mathrm{Mg}}}{a_{\mathrm{Ca+Mg}}}$$

were not entirely from differences in the total cation-exchange capacities of the soils. The Ca–Mg equilibria of an illite and a bentonite were almost identical, but Mg was held much less strongly by a fen peat soil, suggesting that some of the variations between Ca–Mg activity ratios may be associated with different organic matter contents.

Exchangeable soil Mg was poorly correlated with Mg contents of ryegrass in glasshouse experiments. The % Mg in the crops was, however, related to the cation-activities in soil solutions; the effects of varying exchangeable Mg, Ca, K and of soil pH can be explained by ionic competition in the soil solutions from which Mg is taken up. Ion activity ratios of the form

$$\frac{\sqrt{a_{\mathrm{Mg}}}}{\sqrt{a_{\mathrm{Ca+Mg}}} + \mathrm{B}.a_{\mathrm{K}} + \mathrm{C}.a_{\mathrm{H}}}$$

obtained by analysing equilibrium soil solutions, were well correlated with Mg contents of the ryegrass. The proportionality factors B and C in the denominator take account of the relative abilities of "antagonistic" ions to compete with the dominant Ca + Mg soil cations in uptake processes. Their values depend largely on the crop grown, and they can be determined for each experiment.

When relating plant composition to cation activity ratios the main *practical* difficulty is that activity ratios determined before cropping alter to varying extents in different soils during cropping. This effect is particularly important with ions such as K, of which large amounts are removed. When other active ions, such as Na or NH_4, are considerable their competitive influence on Mg uptake will also have to be considered. (Salmon and Arnold)

Potassium–magnesium relationships. Field experiments at Rothamsted and Woburn testing potassium (as K_2SO_4) and magnesium (as $MgSO_4$) (*Rep. Rothamst. exp. Sta.* for 1961, p. 57) were sown with red clover in spring 1962. At Rothamsted the crop grew badly. At Woburn the clover yield was increased three times by K and there was a small but significant response to Mg. The % Mg in the second harvest of dry clover at Woburn ranged from 0·19 to 0·43, the % K from 0·91 to 2·8 and the % Ca from 2·0 to 2·7; Table 11 gives K : Mg ratios for this second harvest. (Arnold and Penny)

TABLE 11

Effects of K and Mg dressings on the ratios of K: Mg in red clover at Woburn

	Mg applied (lb/acre)		
	0	29	58
K applied (lb/acre)	Ratios of K : Mg (in equivalents)		
0	1·64	0·80	0·70
95	3·38	1·82	1·32
190	4·94	2·93	2·49

Cation–Anion Relationships in Crop Nutrition

Previous work (*Rep. Rothamst. exp. Sta.* for 1961, p. 60) showed that the sum of the cations ($Na + K + Ca + Mg$, expressed in m.e./100 g dry matter) ranged widely in several samples of Italian ryegrass that were grown at different places in Britain. Work with over 100 grass samples showed that total cations were positively correlated with total anions and with % N, and depended on the form of N (NH_4-N or NO_3-N) taken up by the grass. The greatest value obtained for total cations was 205 m.e./100 g when NO_3-N was added, but the regression equation of the relationship between total cations and total anions suggested that the maximum cation content had not been reached.

The total cation : total anion ratios $\left(\frac{Na + K + Ca + Mg}{N + P + Cl + S}\right)$, termed *R* values, ranged from 0·33 to 0·93. *R* was negatively correlated with % N and depended on the form of N absorbed by the grass; *R* did not depend on % K. Good negative correlation between *R* and % N was obtained when Italian ryegrass was grown in a Rothamsted soil in the glasshouse, but the curve plotting the *R*–% N relationship did not coincide with that of samples grown in a similar soil in the field with the same form of N. Possible reasons for this, such as different soil temperatures, light intensities, water relationships and the effects of rewetting the soil after air-drying, are now being investigated by pot experiments. *R* values in various agricultural and horticultural crops were measured. *R* and % N were negatively correlated and, for the same N level, dicotyledons had greater *R* values than monocotyledons.

Italian ryegrass and kale were grown at three levels of 10 nutrients (Na, K, Ca, Mg, NH_4-N, NO_3-N, P, Cl, S and Si) on a sandy loam and a clay loam. The effects on yields and mineral composition were measured. Changes in mineral composition were greater in the ryegrass and on the sandy loam. "Apparent" ion interactions were caused by secondary or indirect effects, such as increase in yield. The "real" negative-ion interactions (antagonisms) were: Na with K and Ca; K with Na, Ca, Mg; NH_4-N with K; and Cl with S. The "real" positive ion interactions (synergisms) were NO_3-N with Na, K and Mg, and Cl with K. Na and K were the only ion pairs which showed mutual effects. Equivalent replacement of one ion by another ion was not found. (Cunningham)

Pot experiments in the greenhouse in winter 1961–62 and summer 1962 measured the maximum level of cations in Italian ryegrass. Several levels of an NPKCaMg mixture containing NO_3-N was used in the winter experiment; this nutrient mixture and another mixture, similar but containing NO_3-N and NH_4-N in the ratio 3 : 2, were used in the summer experiment. At the same nutrient levels the summer yield was twice the winter yield. With NO_3-N only the maximum levels of cations and anions were 333 m.e. and 415 m.e./100 g dry matter in the winter and 193 m.e. and 284 m.e. in the summer. When the source of N included some NH_4-N the maxima were 177 m.e. and 261 m.e. These results show that the maximum cation value of 200 m.e. (Dijkshoorn, *Neth. J. agric. Sci.* (1957), **5**, 233) is an underestimate and also that the total cations in Italian ryegrass depend on the season and the form of N taken up by the plant. The total cations and the total cation : total anion ratios (R) were correlated with % N in the crop, positively and negatively respectively. The *R*–% N relationship was affected by the form of nitrogen but not by the season. (Karim and Cunningham)

The difference between the *R*–% N relationship curves for Italian ryegrass grown in the greenhouse and in the same soil in the field may be caused by soil temperature among other factors. Ryegrass is therefore being grown in a Rothamsted clay loam at six levels of NO_3-N and NH_4-N in closed pots at 11°, 19·5° and 28°, to test the effect of soil temperature on the *R*–% N relationships. Nitrification of added NH_4-N is stopped by using 2-chloro-6-(trichloromethyl)pyridine. (Nielsen and Cunningham)

Micronutrients in Crops and Soils

Boron in Rothamsted crops. We are beginning to survey the micronutrients in crops grown on the Rothamsted Farm. Values for boron (determined colorimetrically by the dianthrimide method) in several crops from selected plots of the field experiments are below:

Boron in crops

(ppm B in dry matter)

	Grain	Straw
Wheat and barley	1	2–3
	Tops	Tubers or roots
Potatoes	35–40	6
Swedes	35–40	25–30
Sugar beet	30–40	15
Kale	25–40	—
Lucerne	30–40	—

There was no difference between the B contents (in ppm) of wheat (grain and straw) from the farmyard manure plot of Broadbalk (2B) and the plots receiving full fertilisers (7 and 8), nor was there any increase from farmyard manure on barley in the Hoosfield Permanent Barley Experiment. Increasing rates of fertiliser N did not affect the concentration of B in the wheat of the Highfield and Fosters ley–arable experiments. Sodium silicate in the Hoosfield experiment, however, decreased the boron from 3·4 to 2·3 ppm in barley straw where K fertiliser was given; there was no effect on grain. The concentration in tops and roots of swedes was not changed by P or K manuring, but potato tubers contained 2 ppm less B when given P fertiliser. K manuring sometimes diminished the B content of kale and sugar-beet tops. Many of the differences in B content produced by manuring had no effect on uptakes of B per acre. The amounts of B in the crops analysed seem adequate, and the differences found between some samples are unlikely to affect yields. (Chater and Warren)

Interactions of manganese and phosphate in soils. Previous work showed that manganese phosphates of various compositions were precipitated from aqueous solutions at pH values above 5·5–6·0 unless they contained a great excess of Mn. How added phosphates affects the availability of native or applied soil Mn has now been studied. Two alkaline fen soils were incubated after adding monocalcium phosphate and manganese sulphate. At the three levels tested, adding phosphate decreased exchangeable Mn but had no effect on readily reducible Mn. In a pot experiment oats were grown on a Mn-deficient alkaline sandy fen soil; three levels of P and three levels of Mn were tested as monocalcium phosphate and manganese sulphate respectively. Mn without P increased grain yields, whereas P alone lessened them; both effects were highly significant. The effects of two rates of P at two levels of Mn are set out below:

	Gains in dry matter yield (g/pot)	
	Grain	Stalks + leaves
From P at low rate:		
With low Mn	−1·43*	5·7*
With high Mn	−0·05	3·5*
From P at high rate:		
With low Mn	−2·23*	6·5*
With high Mn	−0·16	4·9*

(* $P = 0{\cdot}05$ or less)

Increasing manganese offset the loss in grain yield caused by both levels of phosphate; yields of stalks and leaves were increased by phosphate, but most with the smallest Mn dressing. These results do not support the suggestions of other workers that the availability of Mn on Mn-deficient soils is increased by applying an "acid" phosphate such as monocalcium phosphate or superphosphate.

The amounts of Mn and P in the grain confirmed that moderate phosphate dressings given to this alkaline Mn-deficient organic soil did not liberate enough Mn to reach the grain. (Heintze)

Ion equilibria involving manganese. Preliminary correlations were made between the ion-activity ratio $\frac{Mn^{++}}{Ca^{++} + Mg^{++}}$ (measured in $0{\cdot}01M$-$CaCl_2$ solutions) with Mn taken up by crops. The ratios are considerably less for organic than for mineral soils at equal pH values; when pH was raised above 5·5 the ratios decreased rapidly in all kinds of soil. Some soils showed linear relationships between the equilibrium ion-activity ratios and Mn uptake, but correlations appeared to be complicated by other factors such as soil pH. (Heintze)

Natural Radioactivity in Soils

Work reported earlier (*Rep. Rothamst. exp. Sta.* for 1958, p. 59, and for 1961, p. 62) was extended. Assay with a B24 Geiger–Müller counter, using 450–600 g of soil showed that more than three-quarters of the 45 soils examined had β $(+\gamma)$ radioactivity that was significantly larger (to varying degrees) than was predicted from their chemically determined K contents. Ten of these soils were selected from the 1958 work, which was with a smaller M12 counter holding about 20 g soil. Only four soils gave calculated K contents similar to those observed earlier; the other six gave significantly greater values than were obtained with the M12 counter.

The discrepancy between the K contents of uncontaminated soils calculated from their natural radioactivity measured with Geiger counters (predominantly β-emissions) can be primarily attributed to their U and/or Th contents. The γ-spectra of the U and Th families were used to correct for this excess β-radioactivity to obtain the true K content by radioactive assay. The principle was to select one γ-energy emission from each of the U and Th families which could be efficiently resolved by electronic separation of the γ-energy spectra ("pulse height analysis"). Combining the radioactivity measured in these two γ-energy channels with that in the γ-energy channel for the 1·46-MeV emission from ^{40}K (0·0119% in terrestrial K) or its β radioactivity (1·32 MeV) in a Geiger counter, the true K content of the soil should be calculable provided some conditions hold rigorously. These conditions are: (1) the γ photo-peaks are resolved efficiently and with minimal contribution from the Compton scatter from higher energies; (2) the state of radioactive equilibrium of the U and Th families in the soils and the standards is identical; (3) there is little contamination by "fall-out" elements in the soils; and (4) experimental conditions guarantee the stability of the apparatus and the statistical accuracy of the sample count rate above background.

Five soils having β(+ γ) radioactivity values of more than 20% above that predicted from their chemically determined K contents were used to test this principle. The radioactivity was measured in two γ-energy emissions for each of U and Th families, and the 1·46-MeV γ-emission and the 1·32-MeV β-emission for K. Calculated total K contents from these measurements differed widely from the total K contents by chemical analysis, illustrating the danger of choosing the wrong γ-energies in condition (2) and possibly condition (3) above.

Thus, the only reliable radiometric methods of obtaining the total K contents of soils, weathered to very different extents and containing different amounts of U and Th, are: (1) directly assaying the 1·46-MeV γ-energy of ^{40}K suitably corrected for Compton scatter from the higher energies of the U and Th families, or (2) using the measured radioactivity in the complete γ-spectrum of each soil to correct the β-radioactivity values obtained by Geiger counting. Both methods require better nucleonic equipment than we have. A modest beginning is being made with the first method using present equipment. (Talibudeen)

Apparatus and Experimental Methods

Mass spectrometer. Technique was refined and the instrument modified to determine ^{15}N/^{14}N ratios much more precisely. The D.C. amplifier bought last year is very reliable and sensitive, and all observations were made with it. Over 100 determinations of an isotopically normal nitrogen standard made during 3 months had a standard deviation of ±0·8%; 30 determinations of a ^{15}N-enriched standard containing 30% ^{15}N during the same period had a standard deviation of ±0·5% (with the equipment as previously used the value was ±5%). Increased precision requires corresponding care in the other parts of the procedure. So-called "memory" effects, caused by traces of the previous sample being carried forward to the next determination, were particularly troublesome. Contamination during NH_3 distillation in the usual types of still cannot be eliminated conveniently by blank distillations. Two samples containing 350 μg 30% ^{15}N were distilled successively, followed by three blank distillations in which carrier $^{14}NH_4$ was added to the distillate to provide enough N for the isotopic determination. These blanks contained 0·585, 0·475 and 0·425% ^{15}N compared with a normal NH_4 sample containing 0·393% ^{15}N. About 3 μg, or less than 1% of the original 350 μg, was therefore retained by the still, and this percentage is barely detectable even by careful micro-titration. An isothermal distillation procedure is now being tried; it is similar to that used by J. Tinsley *et al.* (*Analyst* (1951), **76**, 300–310) for determining CO_2, and has the advantage that all parts of the apparatus can be rigorously cleaned after use. Even so, a "memory" effect still occurs, probably because NH_3 is absorbed by both glass and rubber; this may be eliminated by using all-glass apparatus which will be autoclaved between determinations.

The vacuum technique used during the conversion of NH_4 to N_2 was refined; there is now no contamination of a sample of about 300 μg N with air by leakage or by desorption from the conversion vessels. With smaller samples, increasing amounts of argon are observed, and correction is made for the attendant nitrogen by assuming that the argon : nitrogen ratio is the same as for air. But as these impurities are probably mainly derived by desorption rather than from an air leakage, they will not normally be in the same proportions as for air, and this correction may not be accurate. Such uncertainties make the ratios obtained less accurate the smaller the amount of N in the sample; so far the smallest amounts of N analysed have been about 40 μg. Probably the technique could be developed to analyse samples as small as 10 μg, but at this level the basic inaccuracies of the instrument begin to be much more important. (Newman)

Determining nitrate–nitrogen in soil and plant extracts. Work on the Zn–Cu couple method as an alternative to the titanous sulphate method was continued. NO_3-N was completely reduced when a solution of pH 1–2 containing 100 μg NO_3-N was treated for 30 minutes at room temperature with Zn–Cu couple (prepared from Zn dust) and the reduced solution together with the Zn–Cu residue was steam distilled with MgO. Nitrate was not completely reduced to ammonia after 30 minutes at room temperature, and the hot distillation with MgO plus the residue of Zn–Cu couple was needed to recover all the N in the distillate. When an aliquot of the solution free from Zn–Cu residue was taken at the end of the cold reduction period and distilled with MgO only 88–92% of the N was recovered.

When titanous sulphate is used reduction is complete at room temperature and ammonia can be distilled in the cold, as in a Conway unit. (Normally the whole procedure is done here in a constant-temperature cabinet at 25°.) When the solutions contain organic nitrogen it is safer to use cold distillation; the Zn–Cu couple method is not then a satisfactory alternative to the titanous sulphate method, as only 80% of the NO_3-N is recovered in a Conway unit. Nitrate was detected in the early part of the 30-minute reduction with Zn–Cu couple but not at the end; hydroxylamine equal to about 3% of the added NO_3-N was found at the end of the period.

The presence of hydroxylamine did not account for the incomplete recovery of NO_3-N in the Conway unit or when the reduced solution free from Zn–Cu residue was steam distilled. (Titrating the distillate to pH 4 would include nitrogen present as hydroxylamine.)

Nitrate–nitrogen measurements by the titanous sulphate method using steam distillation for 4 minutes agree closely with those by cold distillation of extracts from the soils, farmyard manures and plants examined. Where a hot 4-minute distillation is permissible, the Zn–Cu couple method is a simple and satisfactory alternative to the titanous sulphate procedure, provided that the Zn–Cu residue is transferred along with the reduced solution to the distilling flask. A mixture of powdered Zn and $FeSO_4$ as reducing agent gave satisfactory results (98–100% recovery); it avoids preparing the reducing agent needed for the Zn–Cu method and allows reduction and distillation to be done in one operation. The solution containing nitrate, the reducing agent and MgO is added to the distillation flask and steam-distilled for 4 minutes. An advantage of the Zn–$FeSO_4$ method is that the reagent blank is zero. "Technical" brands of titanous sulphate give a blank equivalent to 15 μg N.

The Zn–Cu couple added direct to the distillation flask with MgO and the nitrate solution also gave 98–100% recovery. The Cotte and Kahane method (*Bull. Soc. chim., Fr.* (1946), 542) uses ferrous sulphate with silver sulphate as a catalyst for reducing nitrate, but is said to work only when strong alkali is used for the distillation. The method works well with MgO instead of NaOH, but we know of no advantage over the Zn and $FeSO_4$ method. (d'Arifat and Warren)

Technical titanous sulphate is no longer obtainable, so a substitute reagent using titanous chloride was developed. Nitrate-N was not reduced quantitatively to NH_4-N either by titanous chloride or by "pure" titanous sulphate. Adding ferrous sulphate to the titanous chloride or sulphate solutions greatly increased the percentage of NO_3-N recovered as NH_3 when distilling standard solutions. In a satisfactory reagent the titanous chloride must be converted to sulphate and the correct amount of ferrous sulphate added (when chloride was present only limited amounts of nitrate were reduced quantitatively). The simplest and quickest procedure for making the reagent is to add iron powder to titanous chloride solution acidified with sulphuric acid and boil the mixture while the iron dissolves to expel as much HCl as possible. (Gasser)