Report for 1972 - Part 1

Full Table of Content

Chemistry Department

G. E. G. Mattingly

G. E. G. Mattingly (1973) *Chemistry Department ;* Report For 1972 - Part 1, pp 44 - 65 **- DOI: https://doi.org/10.23637/ERADOC-1-127**

CHEMISTRY DEPARTMENT

G. E. G. MATTINGLY

Practical implications of the work

Wheat and barley yield better on Clay-with-flints soils at Rothamsted than on Boulder Clay soils at Broom's Barn in Suffolk. In the last two years the soil supplied more mineral N, and wheat stems contained more nitrate, at Rothamsted than at Broom's Barn. Giving enough nitrogen fertiliser lessened differences between both wheat and barley yields. Irrigation had smaller and more variable effects; combinations of nitrogen fertilisers and water diminished, but did not eliminate, differences between yields at the two sites.

A combined spray of herbicide (dichlorprop and MCPA) and liquid N fertiliser (urea and ammonium nitrate) 'scorched' spring barley and winter wheat but only decreased yields appreciably when too little nitrogen was given. Extra nitrogen helped to overcome damage done to leaves by the combined spray. 'Nitro-Chalk' and the herbicide generally gave larger cereal yields than liquid nitrogen fertiliser and a herbicide sprayed together. The combined spray 'scorched' permanent grass and diminished yields; a combination of 'Nitro-Chalk' and the herbicide has consistently yielded more herbage.

Julia barley is more susceptible to soil acidity than Maris Badger and, in 1971 and 1972, failed on very acid soils. Yields increased on liming and experiments in three successive years, at Rothamsted and Woburn, show small but worthwhile benefits from liming above pH 7 when Julia barley is grown.

Small dressings of triple superphosphate decreased, and large dressings increased, yields of cotton and beans at Namulonge (Uganda). This unusual effect, which has been recorded elsewhere, is associated with the phosphorus nutrition of cotton in a manganese-rich soil rather than with the chemical behaviour of triple superphosphate in soil. Cotton, grown in nutrient culture and in soil, showed symptoms of manganese toxicity when the supply of calcium was restricted. The extra Ca from large dressings of triple superphosphate seems to counteract the harmful effects of soil manganese. On such soils, phosphate fertilisers with a larger Ca : P ratio than triple superphosphate should be more effective.

Better methods are needed to predict the rate of release of potassium from residues of fertilisers or from the weathering of soil minerals. We describe a laboratory method, using calcium-saturated resins, which measures the rates of release of three different categories of soil potassium, all of which contribute, at different stages of growth, to the nutrition of plants.

Ion-selective electrodes, sensitive to K and NO_3 ions, have been used this year to measure changes in the nitrate and potassium concentrations in soil water without disturbing plant roots. Changes in nitrate concentrations were large and periodic and more nitrate was removed from deeper soil than from surface soil. Potassium concentrations changed less during growth and, where depletions were observed, they lagged behind those for nitrate. With winter wheat, changes in soil nitrate concentrations were largest during the later stages of growth and they probably coincide with a period of rapid root extension.

Experiments with ^{14}C-labelled compounds show that the herbicide 2,4-D breaks down differently in soils which have been sprayed with 2,4-D than in comparable soils which have never been sprayed. The more rapid decomposition of the side-chain in sprayed soils suggests that the microflora have become adapted even to small annual applications of this (or related) herbicides.

Nitrogen fertilisers

Placement of liquid fertilisers for barley. The experiments begun in 1971 to test the value of injecting liquid NPK fertilisers were extended. A liquid fertiliser rig was modified so that, simultaneously with sowing the seed, liquid fertiliser could be (1) injected 7–8 cm deep, midway between pairs of seed coulters spaced 15 cm apart, (2) combine-drilled with the seed, and (3) sprayed over the seedbed in front of the drill. One liquid, rich in urea, contained 14% N, 6% P_2O_5 and 8% K_2O (described as 14–6–8); it supplied all the N needed. The other, with little urea (4–10–10), supplied one-fifth of the N (the balance was broadcast over the seedbed as 'Nitro-Chalk'). Granular 20–10–10 fertiliser was broadcast by the drill to act as the standard. Each was applied to give either 63 or 126 kg N/ha in each of four experiments, two on light loams over Chalk, one on sandy loam over Greensand and one on clay loam over Clay-with-flints.

Visual scores in late April showed a 20–25% improvement in growth (relative to unmanured plots) from broadcasting the granular 20–10–10, from injecting or spraying the liquid 14–6–8 and from injecting the liquid 4–10–10 (with broadcast 'Nitro-Chalk'), but a 60% improvement from combine-drilling the 4–10–10 to act as a starter. By contrast, combine-drilling liquid 14–6–8 diminished growth by 20% with the single amount and by 70% with the double amount; it also killed many plants. However, differences in crop growth became less obvious later in the year.

TABLE 1

Yields of barley grain from four experiments testing liquid fertilisers in 1972

Yields of grain at 15% moisture content (t/ha)
Without fertiliser 3·12

Fertiliser tested		Fertiliser applied to give 63 kg N/ha	Fertiliser applied to give 126 kg N/ha
Granular 20–10–10			
Broadcast		4·78	5·03
Liquid 14–6–8			
Injected		4·62	4·88
Combine-drilled		4·64	4·47
Sprayed		4·43	4·98
Liquid 4–10–10			
Injected	+ 'Nitro-Chalk' broadcast	4·59	4·94
Combine-drilled	+ 'Nitro-Chalk' broadcast	4·83	5·13

Combine-drilled liquid 4–10–10 plus 'Nitro-Chalk' was the only treatment involving liquids which gave a larger yield than the granular 20–10–10, though the advantage was small (Table 1). Combine-drilling rather than spraying the double amount of 14–6–8 lessened yields on the sandy soil by 1·5 t/ha; injected dressings, though safe, did not give consistently larger yields than sprayed dressings and each gave smaller yields than the broadcast 20–10–10 fertiliser. Our conclusion is, therefore, that P and K in the injected dressings was too far from the young roots to be fully effective. (Widdowson, Penny and Flint)

Aqueous ammonia as a fertiliser. Nitrogen in the form of ammonia is applied to much grassland in eastern England, commonly in a single injection early in Spring. Immediately after injecting NH_3, much nitrogen can be taken up quickly, but grass grows poorly later if no more is applied.

Aqueous NH_3 was injected on 15 March under grass (Highfield, grazed Reference Plots enclosure) at 155 kg N/ha, either as 4·7 g N/m of slit, with slits 30 cm apart, or 9·3 g N/m at 60 cm spacing; each treatment was applied to two plots. The K_2SO_4-exchangeable NH_4-N remaining around an injected band was measured in sub-samples of the soil from a 20 cm square profile surrounding the injection slit. The numbers of nitrifying bacteria in the sub-samples were also measured by Soriano's method (*Soil Biology* No. 9, 7–8, International Society of Soil Science, July 1968). Contour diagrams, obtained by fitting a cubic equation to the square array of results and interpolating values over the whole cross-section, showed that both NH_4-N and nitrifiers were radially distributed around the injected band.

Five weeks after injection, 7·1 ± 0·5 g N/m (76%) and 1·7 ± 0·1 g N/m (36%) remained of the large and small doses respectively, corresponding to 118 and 57 kg N/ha. The relative rates of disappearance of the two doses, after five weeks, were very similar. After 13 weeks, the amounts remaining were 11 and 3 kg N/ha. The increases in population of nitrifying organisms (counted once only), caused by the NH_3, were 42×10^6/m of slit receiving the high dose and 17×10^6/m with the low dose after five weeks, and 27×10^6 and 28×10^6/m respectively after 13 weeks. These counts are subject to large experimental errors but they suggest that soil sterilised by NH_3 is quickly re-occupied by nitrifiers which persist in large numbers until NH_4-N is exhausted. Grass was cut from the four plots after 10, 21 and 32 weeks when dry matter yields were 399 ± 20, 264 ± 9 and 53 ± 3 g/m^2 (high dose) and 482 ± 76, 169 ± 53 and 65 ± 1 g/m^2 (low dose) respectively. Nitrogen contents of the dry matter were closely similar.

These results suggest that a large dose of NH_3 injected under grass, is taken up and nitrified more slowly than a small dose and apparently causes more even growth of grass. (Ashworth and Flint)

Reactions of ammonia with soils and clays. Work on the sorption of ammonia from aqueous solutions by soils and clays was continued to assess better the contribution that exchangeable cations make to the mechanisms of the process.

Sorption by 1% and 3% suspensions of homoionic montmorillonite (Wyoming bentonite, $<2\ \mu$, CEC 92 meq/100 g) was measured by mixing in a centrifuge tube at 25°C the clay suspension (4 ml) and NH_3 solution (0·01M, 0·02M or 0·04M; 2 ml), centrifuging at 25°C and analysing NH_4-N colorimetrically in an acidified portion of the supernatant. Separate experiments measured the heats evolved on mixing the above quantities of clay suspension and NH_3, relative to suspension and water, at 25°C in a microcalorimeter. Sorption was measured as above, but using 0·2 or 0·4 g soil and 5 ml NH_3 solution, on Na- and K-saturated soils from two series with contrasting clay mineralogy (Batcombe Series, mainly interstratified montmorillonite-vermiculite and Speller Series, mainly illite) each containing <1% organic C and CECs of 12 and 18 meq/100 g respectively.

In experiments with clays or soils saturated with the alkali metals, the cation concentration in the supernatant from the NH_3-treated suspensions was also measured and compared with that of control suspensions in water. NH_3 sorption, at a given equilibrium NH_3 concentration, was much less on Ca, Mg and $N(CH_3)_4$-saturated clays (1–10 meq/100 g) than on Li, Na or K-clays (5–20 meq/100 g). In 1% suspensions of Li, Na and Ca-clays, ion displacement was approximately stoichiometric with each equivalent of NH_3 sorbed, attributable to protonation of NH_3 and subsequent ion exchange.

However, 3% suspensions gave different sorption isotherms from the 1% suspensions; they sorbed less NH_3/g of clay and the ratio of the amounts of alkali metal cation displaced and NH_3 sorbed was less than one. Sorption isotherms with Na- and K-saturated soils changed with the soil : solution ratio, the more soil used, the less the sorption per gram. The ratio of the amounts of cation displaced and NH_3 sorbed also varied with the mass of soil used and was less than 0·5, except with 0·2 g Na-saturated illitic soil, where it was about 0·7. The differences were not resolved by plotting NH_3 sorption against NH_4^+-ion concentration at equilibrium (calculable from the equilibrium pH).

The free electrolyte in solution at equilibrium with the soil or clay increases with the density of the suspension and this increase does not favour NH_3 sorption by the exchange mechanism. Separate experiments with Na montmorillonite, to measure the effect of increasing Na^+ concentrations in solution on NH_3 sorption by clay and soil, showed that the decrease in NH_3 sorbed was too little to account wholly for the different adsorption isotherms obtained with 1% and 3% clay suspensions.

Experimentally measured heats of NH_3-sorption on 3% clay suspensions from 0·02*M* solution were less than from 0·01*M* solution presumably because more molecules are sorbed at the higher concentration, so some must occupy less reactive sites than those available for adsorption from more dilute solution. Heats of sorption from 0·04*M* NH_3 solution, however, were greater than at the more dilute concentrations. Possibly the more concentrated NH_3 aggregated or flocculated clay particles when sorbed on them and produced more heat.

Apparent heats of sorption were approximately 30–40 kJ mol^{-1} on the alkali metal clays, and 40–60 kJ mol^{-1} on Ca, Mg and $N(CH_3)_4$-clays. (Ashworth)

Effects of compounds of nitrogen and phosphorus on crops

Phenylphosphonic acid. In an experiment at Rothamsted with Julia barley given either 56 or 112 kg N/ha (as 'Nitro-Chalk' in the seedbed) we measured the effects on yield of phenylphosphonic acid (PPA) either applied as a seed dressing (at 0·2, 0·4 or 0·8% by weight) or sprayed at equivalent amounts over the barley at the 'five-leaf' stage.

Applying 0·8% by weight of PPA on the seed badly checked emergence (in mid-April), killed some plants, and decreased crop height (by 7 cm by mid-June); the smaller seed dressings were safer. PPA sprays did not affect the growth of the barley. Barley given 112 kg N/ha lodged and yielded slightly less (6·05 t/ha) than with 56 kg N/ha (6·11 t/ha). Averaging both amounts of N, yields of barley grain (t/ha) were 5·88 without PPA, 6·24 with the single amount on the seed and 6·08 with it sprayed, 6·31 with the double amount on the seed and 6·25 with it sprayed, and only 5·71 with the quadruple amount (0·8% level) on the seed but 6·29 with it sprayed. There was little advantage in this experiment in applying more than 0·2% by weight to the seed, though twice as much was needed as a foliage spray to obtain an equivalent yield. (Gasser and Penny)

An experiment in 1971 at Saxmundham with seed dressed with a PPA derivative was repeated in 1972. Julia replaced Sultan barley, but Midas was grown again. Brown rust was much less evident than in 1971, Midas yielding 4·22 t/ha grain (compared with 2·45 t/ha in 1971) and Julia 4·64 t/ha. Barley yields were 4·03, 4·59 and 4·67 t/ha with 50, 100 and 150 kg N/ha respectively. N was more effective in the seedbed (4·68 t/ha) than as a top-dressing (4·18 t/ha). PPA diminished yields, irrespective of the amounts of N given, time of application or variety. Mean grain yields were 4·61 t/ha without and 4·25 with the seed dressing. No obvious checks in growth, or differences in appearance of the crop, explain this loss of yield. (Widdowson, Penny and Flint)

Experiments on growth and yield of wheat and barley at Rothamsted and Broom's Barn

Experiments begun in 1971 to compare growth rates, crop mineral contents and yields of cereals were repeated in 1972. Unlike 1971, when the Rothamsted wheat followed potatoes and the Broom's Barn wheat a one-year ley, both wheat crops followed beans and the barley again followed wheat. Soil samples taken in October, and again in March, contained little mineral-N, though there was more in Rothamsted than in Broom's Barn soil. (Gasser)

Wheat stems at Rothamsted, sampled in December and again in March and in April (before the N was applied) contained more NO_3-N (48, 10 and 33 ppm at the three times) than wheat at Broom's Barn (29, 0·3 and 1·5 ppm). In late May, after top-dressing with N, NO_3 contents ranged from 20 ppm (with 31 kg N/ha), to 570 (with 186 kg N/ha) at Rothamsted and from 8 to 720 ppm at Broom's Barn. Barley stems at Rothamsted, sampled in mid-May (the N was applied in March) had NO_3 contents ranging from 170 ppm (with 31 kg N/ha) to 800 ppm (with 186 kg N/ha); NO_3 contents at Broom's Barn were 7 to 640 ppm. In mid-June they ranged from 30 to 240 ppm at Rothamsted and from virtually none to 170 ppm at Broom's Barn, so that Rothamsted soil supplied more N and for longer than Broom's Barn soil. (Williams)

Rainfall was ample during May, but a soil moisture deficit developed from 2 June onwards; water was added from then until mid-July to bring the soils near to field capacity. Water increased yields of wheat grain at Broom's Barn (by 0·51 t/ha), but not at Rothamsted; yields of wheat straw were increased at Rothamsted (by 0·23 t/ha), but not at Broom's Barn. Water decreased yields of barley grain at Rothamsted (by 0·42 t/ha), but increased them at Broom's Barn, providing that no more than 93 kg N/ha was given. With more N than this, water decreased yields there too.

The largest amount of nitrogen needed for wheat on either farm was 93 kg N/ha though straw yields were larger with more. Without water, best wheat grain yields at Rothamsted (8·23 t/ha) were 1·86 t/ha larger than at Broom's Barn, and with water (8·02 t/ha) 1·31 t/ha larger, so neither water nor N eliminated the difference between the farms though they did diminish it.

Without water, 93 kg N/ha was enough for the barley at Rothamsted, but 155 kg N/ha was needed at Broom's Barn. With water, only 62 kg N/ha was needed by the barley at either farm. More N was needed to achieve maximum yields of straw than of grain. Without water, the largest barley grain yield at Rothamsted (6·95 t/ha) was 0·76 t/ha more than at Broom's Barn and with water (6·79 t/ha), 0·69 t/ha more; neither N nor water completely eliminated the difference between the farms. (Widdowson, with Welbank, Botany Department, see p. 90)

Herbage crops at Saxmundham

Yields of grass and lucerne. The plots of the Rotation I experiment at Saxmundham were halved in 1970 and one-half of each plot was sown with lucerne, the other with a mixture of timothy and meadow fescue. The reasons for stopping the arable four-course rotation with which the site was cropped between 1899 and 1969 were given by Cooke and Williams (*Rothamsted Report for 1970*, Part 2, 94). The P and K manuring was modified in 1966; P was tested at 22 (P1) and 44 (P2) kg P/ha and K, at 0 and 104 kg K/ha, both given in one dressing in early spring. These dressings were continued in 1970, 1971 and 1972. Farmyard manure (FYM) was applied in a single dressing (60 t/ha), ploughed down in autumn 1969; bone meal was given at 500 kg/ha each spring. In addition, the grass received a uniform dressing of nitrogen, 100 kg N/ha, for each cut taken at silage stage.

Both crops established very slowly in 1970 because May and June were drier than usual. The lucerne was cut once, the grass not at all. Lucerne yielded about 50% more on the FYM treated plots (3·2 t/ha) than on the plots given fertilisers. Once established, however, both crops grew well. Total yields in 1972 (two cuts) were less than in 1971 (three cuts). The ratios of the yields in 1971 and 1972 for grass and lucerne were the same as the total rainfall (between April and October) in the two years.

	Mean yield, t/ha		Rainfall, mm (Apr.–Oct.)
	Grass	Lucerne	
1971	12·1	13·0	358
1972	9·7	9·3	262

TABLE 2

Mean annual yields of lucerne and grass, Rotation I
Saxmundham, 1971–72

	Dry matter, t/ha					
Treatment	Bone meal	Farmyard manure	P1	P1K	P2	P2K
Lucerne	10·43	12·50	10·42	11·42	10·79	11·60
Grass given 100 kg N/ha for each cut	10·38	11·98	10·65	10·88	10·82	10·82

Table 2 shows the average yields of grass and lucerne in 1971–72. Both crops gave very similar yields of dry matter with each treatment. Although yields were most where FYM was given, fertilisers yielded almost as much. The 50% increase in yield of lucerne with FYM in 1970 was probably due, therefore, to quicker establishment of the plants. Compared with the treatment receiving most fertiliser (P2K), FYM increased dry matter yields, on average, by 1·16 t/ha (grass) and by 0·90 t/ha (lucerne). Bone meal, together with basal N, gave smaller yields of grass (−0·44 t/ha) and, without N, of lucerne (−1·17 t/ha). Increasing the P dressings from 22 to 44 kg P/ha and giving some K, 104 kg K/ha, further increased yields but much less with grass than with lucerne. Extra P increased yields of lucerne by 0·28 t/ha but gave only another 0·06 t/ha of grass. The K dressing was more effective and lucerne yields increased by 0·90 t/ha, grass by only 0·12 t/ha. The results from the first two years of this experiment confirm previous indications that herbage crops, especially lucerne, grow well on the poorly structured Chalky Boulder clay at Saxmundham and benefit from more K than was needed by crops in the preceding arable rotation. (Johnston and Flint)

Soil nitrogen

Rothamsted soils, with differing amounts and types of organic matter, from Barnfield (FYM or fertilisers) and the Ley–Arable experiment on Highfield (lucerne, grass–clover, grass leys, permanent grass and permanent fallow) and Woburn soils from the Organic Manuring experiment (grass–clover, grass leys, FYM, straw, peat, green manures and soils given only fertilisers), were used to measure available-N in the laboratory and to grow ryegrass, with or without additional fertiliser-N, in the glasshouse. The laboratory measurements were: (i) mineral-N produced on aerobic incubation of soil; (ii) ammonium-N produced on anaerobic incubation of soil; (iii) total-N extracted by boiling water; (iv) soluble carbohydrate, measured as glucose, extracted by 0·1N barium hydroxide; (v) total-N and (vi) organic-C.

The grass was cut three times and yields measured and N uptakes calculated. Crop performance in the glasshouse was related to individual measurements of available soil-N. All methods were highly correlated ($r > 0{\cdot}9$) except those between reducible sugars, extracted by barium hydroxide, and total-N and organic-C in the soil.

Yields of dry matter and N taken up by the grass correlated better with laboratory methods for measuring available-N in the absence than in the presence of fertiliser-N. Adding fertiliser-N decreased the differences between soils so that ranges of dry matter produced and N removed by the grass were smaller in the presence of fertiliser-N than in its absence. N uptake was usually better correlated than dry matter produced with laboratory measurements of available-N. (Kalembasa, Gasser and Mitchell)

Soil phosphate

The Langmuir equation as a model for phosphate adsorption by soils. The Langmuir equation, used previously to describe P adsorption isotherms (*Rothamsted Report for 1971*, Part 1, 64–65) assumes that P is adsorbed on a surface with a uniform bonding energy (inherently unlikely in soils) and underestimates adsorption at the largest P concentrations. P adsorption can be described more adequately by postulating two types of surface with different bonding energies (k' and k''). The validity of this hypothesis was tested by fitting 10-point isotherms to four soils varying widely in bonding energies, adsorption maxima and degrees of P saturation. Initial P concentrations of equilibrating solutions (KH_2PO_4 in $0{\cdot}02M$ KCl) ranged from 0·8–31·0 μg/ml. Residual variances between observed and predicted adsorption were much smaller after fitting four Langmuir parameters (composite surface equation) instead of the usual two (uniform surface equation). Moreover, the composite surface equation gave larger and more reliable values for the maximum surface adsorption ($x_m' + x_m''$). Equations of this type were satisfactorily fitted to adsorption isotherms on a further 37 soils from Southern England and Eastern Australia.

The relative magnitude of the parameters suggests that (i) P is adsorbed initially on a relatively small surface of high bonding energy which generally accounted for about one-third of the total P adsorption maximum; observed adsorption and that predicted by the Langmuir equation agreed very well; (ii) P is adsorbed more slowly on a second larger surface characterised by a small bonding energy. The slight positive divergence of observed from predicted adsorption at the highest solution P concentration was probably caused by the small decrease in pH when HPO_4^{2-} ions were adsorbed. (Holford and Mattingly, with Wedderburn, Statistics Department)

Plant availability of soil phosphate in relation to P adsorption parameters. The instantaneous P buffer capacity (dQ/dI) and the theoretical maximum buffer capacity of soils $(dQ/dI)_{I\to 0}$ can be calculated by differentiating the composite surface Langmuir equation. The major components of the maximum buffer capacity are the Langmuir adsorption parameters for the high energy surface.

Multiple regression with buffer capacity, calculated in this way, and either the intensity (I), or the quantity (Q) of labile P as independent variables, accounted for up to 94% of the variance in P uptake by ryegrass from two different groups of soils. With a buffer capacity term in the regression, the extensive parameter, Q, was generally better related to P uptake than the intensive parameter, I.

Both intensity and quantity parameters are required to measure the plant availability of soil P. If phosphorus is measured as an intensity (e.g. P concentration), the extensive component of buffer capacity, x_m, contributes most to plant availability, because it tends to be closely correlated with Q. If phosphorus is measured as a quantity (e.g.

labile P), the intensive component, k, is the major factor in buffering. The Langmuir constant, k, which is related to bonding energy, has a negative effect on the availability of labile P; the higher the value of k, the more the Q/I equilibrium moves in the direction of Q, so that I is inversely correlated with k.

The levels of Q or I which are optimal for plant uptake vary with the buffer capacity of the soil and the length of time during which P is removed from the system. Optimal levels of Q increase, and of I decrease, as the buffer capacities of soils increase. It is not, therefore, possible to set universal optimal levels for either Q or I in all soils unless the buffer capacity and time factors are uniform. (Holford and Mattingly)

Organic phosphorus in soils. Previous results (*Rothamsted Report for 1969*, Part 1, 61–62) showed that repeated dressings of superphosphate and FYM scarcely changed the organic P in arable soils from Barnfield at Rothamsted. Organic P was measured both by ignition and extraction methods on air-dried soils (0–23 cm) taken from the Classical Barley experiment at Woburn, to which FYM and fertilisers were applied from 1877–1926 and their residual effects measured from 1927–58. Yields during this latter period were often very small ($<$ 1·25 t/ha) and the site was fallowed in nine of the 32 years. Total soil carbon decreased from about 1·5% C in 1876 to 0·5–0·8% in 1959.

TABLE 3

Total and organic phosphorus contents of soils from the Classical barley experiment, Stackyard, Woburn, 1888–1959

Treatment	Plot	Year	Total P (mg/kg)	Organic P[a] (mg/kg)
No phosphorus since 1876	1, 2, 3, 7	1888	715	230
		1927	695	215
		1959	620	205
Superphosphate (1876–1926)	5, 6, 8, 9	1888	810	245
		1927	930	255
		1959	810	240
Farmyard manure (1876–1926)	11b	1888	820	260
		1927	900	290
		1959	795	245

[a] Means of estimations by extraction and ignition

Changes in organic P were much smaller (Table 3). Plots without P lost organic P continuously from 1888–1927; the total loss, however (25 mg P/kg), represented only about 10% of the amount present in 1888. Where superphosphate was given for 50 years, organic P contents of the soils scarcely changed. With FYM, organic P increased by 30 mg P/kg between 1888–1927 but declined steadily between 1927–59 when none was given. The average annual rate of mineralisation since 1927 has ranged from 1 kg P/ha, in soils without P, to nearly 5 kg P/ha in soils given FYM for 50 years. Residues from FYM appear to mineralise rapidly enough in these soils to supply most of the P needed by small crops of barley. (Chater and Mattingly)

Responses to triple superphosphate in Uganda soils. Work continued on the causes of unusual effects of triple superphosphate on yields of cotton and beans at Namulonge (Uganda), where small dressings decreased, but larger amounts increased yields. Last year's experiments showed that both the acid triple-point solution and dicalcium phosphate, derived by hydrolysis from monocalcium phosphate, increased Mn concentrations in ryegrass grown in a Namulonge soil. It is, therefore, unlikely that the results observed at Namulonge were caused by the triple-point solution dissolving soil Mn. They appear, rather, to be associated with phosphorus nutrition in a manganese-rich soil. This year's experiments studied interactions between P, Ca and Mn in cotton, grown in solution culture and in Namulonge soil in Saxcil cabinets.

Nutrient solutions containing 0·065 and 1·00 *mM* P, 0·15 and 2·25 *mM* Ca and 0·009, 0·082, 0·155 and 0·300 *mM* Mn were given to cotton growing in quartz chips. Total dry matter yields, with and without P, were closely related to nutrient Ca : Mn molar ratios which ranged from 0·5–27·5. With a nutrient solution 1·00 *mM* in P the yields ranged from 4·5–15·2 g/pot; with solutions 0·065 *mM* in P, yields were 1·9–3·1 g/pot. 'Crinkle leaf', the typical symptom of Mn toxicity in cotton, was inversely related to the Ca : Mn ratios in the nutrient solutions; at the larger P concentration, 'crinkle leaf' was severe with small ratios but was eliminated with large ratios. With the largest P, Ca and Mn concentrations, leaves contained over 2000 ppm Mn but yield was good, probably because much Mn precipitated. Nodules of MnO_2 were observed and identified in the lower leaves.

Cotton was grown in Namulonge soil treated with all combinations of 0, 0·2, 0·4 and 0·8 *mM* P and 0, 0·1, 0·2, 0·4 and 0·8 *mM* Ca in nutrient solutions adjusted to the soil pH (5·75); Mn was not given. Yield was 3·4 g/pot without P and 12·0 g with all P concentrations; Ca did not affect yield. Without Ca, phosphate increased the Mn concentration in leaves from 240 ppm without P to 1030 ppm with 0·8 *mM* P. With Ca, Mn concentrations decreased and, with the largest Ca concentrations tested, the Mn content of the leaves was 150 ppm at all phosphate concentrations. At each Ca : P ratio the smallest solution concentrations of P and Ca increased leaf Mn but larger concentrations, at the same ratio, decreased it. As nutrient Ca : P ratios increased, leaf Mn concentrations diminished.

These experiments indicate that small dressings of triple superphosphate decreased seed cotton yields at Namulonge because P induced Mn toxicity; with more fertiliser, the extra Ca counteracted the Mn and yield increased. The results show that in soils with much Mn and little Ca, phosphate fertilisers should be used in which the ratio of Ca : P is large. (Le Mare)

Liming experiments and limestones

Effects of liming on barley yields. Barley was grown on the long-term liming experiments at Rothamsted (Sawyers) and Woburn (Stackyard) from 1965 to 1967 (*Rothamsted Report for 1970*, Part 2, 98). A second sequence of three barley crops has been grown since 1970 on the same plots without further applications of lime but with and without annual dressings of phosphate and potassium fertilisers. Crops on the unlimed plots were poor at both sites in 1970 and failed in 1971 and 1972. These plots were more acid than in 1967 but not sufficiently so to account fully for the crop failures. A more probable cause was the change in variety from Maris Badger to Julia in 1970. Barley varieties vary widely in their susceptibility to soil acidity and those yielding more in less acid soils (Julia outyields Maris Badger) are usually more sensitive to soil acidity.

Yields of both varieties declined rapidly below pH 6 (in water); above this, liming generally increased yield especially when phosphate and potassium were given (Table 4). As in previous experiments, phosphate fertiliser increased yields more at low than at high pH. Mean yields increased rather than decreased during the three years, perhaps because a systemic fungicide was used to control mildew in 1972. (Bolton)

Effects of lime and potassium on growth of carrots. Previous work with potatoes and ryegrass showed that liming acid soils lessened K uptakes and increased responses to K fertilisers. Two pot experiments were made to study interactions between liming and K responses, using carrots (which remove much soil K) grown for ten weeks on acid

TABLE 4

Effects of liming on the yields of spring barley (Julia), 1970–72

		Limestone t/ha in 1962				Standard errors
		0	5	10	20	
Sawyers, Rothamsted						
pH (water)	1970	4·5	5·2	6·0	7·4	
	1971	4·7	5·4	6·3	7·6	
	1972	4·5	5·2	6·0	7·2	
		t/ha grain at 85% dry matter				
Mean yield	1970	0·31	2·87	3·64	3·58	±0·188
	1971	—	3·54	4·34	4·53	±0·273
	1972	—	3·67	4·55	4·90	±0·400
Response to P	1970	0·31	0·70	0·54	0·32	±0·376
	1971	—	1·34	0·90	0·76	±0·546
	1972	—	1·91	1·27	1·33	±0·799
Response to K	1970	0·07	0·56	0·42	0·09	±0·376
	1971	—	0·46	0·60	0·38	±0·546
	1972	—	0·58	0·83	1·28	±0·799
		Limestone t/ha in 1962				
		0	5	12	19	
Stackyard, Woburn						
pH (water)	1970	5·0	6·0	6·9	7·5	
	1971	4·9	5·9	6·7	7·1	
	1972	4·7	6·0	6·7	7·3	
		t/ha grain at 85% dry matter				
Mean yield	1970	1·52	3·77	4·09	4·24	±0·093
	1971	—	4·13	4·19	4·24	±0·096
	1972	—	4·81	5·28	5·83	±0·132
Response to P	1970	1·19	0·38	0·45	−0·12	±0·185
	1971	—	1·07	0·33	0·39	±0·191
	1972	—	0·56	0·62	0·16	±0·263
Response to K	1970	0·09	0·54	0·15	0·54	±0·185
	1971	—	0·07	0·75	0·98	±0·191
	1972	—	1·12	0·18	0·80	±0·263

Rothamsted soil (pH 4·6 in 0·01*M* $CaCl_2$) and Woburn soil (pH 4·7) given none or four amounts of lime (pure $CaCO_3$), with and without potassium fertiliser.

Yields of carrot tops were increased only 11% by the added K, although both soils contained less than 0·15 meq/100 g exchangeable K. When the tap root started to store carbohydrate, K-deficiency symptoms appeared on the leaves and root yields were more than doubled by the added K. Liming increased yields of tops slightly (up to pH 6·3) but most roots were harvested in the range pH 5 to 5·5. K fertiliser increased yields of tops similarly at all levels of liming but the largest increases in root yields were at the optimum pH (5·0–5·5). There was some evidence that insufficient K was given for maximum yields. In both experiments liming decreased % K and increased % Mg in the tops. In the roots % K was unaffected by liming but % Mg was much increased. (Bolton)

Acid-insoluble constituents of limestones. The composition of the acid-soluble fraction of 89 British limestones and three shell sands was reported last year (*Rothamsted Report for 1971*, Part 1, 68–69). The fraction insoluble in cold 5*N* HCl was analysed semi-quantitatively by emission spectrography using a D.C. carbon arc cathode layer method. Na, K and Mg were measured after digestion with H_2SO_4 and HF in 51 samples, the insoluble fractions of which exceeded 1·5%. The amounts present were calculated as mg/kg and, for Na, K and Mg, as % in the original limestone (Table 5).

TABLE 5

Minimum, maximum and mean concentrations of constituents of acid-insoluble matter in limestones determined semi-quantitatively by emission spectrography

	Amounts insoluble in cold 5*N* HCl (mg/kg of original limestone)			
	Min.	Mean	Max.	Mean in three Shell sands
Barium	0·7	122·0	2115·0	408·0
Cobalt	0·0	0·7	6·0	3·2
Copper	0·1	1·3	10·7	5·8
Chromium	0·1	5·7	47·0	16·3
Gallium	0·1	1·2	8·4	7·5
Lead	0·1	1·7	12·6	6·4
Manganese	0·2	13·2	370·0	108·5
Molybdenum	0·0	0·5	4·2	<2·6
Nickel	0·1	3·7	25·6	10·0
Strontium	0·1	10·9	239·0	17·8
Tin	0·0	0·6	12·6	476·0
Titanium	4·8	222·0	4230·0	850·0
Vanadium	0·1	2·7	18·0	8·5
Yttrium	0·0	0·8	10·6	7·9
Zirconium	0·1	8·8	55·0	48·3
		(per cent)		
Sodium*	0·001	0·042	0·571	0·080
Potassium*	0·017	0·188	2·157	0·370
Magnesium†				
Calcitic limestones	0·006	0·076	0·566	0·225
Dolomitic limestones	0·012	0·063	0·159	

* Determined by flame photometry on the H_2SO_4-HF extract
† Determined by atomic absorption on the H_2SO_4-HF extract

Ba, Mn, Sr, Ti, Na, Mg and K were present in the largest amounts but individual samples varied considerably; the micronutrients Co, Cu and Mo were present in small amounts. Sn was less than 13 mg/kg in the limestones but much more in the shell sands (mean 476 mg/kg), one sample from Perranporth containing 1420 mg/kg Sn.

Mean concentrations of K (0·004%) and Na (0·019%), soluble in cold 5*N* HCl, were much less than those in the insoluble fractions. Mean K in the acid-soluble fraction of the shell sands (0·01%) was less than in the acid-insoluble fraction, but Na (0·36%) was more, presumably due to contact with seawater. Mg concentrations were less in the acid-insoluble than in the acid-soluble fractions; about one-third of the total Mg in the shell sands was in the acid-insoluble fraction.

Acid-soluble B, determined on the original limestones by procedure A of Spicer and Strickland (*Analytica Chimica Acta* (1958), **18**, 523), averaged nearly 4 mg/kg (a range of 0·2–73 mg/kg) in limestones; the largest concentrations were in the magnesian limestones. The mean concentration in three shell sands was 13·3 mg B/kg.

Mean concentrations of Co and Cu were similar in both fractions analysed. There was little Mo in the acid-soluble fraction but more in the insoluble fraction. The amounts of K in the two fractions differed more than any other element and clearly depend on the proportion and nature of the insoluble matter. Much less Mn, about one-tenth, was present in the insoluble fraction than in the soluble fraction. These analyses emphasise that results based on total elemental analyses of limestones could sometimes overestimate their potential use as sources of trace elements in agriculture. (Chater and Williams, with Le Riche, Pedology Department)

Cations in soils

Potassium reserves in soils from the Classical experiments. The use of calcium-saturated resins to measure reserves of potassium in soil was described earlier (*Rothamsted Report for 1968*, Part 1, 55). The method was extended to soil from the 'Nil' plots and plots given K fertiliser (without N) from Broadbalk, Hoosfield and the limed and unlimed sections of Park Grass.

Exchange kinetics were analysed by relating 'cumulative K extracted' (mg K/100 g/soil) to (reaction time in hours)$^{1/2}$. Soils from plots not given K for more than 100 years gave a non-linear exchange reaction up to 10–20 hours, a slow linear exchange up to 1500 hours and a very slow linear reaction up to at least 7000 hours. Soils from K-treated plots gave similar exchange patterns to the 'Nil' plots, except that the rates of release in the initial two reactions were usually more rapid.

The amounts of K associated with the initial non-linear reaction were similar to those exchangeable to neutral M ammonium salts. Rate constants for K exchanging by the slowest linear reactions for 'Nil' and 'K' soils were identical and were attributed to K release from micaceous minerals in the clay and silt fractions ('matrix' potassium). These constants were similar for Broadbalk, Hoosfield and Park Grass (limed) ($0{\cdot}23 \pm 0{\cdot}02$ mg K/100 g soil/unit change in (reaction time in hours)$^{1/2}$. Rate constants for Park Grass (unlimed) were slightly smaller ($0{\cdot}20 \pm 0{\cdot}02$). These constants can be predicted approximately if the clay and silt contents of the soil, and their mineralogical composition, are known.

In soils from K-treated plots, the intermediate linear reaction proceeded appreciably faster (rate constants ranging from 9 to 29) than in 'Nil' soils (8 to 17). The extra K associated with this reaction in K-treated soils, together with the 'exchangeable K' (i.e. the initial non-linear reaction), comprises the total 'residual' K. The rate of exchange of this reaction in K-treated soils is nearly twice that in 'Nil' soils from Broadbalk and Hoosfield (13 : 8 and 29 : 17 respectively), but not significantly greater in the limed and unlimed plots from Park Grass (13 : 12 and 9 : 10 respectively.) Potassium exchanges by this reaction more slowly in the acid unlimed plots than in the limed plots (8 : 10 and 7·5 : 11 for the 'Nil' and 'K' plots respectively).

The release of K to crops in glasshouse and field experiments is thus governed by the simultaneous equilibria: Solution K $\rightleftharpoons$ surface and sub-surface K $\rightleftharpoons$ Soil 'Matrix' K (surface and sub-surface K includes residues from crops and fertilisers). The rate of K uptake by unit weight of the crop depends on the proportions of these categories in the soil and their rates of release when the K concentration in the soil water tends to zero during cropping. (Talibudeen)

Potassium and nitrate concentrations in soil pastes. In electrolyte solutions in the range 3×10^{-2} to $3 \times 10^{-5}M$, ion-selective electrodes gave linear calibration curves with a slope of 60 ± 5 mV per ten-fold change in concentration, compared with a theoretical value of 59·2 mV. In more dilute solutions, the calibration was much less linear and became insensitive to changes in concentrations below $1{\cdot}6 \times 10^{-6}M$. K standards buffered with $0{\cdot}1M$ ethanolamine hydrochloride (recommended by various workers and manufacturers) gave a slope of only 45 mV in the range 10^{-2} to $10^{-4}M$.

To extend measurements of K concentration to soil pastes, the effects of various salt bridges in the reference half-cell, three soil : water ratios and interferences by Ca^{2+} and NH_4^+ ions were investigated. Bridges of M ethanolamine hydrochloride, $2M$ Na_2SO_4 (used by manufacturers) and $4{\cdot}5M$ NaCl gave either poor reproducibility or much higher values in soil pastes than those measured by flame emission in the supernatant solution. NH_4^+ concentrations of $3 \times 10^{-5}M$ did not interfere but $3 \times 10^{-4}M$ NH_4^+ made K measurements less sensitive. $10^{-2}M$ Ca only decreased the sensitivity a little but extended the linear response to more dilute solutions.

Potassium concentrations in soil water, measured by the K electrode directly inserted into soil : water pastes at a 2 : 1 ratio and in the supernatant extract by flame emission, agreed well. At higher dilutions, the electrode method gave smaller values than those by flame emission. (Nair and Talibudeen)

Potassium and nitrate-N depletions in soil water during crop growth on Broadbalk

Measurements with ion-selective electrodes. Changes in the concentrations of nutrient ions in soil water indicate, most sensitively and rapidly, changes in the nutrient status of soils caused by crop uptake, leaching, etc. Monthly measurements of soluble P and K reported earlier (*Rothamsted Report for 1965*, 59) on soil samples taken from field and microplot experiments, showed seasonal changes during the year but they were not sensitive enough to detect changes during crop growth. Also, NO_3 concentrations would be more difficult to measure accurately by such means. For all ions, avoiding contamination of samples taken from lower depths presents serious difficulties. Ion-selective electrodes, which seem to solve these problems, at least for K and NO_3 ions, were used this year on Broadbalk.

Potassium and NO_3-N concentrations in soil water were measured during May to August at ten-day intervals with such electrodes, placed 3–45 cm laterally from rows of winter wheat (Cappelle) and at depths of 5–20 cm vertically in the soil. Duplicate sets of sites were installed on Plots 7 (N_2PKNaMg), 9 (N_4PKNaMg) and 17 (N_2, $\frac{1}{2}$PKNaMg) in Broadbalk, Section I (continuous wheat). Three such sets were distinguished—'Between Rows', 'Internal Boundary' (between the guard row and the harvest area) and 'External Boundary' (between Sections). Depletions of each ion in the soil water by crop uptake were calculated from the measurements, assuming that values at the '45 cm lateral' distance in the 'External Boundary' were not affected by the crop ('control' sites).

Concentration changes, especially of NO_3-N at 'control' sites, reflected 'wet' and 'dry' cycles during the growing season, indicating leaching to lower depths when wet and recovery during dry periods. At sites affected by roots, calculated 'depletion' value showed well-defined changes, most at 'Between Rows' sites and least at 'External Boundary' sites. These changes were markedly periodic and large for NO_3, but much smaller for K. Potassium depletions, when observed, always *followed* NO_3 depletions, suggesting a rhythmic growth pattern: NO_3-uptake → root extension → K uptake. The smaller and less frequent K depletions support earlier observations (*Rothamsted Report for 1970*, Part 1, 53) that little K stress occurs in the soil when fertilised with K.

These results showed that soil NO_3 depletion by the crop was much more at lower depths (12·5–20 cm) than at the surface (5 cm). Maximum NO_3 depletion was observed during the later stages of crop growth, before 'panicle emergence' and 'grain filling'. The rate of depletion then decreased and soil NO_3 levels recovered partially as the crop reached maturity. Soil K concentrations started to recover at the 'grain filling' stage, about a month earlier than with NO_3. Changes in NO_3 and K concentrations seem to relate more to the amounts of each nutrient given than to the N : K ratios of the fertiliser treatments. (Nair and Talibudeen)

Nitrate concentrations in wheat and soil on Broadbalk. Concentrations of nitrate-N in the lower stems of wheat grown on Section I on Broadbalk, and in soil at different depths, were measured during May and August, using a field method described elsewhere (*Chemis-*

try and Industry (1969), 1735). Crop samples were taken from the centre rows of the discard areas, and soil from different depths between these rows.

Nitrate concentrations in the soils of the control and PK treatments did not exceed 6 ppm between 24 May and 23 August and the mean concentrations of NO_3 in stem tissue were 1 ppm or less. Soil given 96 kg/ha N had the largest concentrations of nitrate (50 ppm) on 24 May at 0–7·5 cm depth; at later samplings, concentrations were less than 5 ppm at all depths sampled. Nitrate in the crop diminished rapidly after 6 June to less than 1 ppm. With larger application of N (193 kg/ha) the soil had more NO_3 up to 6 June. The concentration of NO_3 in the crop exceeded 200 ppm until 5 July and, up to 23 August, remained greater than in crops given the smaller application of N.

Soil moisture (0–23 cm) varied from 13–17% w/w during the period of measurement; it was less in treatments receiving N fertilisers than in controls. Soil NO_3 measurements indicated that little of the applied N had leached, except from the larger application; when sampled on 6 June, after 19 mm of rain during the previous ten days, the subsoil (23–30 cm) from plots given most N had more NO_3 than the controls or soil given the smaller N application. (Williams and Rangeley)

Ion interactions in potato nutrition

When the amount of K given to potato plants is increased, the distribution of other nutrients between the tubers and the rest of the plant alters to the benefit of the tubers; K also *increases* the % Mg in the dry matter of tubers and of young, just unfurled leaves, which also act as 'sinks' (*Rothamsted Report for 1970*, Part 1, 55; *for 1971*, Part 1, 67).

Effect of K and Mg concentrations in nutrient solutions. Potato plants were grown in culture solutions of constant composition until tubers formed. They were then divided into four groups and given the following treatments for 23 hours: control, extra K, extra Mg, extra K + Mg (given as sulphates); for the first five hours the tops were exposed to $^{14}CO_2$. Tubers were separated into three or four segments, macerated under distilled water and the suspension assayed for ^{14}C by liquid scintillation counting and analysed for water-soluble K, Mg and phosphate (assumed to be that freshly acquired). Within individual tubers, ^{14}C and K concentrations increased from the heel end (attached to the plant) to the rose end. Mg and phosphate concentrations were smaller in the middle of the tubers than at the ends.

Concentrations of ^{14}C varied considerably between tubers and probably reflected the positions on the plant of the leaves by which the tubers were fed. K concentrations varied little between tubers; Mg concentrations varied somewhat more but were unrelated to ^{14}C concentration (cpm/g fresh weight). Phosphate concentrations also varied between tubers and were positively related to ^{14}C concentrations, probably because there was the greatest turnover of energy-storing phosphate compounds involved in starch synthesis in the tubers that received most assimilate.

Giving extra K, extra Mg or both had no effect on mean K concentrations in the tubers of each plant, but all three treatments increased the mean ^{14}C, Mg and phosphate concentrations. All treatments increased the quantity of ^{14}C in the tubers of each plant. This was probably mainly due to the K ion, because the quantity of ^{14}C in the tubers and the quantity of K in the stems and petioles were highly correlated ($r^2 = 0{\cdot}98$) and extra $MgSO_4$ increased the quantity of K in the plant about as much as extra K_2SO_4 (presumably due to extra SO_4^{2-} uptake). In a subsidiary experiment, increasing the K^+ concentrations in the solution bathing discs of fresh-cut tuber stimulated them to absorb extra ^{14}C-labelled sucrose but did not cause them to absorb more Mg.

The influence of K nutrition on % Mg in the dry matter of sinks probably occurs as a result of effects in translocation rather than within the sinks because (i) the increase in Mg concentration in the tubers caused by the extra K seemed unrelated to the ^{14}C concentration, and (ii) extra K did not stimulate the discs of tuber to absorb more Mg.

Theoretical treatment of effects in translocation. The xylem and phloem elements in the stems of potato plants (and other species) are arranged in vascular bundles and are often separated by only a few cells, suggesting that ions and other solutes may be transferred from one to the other. If increasing the amount of K given to a plant, and thereby increasing the K concentration in the phloem, were to increase the fluxes of other nutrients through phloem sieve tubes, the fluxes of these nutrients in the xylem would decrease. This would change the distribution of the nutrients between the sinks and the rest of the plant in ways similar to those described in previous experiments.

In Professor Spanner's electro-osmotic theory of phloem translocation (*Journal of Experimental Botany* (1958), **9**, 332), circulation of K^+ ions about each sieve plate impels the translocation stream through the phloem sieve tubes. Calculations were made, using Spiegler's frictional formulation of transport processes (*Transactions of the Faraday Society* (1958), **54**, 1408), to find whether the effects of increased phloem K concentrations on fluxes of nutrients and sucrose could explain the changes in nutrient distributions and the % Mg in the dry matter of 'sinks'. Professor Spanner's theory explains the observed changes better than alternative theories that do not involve K^+-intervention in translocation. (Addiscott)

Nitrogen nutrition of conifers

Effects of NO_3-N, NH_4-N and Fe on crop size and composition. Nursery-raised one-year seedlings of Sitka spruce (*Picea sitchensis*) and Scots pine (*Pinus sylvestris*) were transferred to nutrient solution in the greenhouse and grown for 11 weeks, from 1 February to 25 April 1972. Three N sources (ammonium, nitrate and ammonium + nitrate) and two Fe levels (none and 1 ppm as ferric ethylene diamine di-*o*-hydroxyphenylacetate, FeEDDHA) were combined factorially to give six treatments. At harvest, colour, plant height and dry weights of various plant parts were determined. The tissues were also analysed for total N and Fe, as well as for cations and anions in order to estimate organic acid contents. (New roots were separated from old roots only for the work described below on arginine contents.)

The newly formed needles of the NO_3-N treated trees were lighter in colour than those grown with NH_4-N; Fe tended to darken them slightly, with both N fertilisers.

Height increments and dry weights of tops (newly formed tissue) were greater for both species when the plants were supplied with ammonium or the combination of ammonium plus nitrate than with nitrate alone. For Sitka spruce, the dry weight of the whole root was greater with NO_3-N than with NH_4-N, even though top growth was less. In the spruce, Fe tended to increase the dry weight of new top growth slightly, irrespective of N sources, whereas in the pine Fe increased it only with the NO_3 source.

Total N concentrations in plant tissue of both species were least in those plants receiving NO_3-N and most in those receiving NH_4-N; the combination gave intermediate values. Newly formed top tissues had smaller Fe concentrations than the older tissues or the roots ranging, for Sitka spruce, from 100 ppm in new tops to 900–1300 ppm in whole roots. These concentrations, in new tissue, tended to be smaller with the NO_3 source in Scots pine but not in Sitka spruce.

Organic acids, estimated from the difference between total cations and total anions, were larger in plants receiving NO_3-N; adding Fe decreased the level of organic acids, especially in the new tissues of Scots pine. Maximum growth occurred at 0·35 meq of organic acids per gram of dry tissue for pine and 0·60 meq/g for spruce.

The data are consistent with other published results in that Fe chlorosis (in our experiment only a very slight lightening of colour) and organic acid accumulation are associated with NO_3-N nutrition. They do not indicate, however, whether the NO_3-N source of nitrogen is the direct cause of the accumulation of organic acids, which in turn give rise to paler plants, or if a disturbed Fe metabolism is the cause of the organic acid accumulation. (Nelson and Selby)

Arginine accumulation in conifers. Arginine was the predominant free amino acid in both species and was also the amino acid most affected by the form of nitrogen supplied. Table 6 shows that in both species, the arginine concentration (μg/g dry matter) in the new top growth and in the new roots was largest when nitrogen was given as NH_4-N and smallest with NO_3-N. Except when nitrogen was supplied as NO_3-N, the arginine concentration in both species was much larger in the new roots than in the new top growth. With all nitrogen sources, the arginine concentration in the new top growth and the new roots was much larger in Sitka spruce than in Scots pine. This work suggests that in these conifers arginine may function, like asparagine, as a compound detoxifying ammonia. The accumulation of arginine is of interest in relation to pathways of amino acid metabolism, and also because it may control plant growth through its effects on the utilisation of other amino acids. (Nowakowski, Nelson and Lazarus)

TABLE 6

The effect of the form of nitrogen fertiliser on the amount of arginine in Sitka spruce and Scots pine

	Treatment	Arginine-N concentration μg/g DM	Arginine-N	
			% of total soluble organic-N	% of total N in free amino acids
Sitka spruce				
New top growth	NH_4	1029	35·7	45·9
	NO_3	165	15·1	21·8
	$NH_4 + NO_3$	317	20·0	29·3
New roots	NH_4	1818	37·6	49·9
	NO_3	184	9·6	18·7
	$NH_4 + NO_3$	1726	41·9	53·1
Scots pine				
New top growth	NH_4	630	25·9	33·7
	NO_3	152	9·9	15·6
	$NH_4 + NO_3$	183	11·9	16·7
New roots	NH_4	939	15·7	19·3
	NO_3	141	4·6	8·5
	$NH_4 + NO_3$	611	17·6	20·2

Nutrient concentrations in healthy nursery-grown seedlings and transplants of conifers

The approximate range of nutrient concentrations in plant tissues for conditions of deficiency can be defined more easily than for those of sufficiency. However, with such high-value crops as British nursery conifers, fertilisers constitute less than 5% of the production cost and the main consideration in manuring them is to achieve good survival and growth after forest planting. To meet this need, reliable analytical values are required which are consistent with the production of green, healthy trees. There is, at present, little relevant published information of this kind, especially for Western American species, some of which are widely planted in Britain.

Concentrations of N, P, K, Mg, Ca and Mn were determined in whole-plant samples of healthy one-year seedlings and two-year (one-plus-one) transplants of Sitka spruce (*Picea sitchensis*), Norway spruce (*Picea abies*), Grand fir (*Abies grandis*) and Western hemlock (*Tsuga heterophylla*). The conifer crops were grown with inorganic fertiliser supplying N, P, K, Mg and Ca, using standard manuring methods developed during an extensive experimental programme. The samples were taken between 1967–69, at the end of the growing seasons, from nursery beds on four contrasted soils in south-east England. The soils ranged from a nutrient-poor very acid sandy podsol (Wareham) to a soil which, though well supplied with nutrients, had near-neutral pH, i.e. conditions where good plants of the species listed could be grown only if the soil had previously been acidified or treated with partial sterilants.

N, P and K concentrations (but not those of the other nutrients) were consistently smaller in transplants than in seedlings, and all nutrient concentrations tended to vary less in the older plants. With plants of both ages, Norway spruce had larger concentrations of N, P and Ca than Sitka spruce, but smaller concentrations of K. Most of these differences were well supported by our earlier experiments.

Manganese was the only nutrient which showed large differences in tissue concentrations between nurseries. The values of 20–80 ppm Mn at Wareham, unusually small for such an acid soil, are related to the exceptionally small Mn reserves in soil and parent material.

Many of the analytical values derived from this work agree remarkably well with the few published elsewhere for the same species grown in nurseries or in solution culture; where the values diverge, there is often a plausible explanation. However, there is a risk that what appear to be matching results are in fact fortuitous. Until more detailed compilations are published, with conditions of growth carefully described, these nutrient ranges may not be generally valid. (Benzian and Smith)

Experiments with herbicides

Herbicides and liquid fertilisers combined. One experiment with winter wheat and one with spring barley repeated those described in our Reports for 1970 and 1971. A new experiment was begun with permanent grass. All were at Rothamsted and all compared a liquid with a granular N fertiliser, with and without a herbicide.

The liquid fertiliser, a mixture of urea and ammonium nitrate containing 26% N, was sprayed over the leaves to supply 38, 75 and 113 kg N/ha; it was compared with the same amounts of N as 'Nitro-Chalk' (21% N) given as top-dressings.

The herbicide, a mixture of dichlorprop and MCPA, was sprayed at 2·8, 5·6 (recommended dose) and 8·4 litres/ha (1·4, 2·8 and 4·2 kg acid-equivalent per ha) either alone (on plots given 'Nitro-Chalk') or mixed with the liquid N fertiliser. All treatments in individual experiments were applied on the same day; they were repeated for the second cut of grass. The methods used were described in the *Rothamsted Report for 1970*, Part 1, 59.

Winter wheat (Joss Cambier). Treatments were applied on 2 May. Next day none of the leaves of wheat given 'Nitro-Chalk' (with or without herbicide) was scorched. Those sprayed with liquid N alone were either not, or only slightly, scorched whereas all those sprayed with liquid N and herbicide together were scorched. Scorch was bad only with 75 kg N/ha plus 1·5 times the recommended dose of herbicide and with 113 kg N/ha plus either the recommended, or 1·5 times the recommended dose of herbicide. Scorch was less severe in 1972 than in 1970 and 1971 and symptoms had diminished by 12 May except on wheat sprayed with the largest combined amounts of liquid N and herbicide.

Visual estimates of the weed population in late May and in the stubble after harvest confirmed that the few weeds present had been controlled slightly better by herbicide sprayed together with liquid N than by herbicide sprayed alone.

The height of the wheat was irregular before treatments were applied, perhaps because of residues of fertiliser applied for potatoes the year before. A severe attack of yellow rust (*Puccinia striiformis*) also increased irregularity in the experiment. 'Nitro-Chalk' produced larger yields than liquid N in only five of 12 comparisons (Table 7) in contrast to 1970 and 1971 when it was consistently superior. Herbicide sometimes increased and sometimes decreased yields.

TABLE 7

Comparisons of 'Nitro-Chalk' and a separate herbicide spray with a spray combining N fertiliser and herbicide

	'Nitro-Chalk' (N kg/ha)			Liquid N fertiliser (N kg/ha)		
Herbicide litres/ha	38	75	113	38	75	113
	Winter wheat, t/ha of grain (with 15% moisture)					
None	5·21	5·77	5·38	5·27	5·08	5·61
2·8	5·22	6·26	5·60	5·30	5·96	5·84
5·6	5·45	5·45	5·45	4·92	6·02	5·67
8·4	5·67	5·40	5·55	4·81	5·38	5·60
Standard error			±0·233			
	Spring barley, t/ha of grain (with 15% moisture)					
None	6·49	6·86	6·12	6·32	6·32	6·71
2·8	6·49	6·87	6·61	6·47	6·40	7·50
5·6	6·56	6·56	6·63	6·40	6·39	6·78
8·4	6·32	6·58	6·70	6·04	6·37	6·89
Standard error			±0·193			
	Permanent grass, t/ha of dry matter (total of two cuts)					
None	8·95	9·84	11·35	8·11	9·47	10·06
2·8	9·93	10·77	10·76	8·06	8·80	9·42
5·6	8·47	10·06	10·94	7·97	9·13	10·16
8·4	8·52	9·48	10·46	8·27	8·80	9·66
Standard error			±0·504			

The treatments were applied for both cuts of permanent grass

***Spring barley* (*Julia*).** Treatments were applied on 18 May. Five days later none of the barley given 'Nitro-Chalk' (with or without herbicide) was scorched. Liquid N alone scorched the leaves only very slightly. Increasing amounts of both liquid N and herbicide sprayed together increased leaf scorch, which was not severe, even with the largest amounts of both.

There was little difference in weed control in late June between herbicide sprayed alone (on 'Nitro-Chalk' plots) and combined with liquid N, but there were slightly fewer weeds in the stubble after harvest where herbicide had been sprayed alone.

With 38 or 75 kg N/ha, 'Nitro-Chalk' consistently gave larger yields than the liquid N;

with 113 kg N/ha, 'Nitro-Chalk' lodged the barley more and liquid N then gave larger yields (Table 7). With 'Nitro-Chalk', herbicide affected yields inconsistently; with liquid N, yields were always largest with half the recommended dose of herbicide.

Conclusions. Our three experiments with winter wheat, and three with spring barley, reported between 1970–72 show that spraying herbicide and liquid N together, rather than the liquid N alone, increases the intensity of leaf scorch. The damage done, however, was not sufficient to decrease yields appreciably, except when the smallest amount of N (38 kg/ha) was tested. It appears, therefore, that extra N helped to overcome the damage done to the leaves by the mixture. During 1970–72, 'Nitro-Chalk' gave larger yields of wheat grain than the liquid N in seven of nine comparisons without herbicide and in 20 of 27 comparisons with herbicide. 'Nitro-Chalk' gave more barley grain in five of nine comparisons without herbicide and in 15 of 27 comparisons with herbicide.

Permanent grass. The sward used was in Ver Meadow (a soil of the Gade complex) and contained many weeds. The three most dominant were chickweed (*Stellaria media*), plantain (*Plantago lanceolata*) and yarrow (*Achillea millefolia*). Treatments were applied on 13 April and 28 June and the grass cut on 8 June and 28 September. The scorch pattern was the same five days after the April and seven days after the June sprayings; the leaves of grass were not scorched by 'Nitro-Chalk' (with or without herbicide), slightly scorched with liquid N alone, but increasingly scorched with increasing amounts of both liquid N and herbicide sprayed together. Scorch was never bad, and was less in April, when the day after spraying was wet, than in July. There was little difference in weed control on 31 May between herbicide sprayed alone and combined with liquid N.

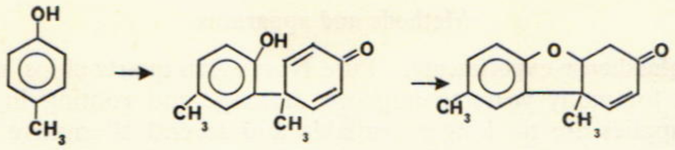
Grass responded to each increment of both 'Nitro-Chalk' and liquid N. Herbicide irregularly affected yield but did not alter the comparison between the two fertilisers; 'Nitro-Chalk' was superior in all 12 comparisons (Table 7). At the second cut, herbage from each plot given 75 kg N/ha was separated into grass and weeds. Weeds contributed 11% of the fresh weight of herbage from plots given 'Nitro-Chalk' alone, 15% from plots given liquid N alone, but less than 2% of the weight of fresh herbage from plots sprayed with herbicide. (Penny and Freeman)

Interactions with soil organic matter

Phenolic compounds. Aromatic amines added to soil, or generated there by degradation of acyl derivatives, such as the phenylurea herbicides, are now known to be extensively incorporated into soil organic matter. The free radical mechanism proposed previously for amine oxidation (*Pesticide Science* (1971), **2**, 165) should be equally applicable to phenols in soils and one would expect that pesticidal phenols would be incorporated into soil organic matter with self-polymerisation products formed if the concentration of phenols is large. Similar reactions have long been suggested to explain the formation of soil organic matter, but their significance for pesticidal materials, present at very small concentrations and providing insignificant amounts of carbon for microbial growth, seems to have been missed.

When *p*-cresol was incubated in Rothamsted and Woburn soils at 25 and 500 ppm, one major neutral product and a minor acidic one were detected, even after one hour. The neutral product was shown from its chromatographic properties and from its nmr spectrum to be Pummerer's ketone (II) the major product of oxidation of *p*-cresol with many one-electron oxidising agents. It is known to be formed by an initial *o, p* coupling to give (I) followed by addition of the phenol to the dienone system.

https://doi.org/10.23637/ERADOC-1-127



I II

It was not possible to establish that *p*-cresol is incorporated into the organic fraction without using radioactive material, so experiments were done with ^{14}C-labelled phenol and benzoic acid in soil at concentrations of 0·1 and 1·0 ppm. In pure culture, both compounds are metabolised via catechol which should be incorporated very readily into organic matter. $^{14}CO_2$ evolution from carboxyl-labelled benzoic acid was almost complete ($> 90\%$) overnight although about 5% of added ^{14}C was still present after five months. Almost all the $^{14}CO_2$ evolved from Rothamsted soils treated with ring-labelled benzoic acid (70%) or phenol (30–40%) was detected within the first 24 hours. However, about 20% of the benzoic acid carbon and 50% of the phenol carbon remained in Rothamsted soil after five months. More remained in other soils which had previously been shown to incorporate aromatic amines readily into the organic fraction. Jenkinson (*Journal of Soil Science* (1966), **17**, 280) has estimated the biomass in soils from the size of the flush of decomposition following partial sterilisation. This method should be applicable to determining the fraction of labelled material incorporated in the biomass, assuming that $^{14}CO_2$ evolved during the flush comes from decaying microbial tissue. Partial sterilisation, two weeks after addition of benzoic acid or phenol to soil, showed that only a small fraction of radiocarbon remaining was in the biomass, providing further evidence for incorporation into the stable organic fraction.

2,4-Dichlorophenoxyacetic acid. The degradation of 2,4-D by micro-organisms in pure culture has been extensively investigated but little work has been done in soils except bio-assays which show that this herbicide is decomposed rapidly. Ring-labelled 2,4-D (5 ppm) was decomposed at about equal rates in soils from sections of Broadbalk which have either been sprayed periodically since 1963 with hormone weed killers or from sections never sprayed. Total $^{14}CO_2$-evolution increased with time (up to 14 days) and solvent-extractable radioactivity remaining in soil decreased with time; only about half of the total radioactivity added was evolved as $^{14}CO_2$. $^{14}CO_2$-evolution from herbicide labelled either in the carboxyl or methylene carbon of the side-chain was very different from ring-labelled herbicide. In the unsprayed soil, a steady slow evolution of $^{14}CO_2$ was observed for several months. In the sprayed soil, there was a five-day lag period, followed by a very rapid evolution of $^{14}CO_2$ for about ten days, by which time extractable radioactivity was very low. $^{14}CO_2$ was evolved at about the same rate as from the unsprayed soil after this time. A considerable fraction of carbon, which was not metabolised after partial sterilisation, remained in both soils.

Decomposition probably proceeds by two competing processes: (1) a non-specific ring hydroxylation followed by further metabolism or by incorporation into organic matter; this proceeds without a lag period and removes the herbicide without much side-chain metabolism; (2) specific hydroxylation of the methylene carbon followed by hydrolysis to 2,4-dichlorophenol and glyoxylic acid which is easily metabolised further. The lag period is short in the soil previously sprayed at normal field rates with related compounds but longer than the life of the herbicide in the unsprayed soil, because of removal by the alternative pathway. The more rapid breakdown in the sprayed soil is presumably due to the development of a microflora which has become adapted to annual applications of the herbicide. (Briggs)

Methods and apparatus

Soil diluents in glasshouse experiments. Pure Norwegian quartz chips, mixed with soils, have been used for many years to improve drainage and rooting in our glasshouse experiments. Supplies are no longer available and several alternative were evaluated. Table 8 gives yields of ryegrass and N uptakes from Rothamsted soil, mixed with equal *volumes* of diluents, and given adequate N, P and K. Three materials, Leighton Buzzard sand, Cornish grit and polythene beads all gave the same yields as soil mixed with Norwegian quartz. Vermiculite gave larger yields than quartz when mixed with Rothamsted soil. There were no differences between any of the materials when mixed with Woburn soil. N uptakes were the same with all materials on both soils. Another source of quartz from Portugal, available in seven grades, has been used successfully in experiments this year. (Mitchell and Avery)

TABLE 8

Effects of diluents on yields of, and N uptakes by, ryegrass grown in Rothamsted soil

Material	g/pot	
	Dry matter	N uptake
Norwegian quartz, water washed	13·87	0·49
Norwegian quartz, acid washed	14·08	0·50
Sand, water washed	13·96	0·52
Sand, acid washed	13·96	0·50
Cornish grit, water washed	13·86	0·50
Cornish grit, acid washed	12·75	0·49
Vermiculite, water washed	16·17	0·50
Polythene beads, water washed	13·62	0·48
Standard error	±0·327	±0·016

Calculations of ion activities in soil solutions. In solutions containing many different cations and anions, e.g. soil solutions, restraints on the composition are caused by solubility products, ion-pair formation and dissociation constants. In all these equilibria, activities rather than concentrations are important. A computer program to calculate ion activities in such complex solutions, described by Professor F. Adams (*Proceedings of the Soil Science Society of America* (1971), **35**, 420) has been tested on our ICL 4-70 machine. With a few minor corrections, the program was used successfully to calculate ion activities in drainage water. The effects of temperature on equilibrium constants have caused some problems not yet resolved. (Bolton)

Analysis of radioactive samples

Liquid scintillation counting. About 25 000 samples were analysed for six radioisotopes on the Beckman scintillation spectrometer, half as many again as in the previous year. This increase arises partly because our automated solid counting system became increasingly unreliable. (Elsmere)

Polythene vials for scintillation counting. Commercial polythene vials cost less than 'low background' glass vials and are claimed to be unaffected by organic solvents. However, after contact for 24 hours with our 'toluene-base' phosphor the counting efficiency of ^{14}C samples decreased significantly by 1·5% (5·0% for tritium) with the phosphor alone, 1·0% (3·5%) with phosphor + Triton X-100 emulsifier and 1·0% (3·5%) with phosphor + emulsifier + water. This change occurred in the first 24 hours of contact, making the vials unsuitable for accurate work. After 20 days contact, the vials became so brittle and dry that they were difficult and hazardous to use in the Beckman spectrometer. (Elsmere)

Liquid phosphors. The effects of water and light were compared on three commercial emulsifying phosphors (Koch Light's *Unisolve* and *KL 354*, dioxan-base, and NEN's *Aquasol*, xylene-base) and our 'toluene-base' phosphor with and without Triton X-100 emulsifier. Without previous exposure to light, all phosphors gave similar background count-rates, which were unchanged by fluorescent laboratory lighting. However, six hours of diffuse daylight increased the background count-rates of three commercial phosphors from 40 cpm to 170–90 000 cpm, the largest increases being with the 'dioxan-base' phosphor *KL354* + water. These 'backgrounds' only returned to normal after 20–50 hours in the dark. The efficiency of ^{14}C assay in water-free solvents was best in our 'toluene-base' phosphor. With aqueous solvents, the 'dioxan-base' phosphor was the most efficient. (Elsmere)

Crops, fertilisers and soils. The 'Technicon AutoAnalyzer' handled 33 000 samples, including analyses for NH_4-N, NO_3-N and P, Cl, S, K and Al. Automated analyses of 18 000 samples (that included ten cations) were also done by atomic absorption on the SP90. More than 10 000 Kjeldahl digestions were done, 1600 were analysed manually by distillation and the rest on the 'Technicon AutoAnalyzer'.

The number of analyses in all sections were a fifth more than last year; about an eighth of the total were for other Departments. (Avery, Cosimini and Messer)

Automated phosphorus analysis. The automated version of the phosphovanado-molybdate method for determining phosphorus in solution in the range 1–80 ppm (Varley, J. A. (1966) *Analyst* **91**, 119) was used successfully as an alternative to the automated version of the molybdenum blue method of Fogg and Wilkinson (*Analyst* (1958), **83**, 406). Samples need to be diluted less, fewer pump tubes are required and the manifold can be used to measure P and K simultaneously. (Messer)

Staff and visiting workers

Following the sudden death of Sir Frederick Bawden in February 1972, G. W. Cooke became Acting Director and G. E. G. Mattingly Acting Head of the Chemistry Department.

J. K. R. Gasser left to take up a full-time appointment as a Scientific Adviser to the Agricultural Research Council and Lucretia Scotland left to go to Reading University.

The following visitors worked in the Department during the year: Dr. M. J. Abedi (Iran), Mr. I. C. R. Holford (Australia), Dr. S. J. Kalembasa (Poland), Dr. P. K. R. Nair (India) and Professor L. E. Nelson (U.S.A.). C. Hinson and W. Symonds spent six months as sandwich course students.

P. H. Le Mare visited Namulonge Research Station, Uganda, financed by the Overseas Development Administration. O. Talibudeen attended a symposium on 'Potassium in Soils' at Landshut, West Germany, as a guest of the International Potash Institute. F. V. Widdowson took part in the Third International Conference on 'Mechanisation of Field Experiments' at Brno, Czechoslovakia, and T. M. Addiscott and G. E. G. Mattingly attended the 25th Anniversary Meeting of the British Soil Science Society in Wageningen, Holland; all were financed by the Agricultural Research Council.

T. M. Addiscott was awarded the Ph.D. degree of London University.