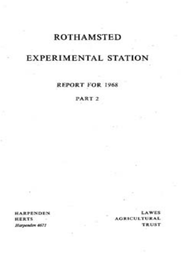
Rothamsted Experimental Station Report for 1968 - Part 2



Full Table of Content

Plant Nutrients in Broadbalk Soils

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minerals have been increased by precipitation of aluminium and iron mobilised from alumino-silicate clay minerals during the various weathering phases. Some of the aluminium freed by acid leaching subsequently entered the interlamellar space of 2:1 layer lattice minerals, and now occurs as hydrated cations in expanding layers, as polymerised aluminium hydroxide in non-expanding layers (chloritised layers), or in mixtures of and intermediates between these two forms. The complexity of X-ray diffraction patterns of the clays results largely from the intermingling of these various layers with non-expanding mica layers and freely-expanding montmorillonite or vermiculite layers. In Table 5·5 the 2:1 layers containing interlamellar aluminium are given as part of the interstratified expanding minerals and chlorite. Complex aggregations of different layers are typical of soil clays, but there is no satisfactory nomenclature for them. Minerals such as chlorite, mica, vermiculite and montmorillonite do occur in soils, but the exclusive use of such terms in describing soil clays inevitably involves oversimplifications.

Plant Nutrients in Broadbalk Soils

By A. E. JOHNSTON

Soil sampling

The principal dates when the soils of all plots were sampled were 1881, 1893, 1914, 1944 and 1966; some plots were also sampled in 1856, 1865, 1904, 1923 and 1936. Although there are still a few samples at Rothamsted taken about the start of the Broadbalk experiment, suitable techniques for taking and storing samples were then unknown and it was not until 1856 that Lawes and Gilbert adopted a procedure they considered satisfactory. Samples were taken during autumn, after the crop had been removed but before ploughing, so that the soil was at its maximum compaction. The procedure, which was rigidly adhered to, was described in detail by Lawes & Gilbert (1882) and by Dyer (1902). It consisted of taking samples with an open-ended metal box of known volume; the depth was always 9 in., the cross-section usually 6 in. × 6 in., occasionally 12 in. × 12 in. The box was driven into the soil until the top edge was level with the surface. The enclosed soil was then carefully removed. Samples below 9 in. were taken by removing the soil from round the box so that it could be driven down again to the full depth of 9 in. Usually 3 or 4 depths were sampled but on some plots in October 1893, after the 50th crop, samples were taken to 90 in. To get these samples large holes 4 to 5 ft in diameter were dug. The soil from each depth was kept separately, back filled in correct order and consolidated with a wooden rammer. Manuscript notes indicate that it was impossible to detect the position of the holes from the appearance of the crop grown in 1894. Lawes and Gilbert subsequently regretted adopting 9 in. as the sampling depth for only shallow cultivations were possible with horses and on Broadbalk the plough layer was less than 6 in.

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deep. However, with the subsequent development and introduction of the tractor and the consequent deeper ploughing the ploughed surface soil has been increased to about 9 in.

It was not until after 1877, when Warington had confirmed that nitrification occured in moist soils, that it was realised that soil samples should be dried as soon as possible after being taken. Though the 1856 and 1865 samples were sieved and weighed as follows they were not dried immediately; for the 1881 and subsequent samples soil from each depth was weighed, broken by hand and dried at about 55° C. The soil was then sieved through sieves of 1 in., 0·5 in. and 0·25 in. square mesh. The stones retained on each sieve were weighed as was the soil passing the 0·25 in. sieve. A sub-sample of soil was dried at 100° C to determine the dry weight and a further sub-sample was finely ground for chemical analysis. Later, and certainly for the 1936 samples, the soils were ground to pass a 2 mm rather than a 0·25-in. sieve.

For the samples taken in 1856, 1865, 1881, 1893, 1904 and 1914 the metal box was used. There were between three and eight sample positions on each plot and from the separate samples a bulked sample was prepared for each depth on each plot. In 1914 duplicate samples of surface soil were taken with a cylindrical sampler. In 1936 a semi-cylinder sampler was used to sample the surface soil of plots 2A, 2B, 3, 5 and 7; 25 cores were taken from each section and the samples from each section were kept separately. In 1944 an attempt was made to repeat the earlier box sampling by taking cubes of surface soil with a spade, but the 9–18 in. subsoil was sampled with a semi-cylinder. Four samples were taken from each section and the pH and $CaCO_3$ contents were determined on each; for further analyses, a bulked sample for each section of each plot was prepared. In 1966 the surface soil of all plots was sampled with a semi-cylinder, (0·75 in. diameter), to a depth of 9 in. Twenty cores were taken from each section and the samples from each section were kept separately. To avoid areas where soils may have been mixed by moving, only the central third of each plot was sampled.

Caution must be used in making use of the soil samples from Broadbalk. Lawes and Gilbert chose to sample each plot in a few places but to take a fairly large sample at each one. This made possible the calculation of bulk densities and weights/acre of stones and fine earth; there was often considerable variation between samples. Small diameter cores taken by semi-cylinders cannot be used to determine the weight of stones and fine soil per acre, but provided enough cores are taken, the sample represents the soil of the plot much better than the box samples for measuring the proportions of N, P and K. Because of the difficulty of getting representative samples for both weight of soil/acre and nutrient content, any calculations that attempt to express N, P and K as absolute quantities per acre are liable to error. Lawes and Gilbert were well aware of this problem and they often made the point that an analytical error of 0·001 % was equal to 25 lb/acre if the 0–9 in. depth of soil weighed 2 500 000 lb. There are some discrepancies between their earlier accounts of nitrogen accumulation and depletion in their experimental soils. However they resolved some of these differences and Dyer (1902), after consultation with Lawes and Gilbert, gave an agreed account for the weight of stones, fine soil, total N and citric acid-soluble P and K in Rothamsted soils up to 1893. He gave separate values for the weights of fine soil per acre for: (i) plots receiving mineral manures; (ii) plots receiving FYM; (iii) the plots receiving rape cake because there were consistent differences. Unfortunately, Hall (1905) later gave a mean value for all plots, and this has been widely used.

Attention must also be drawn to two other factors that can cause discrepancies between various published results, especially in later work. Many authors have characterised the soil of a plot by various analyses and their results have not always agreed. This is because:

1. Their sampling may have been restricted to a particular section, and recent work on the 1966 samples has shown considerable differences between sections. For example, the mean N content for all plots, excluding 20, in each section is—

Section	IA	IB	II	III	IV	VA	VB
% N in air dry soil	0·136	0·128	0·128	0·121	0·127	0·129	0·133

Section III, which was fallowed for four years between 1925 and 1930, whereas the other sections were fallowed only twice, contains least N.

2. Some soil has moved across plot boundaries and though this is less on Broadbalk than on Hoosfield (Warren & Johnston, 1967), results shown in Table 5·7 suggest that at least 3 or 4 feet should be discarded at each edge. Table 5·7 shows the changes in total P across part of plot 5 (PKNaMg) and plots 3 (unmanured), 2B (FYM since 1843) and 2A (FYM since 1885) in sections VA and VB in 1956. As on Hoosfield, soil samples (0–6 in.) were taken about 1 ft apart to measure the extent of soil movement and the results of the analyses when plotted gave surprisingly smooth curves. For ease of presentation the results in Table 5·7 are given at 1 yard intervals.

TABLE 5·7

Change in Total P across plots 2A, 2B, 3 *and part of* 5, *Broadbalk 1956*

Surface soil 0–6 in. total P mg/100 g at yard intervals

Section	Plot 5		Path	Plot 3							Path			Plot 2B					Plot 2A			Path
VA	121	106	86	70	60	60	57	60	60	64	72	80	91	113	132	138	134	129	128	128	118	105
VB	140	110	90	66	62	60	59	59	62	69	82	92	104	130	144	140	129	120	119	109	85	72

Soil reaction and calcium carbonate content

Avery and Bullock (page 67) have described the practice of chalking used in the past to improve Rothamsted arable soils. Applied by hand in amounts that might have been as much as 60–100 tons/acre, the distribution was not uniform, as was shown for Hoosfield (Warren & Johnston, 1967). Table 5·8 shows the calcium carbonate content of the 1944 soil samples and the irregularities in the surface soil. The plots on sections IV and V have, on average, about 1% less $CaCO_3$ than the plots in the other sections. Hall and Miller (1905) analysed soils taken from several plots in 1856, 1865, 1881, 1893 and 1904 and showed that $CaCO_3$ was lost from arable soils containing more than 1% $CaCO_3$. Sampling errors from the few sampling points on each plot, and the initial irregular distribution of the applied chalk, made it impossible for them to estimate the annual loss accurately, but they calculated that between 800 and 1000 lb $CaCO_3$/acre/year was lost and that the loss was greater where ammonium salts were applied.

TABLE 5·8

Calcium carbonate in Broadbalk soils, 1944

Surface soil 0—9 in. % $CaCO_3$ in air dry soil

Plot	Section					Plot mean
	I	II	III	IV	V	
2A	1·6	2·5	2·1	1·2	1·6	1·8
2B	2·8	2·7	2·4	1·1	1·2	2·0
3	2·9	3·1	3·1	1·7	1·4	2·4
5	2·0	2·1	2·7	1·0	0·9	1·7
6	1·0	1·4	2·2	0·4	1·4	1·2
7	0·7	1·3	1·9	0·3	0·1	0·8
8	0·2	0·9	1·0	0·2	0·0	0·5
9	2·2	2·7	2·3	1·1	1·2	1·9
10	1·2	1·5	0·8	0·3	0·4	0·8
11	1·2	1·3	1·2	0·2	0·3	0·8
12	1·6	1·4	1·0	0·2	0·1	0·9
13	1·8	1·5	0·7	0·3	0·0	0·9
14	1·1	1·5	0·8	0·4	0·0	0·7
15	0·5	0·8	1·0	0·3	0·1	0·6
16	1·7	1·5	1·6	1·4	0·9	1·4
17	1·6	2·1	1·7	1·8	1·3	1·7
18	1·6	2·0	2·5	1·9	0·9	1·8
19	1·4	1·9	1·0	0·1	0·4	1·0
20	2·4	1·4	—	—	—	(1·9)
Section mean	1·6	1·8	1·7	0·8	0·7	

When sampled in 1944, the soils of plots 8, 13 and 14 section V contained no free $CaCO_3$ and those of plots 7, 12 and 15 section V not more than 0·1% $CaCO_3$. In March 1954 the crop on parts of plots 8, 14 and 15 section V was very yellow and the soils of all plots in sections IV and V were sampled. The soil reaction on parts of plots 7, 8, 11, 12, 13, 14, 15 and 19, especially in section V, was acid and the Field Plots Committee decided that this should be corrected on section V. The correction was made by dividing section V into halves; the eastern ('B') half received 5 tons $CaCO_3$/acre as ground chalk in autumn 1954 and the 'A' half the same amount in autumn 1963. To prevent further acidity developing, from 1954 chalk was applied annually to the stubble before ploughing on plots receiving ammonium sulphate and rape cake (see Table 2·2). The reaction of the surface soils sampled in 1966 showed that some small areas required further chalking and various amounts of chalk were applied in autumn 1967 to bring the soils to a minimum of pH 7.

Total nitrogen and organic matter

The Broadbalk soils were originally sampled to see how their nitrogen content was affected by manuring and cropping. Table 5·9 shows the mean nitrogen and organic carbon content of the soils of all sections in 1944 and of sections IB, II, III, IV and VA in 1966. For 1966 sections IA and VB are omitted because, being last fallowed in 1951 and 1958 respectively, they were not then in the fallowing cycle.

TABLE 5·9

Organic carbon and nitrogen content of Broadbalk soils, 1944 and 1966

Air-dry surface soil 0–9 in.
1944 mean for all sections
1966 means for section IB, II, III, IV, VA

Plot	Treatment	Organic carbon (%)		Total N (%)	
		1944[1]	1966[2]	1944	1966
3	None	1·09	0·84	0·106	0·099
2A	FYM since 1885	2·05	2·30	0·191	0·216
2B	FYM	2·58	2·59	0·236	0·251
19	Castor meal	1·29	1·17	0·136	0·128
5	P K Na Mg	1·00	0·91	0·105	0·107
6	N_1 P K Na Mg	1·07	0·97	0·112	0·113
7	N_2 P K Na Mg	1·19	1·00	0·121	0·115
8	N_3 P K Na Mg	1·19	1·04	0·123	0·118
15	N_2†P K Na Mg	1·09	0·95	0·118	0·109
17	N_2	1·09	0·99	0·119	0·117
18	P K Na Mg	1·13	1·02	0·122	0·120
9	N_1*P K Na Mg	1·08	0·94	0·114	0·110
16	N_2*P K Na Mg	1·09	0·99	0·117	0·113
10	N_2	1·05	0·91	0·109	0·106
11	N_2 P	1·06	0·96	0·114	0·113
12	N_2 P Na	1·06	1·00	0·120	0·114
13	N_2 P K	1·06	1·02	0·124	0·115
14	N_2 P Mg	1·11	0·99	0·118	0·114
20	N_2 K Na Mg	1·25	1·07	0·131	0·128

[1] Dry combustion. [2] Chromic acid titration.

N Nitrogen as ammonium salts.
N* Nitrogen as sodium nitrate.
N† All nitrogen as ammonium sulphate in autumn.

Organic carbon. Changes in the nitrogen contents of soils (discussed later) reflect changes in the amounts of organic matter. Organic carbon was only determined on soils from all plots in 1944 and 1966. Rickson's (1948) dry combustion method was used in 1944, in 1966 the chromic acid titration method of Walkley and Black (1934). Table 5·9 gives Walkley and Black data multiplied by 1·3 the accepted factor. The organic carbon in the 1966 samples was smaller than in 1944 samples, except on the FYM plots. A loss of carbon is unlikely as there was no significant loss of nitrogen between 1944 and 1966. Most probably the factor of 1·3 is too small for old arable soils without FYM residues (Bremner & Jenkinson, 1960).

Jenkinson (1969) has discussed the results of radiocarbon dating for plot 3. The soil contained no coal or charcoal that could be extracted by flotation in a liquid of S.G.2.00. He concluded, therefore, that the equivalent age of 1385 ± 140 years for the carbon in the 0–9 in. soil sampled in 1881 indicated that much of the organic matter in Broadbalk is very resistant to mineralisation.

Total nitrogen. As on the other Classical arable experiments, the unmanured soil contains about 0·10% N. Fourteen tons/acre/year of FYM since 1843 has increased the N content of plot 2B to 0·25% N and this dressing since 1885 has increased the N content of plot 2A to 0·22% N. It is impossible to determine precisely the effect of castor meal on the N content of the soil because the dimensions of the plot have altered, but slightly more of the added N (80–90 lb N/acre/year) has remained in the soil than where 86 lb inorganic N was given each year. The effect of applying 86 lb N/acre/year as ammonium sulphate was remarkably consistent; plots 7, 11, 12, 13, 14 all have 0·114 ± 0·001% N, only 0·015% N more than the unmanured plot. This increase in the N content of these plots is thought to come from the N in the larger plant residues returned each year to the soil rather than to inorganic-N accumulations. This suggestion is supported by the fact that 86 lb inorganic-N given without PKNaMg (plot 10), or all in autumn (plot 15), has not increased the N content to the same amount; the smaller crops on these plots would return smaller residues to the soil.

Dyer (1902) gave all the nitrogen analyses made on the Broadbalk surface and sub-soils up to 1893 and included figures for some other Rothamsted soils and some subsoil analyses from other localities (including clay taken from below Piccadilly Circus when tunnelling for the underground railway). He pointed out that there had been a change in the method of nitrogen analysis from the soda-lime to the Kjeldahl method (for details see page 50) and that the Kjeldahl method gave slightly larger values for

TABLE 5·10

Total N content of Broadbalk surface soils 0–9 in.

% N in air dry soil

		1865	1881	1893	1893	1914	1936[1]	1944[1]	1966[2]
Method of sampling		Metal box	Metal box	Metal box	Metal box	Metal box	Semi-cylinder	Spade	Semi-cylinder
Method of analysis		Soda-lime	Soda-lime	Soda-lime	Kjeldahl	Kjeldahl	Kjeldahl	Kjeldahl	Kjeldahl
Plot	Treatment								
3	None	0·105	0·101	0·094	0·099	0·093	0·103	0·106	0·099
2A	FYM since 1885	n.s.	n.s.	0·152	0·163	0·196	0·186	0·191	0·216
2B	FYM	0·175	0·184	0·213	0·221	0·252	0·226	0·236	0·251
5	P K Na Mg	0·107	0·098	0·097	0·101	0·103	0·105	0·105	0·107
6	N_1 P K Na Mg	n.s.	0·111	0·108	0·111	0·112	n.s.	0·112	0·113
7	N_2 P K Na Mg	0·117	0·121	0·115	0·122	0·120	0·120	0·121	0·115
8	N_3 P K Na Mg	n.s.	0·126	0·117	0·119	0·129	n.s.	0·123	0·118
15	N_2†P K Na Mg	n.s.	0·118	0·119	0·123	0·118	n.s.	0·118	0·109
17	{N_2	n.s.	0·109	0·112	0·117	0·121	n.s.	0·119	0·117
18	P K Na Mg	n.s.	0·112	0·120	0·123	0·120	n.s.	0·122	0·120
10	N_2	0·106	0·103	0·102	0·106	0·114	n.s.	0·109	0·106
11	N_2 P	0·112	0·112	0·112	0·113	0·128	n.s.	0·114	0·113
12	N_2 P Na	0·116	0·116	0·111	0·119	0·128	n.s.	0·120	0·114
13	N_2 P K	0·115	0·119	0·109	0·116	0·122	n.s.	0·124	0·115
14	N_2 P Mg	0·115	0·116	0·120	0·125	0·119	n.s.	0·118	0·114

n.s. not sampled.

[1] Mean all sections. [2] Mean sections IB, II, III, IV, VA.

N Nitrogen as ammonium salts.
N* Nitrogen as sodium nitrate.
N† All nitrogen as ammonium sulphate in autumn.

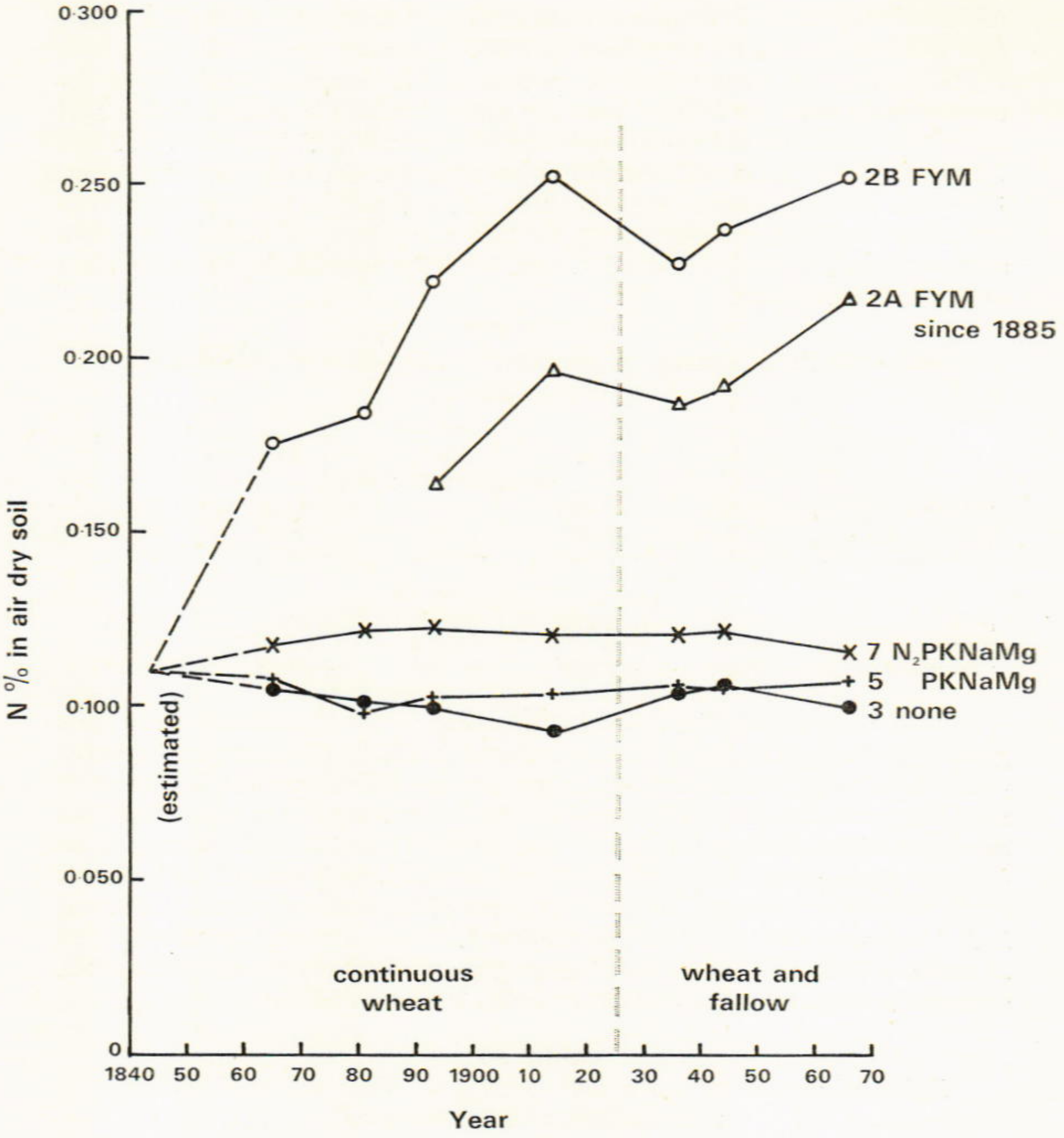

FIG. 5·4. Nitrogen content of Broadbalk soils

the 1893 samples. Not only the method of analysis but, later the method of sampling also changed. Table 5·10, which gives all the measurements of N in the surface soils also shows the method of analysis and sampling. In it corrections are made of a few figures previously transcribed incorrectly by Crowther (1947) and Warren (1956). The results for plots 9, 16, 19, 20 are omitted because there were major changes in manuring that may have affected the N content. The results in Table 5·10 for the treatments, unmanured (plot 3), PKNaMg (plot 5), N_2PKNaMg (plot 7), FYM (plot 2B) and FYM since 1885 (plot 2A) were used to prepare Fig. 5·4, which shows the changes in the nitrogen content between 1865 and 1966. The N content of the unmanured soil remained remarkably constant, and adding PKNaMg had little effect. Soil N increased by 0·015% during the first 20 years with N_2PKNaMg but then remained constant. The increase with FYM increased with time, and hence with the amount of FYM added. Table 5·11 shows that much of the variation in the results in Fig. 5·4 for plots 3, 5 and 7 reflects the methods of sampling and analysis. On only two occasions, 1936 and 1966, and then only for plots 2B, 3, 5 and 7, was the method of sampling and analysis the same, but the changes in N content on each section, for the means of plots 3, 5 and 7 and for plot 2B, is very consistent over the five sections.

TABLE 5·11

Changes in the N content of Broadbalk soils between 1936 and 1966

% N in air dry soil

	Section				
	I	II	III	IV	V
			mean plots 3, 5 and 7		
1936	0·114	0·109	0·103	0·109	0·110
1966	0·113	0·108	0·102	0·104	0·112
1966 minus 1936	−0·001	−0·001	−0·001	−0·005	+0·002
			plot 2B		
1936	0·228	0·220	0·213	0·232	0·236
1966	0·254	0·249	0·241	0·260	0·262
1966 minus 1936	+0·026	+0·029	+0·028	+0·028	+0·026

A major feature of Fig. 5·4 is the decrease in the N content of the soils given FYM after fallowing was introduced in 1926. The two consecutive years of fallowing on all sections, except section III, which was fallowed for the four years between 1926 and 1929, had a much greater effect than the one year in five fallow, for the N content of Plots 2A and 2B started to increase again after 1936. That this effect was largely one of fallowing is confirmed by the changes in the N content of the soils of plots 2A, 2B and 3, 5, 7 between 1944 and 1966 on section I. This section was sub-divided in autumn 1955 so that section IA has grown wheat every year since 1952, whereas section IB was fallowed in 1956, 1961 and 1966.

TABLE 5·12

Effect of continuous wheat and wheat and fallow on the N content of Broadbalk soils on section I

% N in air-dry soil

		Continuous wheat since 1951 on section IA			Wheat and Fallow since 1951 on section IB		
		% N in			% N in		
Plot	Treatment	1944	1966	1966 minus 1944	1944	1966	1966 minus 1944
2A	FYM since 1885	0·191	0·224	0·033	0·191	0·209	0·018
2B	FYM since 1844	0·236	0·266	0·030	0·236	0·243	0·007
	Mean			0·032			0·012
3	None	0·106	0·111	0·005	0·106	0·107	0·001
5	P K Na Mg	0·105	0·117	0·012	0·105	0·112	0·007
7	N_2P K Na Mg	0·121	0·122	0·001	0·121	0·120	−0·001
	Mean			0·006			0·002

Table 5·12 shows that:

1. The mean increase in N content with both FYM and fertilisers was about three times as great under continuous wheat as under the cycle of four years crop and one year fallow.
2. For both systems the increase on the fertiliser plots was only one-sixth that on the FYM plots.

Although the weights of fine soil/acre cannot be determined accurately they are known well enough to calculate the gain in soil nitrogen in the surface soil on each sampling date and to express this as a percentage of the nitrogen added in the FYM given to plots 2A and 2B. Table 5·13 shows that 2B initially accumulated nitrogen rapidly, to be followed by a long period when, under continuous wheat, about 25% of the added N was retained in the surface soil. After the fallowing, the proportion fell to 15% of the added N. Much the same proportions were retained on plot 2A.

TABLE 5·13

Gain in soil nitrogen due to applying FYM to Broadbalk

Gain over the unmanured plot at each sampling date as % of the total nitrogen added since the treatment started

Date	Plot 2B	Plot 2A
1865	37	—
1881	25	—
1893	27	50
1914	25	37
1936	15	20
1944	15	17
1966	16	20

It must be emphasised that the losses of N from the soils of plots 2A and 2B in any year are the sums of the losses from organic matter residues of increasing age.

Phosphorus and potassium

From their early work on nitrogen, Lawes and Gilbert showed that only a very small part of the total nitrogen in soil was available to plants, and they soon realised that, if crops responded to small additions of soluble P and K, then the large reserves of these nutrients present in most soils were also not available to plants. Among the first attempts to determine P and K available to plants was that of H. von Liebig (1872) who obtained soils from five of the Broadbalk plots and determined, in the 0–9 and 9–18 in. depths, P soluble in dilute nitric acid and K soluble in dilute acetic acid. The strengths of the acids used were not given but the amounts of P and K extracted clearly differentiated between soils that had and had not been given P or K fertilisers. During the next few years several workers suggested the use of various dilute acids for extracting soil, and Deherain (1891) used dilute acetic acid to differentiate between plots unmanured and those receiving P since 1875 in an experiment at Grignon. Although Stutzer (1884) suggested the use of 1% citric acid for evaluating the usefulness of phosphatic manures, Dyer deserves the credit for using this reagent to examine soils.

To check that this reagent would differentiate between soils where crops respond differently to P and K, he first examined the soils from the Hoosfield Barley experiment (Dyer, 1894) and then those from Broadbalk (Dyer, 1901, 1902). He compared the amounts of citric soluble-P and K in each surface soil with the total P and K determined by digesting the soil for 48 hours with constant boiling HCl, and showed that, though the total P varied in the ratio 2:1 between manured and unmanured soils, the range of citric-soluble P was much greater, 8 or 9:1. He thus concluded that citric-soluble P was a better index of the P fertility of a soil. For potassium he showed that the K in the boiling HCl extract was only between one-tenth and one-fifth of the total K found by fusing the soil or dissolving it with HF. Also he showed that the K in duplicate HCl extracts was very variable and there was very little difference between the amounts (about 0·21% K, 0·25% K_2O) extracted from K-manured and unmanured soil. However, the range of citric-soluble K was 8 or 10:1. Dyer concluded from his analyses that soils were deficient in P for cereals when they contained less than 0·0044% P (0·01% P_2O_5) soluble in 1% citric acid in the surface soil. He was unable to fix a lower limit for soluble-K content, but concluded that cereals would not respond to extra K when the soil contained more than 0·008% citric-soluble K (0·01% K_2O).

From his analyses of surface soil and subsoil, Dyer concluded that almost all the residual fertiliser P remained in the top 9 in. of soil but there was an indication that on the FYM plots some P had moved into the subsoil. For K the story was quite different and at that time was considered rather unexpected on the Rothamsted soil because of its clay content. On both the fertiliser and FYM plots, much K had moved into the subsoils, even down to 27 in. However, the validity of the result was confirmed by analyses of the Broadbalk drainage waters (Lawes, Gilbert & Warington, 1882), which showed a small loss of K from the soil in the drainage.

The next study of the P and K status of Broadbalk soils was by Hall, begun while he was still at Wye College. In the first paper Hall and Plymen (1902) compared the amounts of P and K removed by 6 extractants from the soils of 7 plots sampled in 1893, and concluded that there was no sharp distinction between available and non-available P and K; also that all the extractants they tested were empirical and the amount of P and K extracted depended on the nature and strength of the extractant. They found, as Dyer had shown, that the differences between the amounts of P and K extracted from manured and unmanured soils were greater with weak than with strong solvents and they favoured 1% citric acid. In the second paper, Hall and Amos (1906) compared successive extractions of each soil by water saturated with CO_2 and by 1% citric acid. They showed that the amount of water-soluble P did not change much with successive extractions but it was difficult to determine accurately the small amounts of P extracted. Successive extractions with 1% citric acid showed that it was not until after the 5th or 6th extraction that the amount of P extracted at each shaking became approximately constant. They also showed that the sum of the P removed in five extractions, when calculated on an acreage basis, was about the amount that would have accumulated in the soil from the residue of the P fertiliser applied.

Phosphorus. Table 5·14 shows the P soluble in 0·01 M-$CaCl_2$, 0·5 M-$NaHCO_3$ and 0·5M-acetic acid-0·5M-ammonium acetate at pH 4·8 (N.A.A.S. 1967) in the soils taken in 1966. None of these methods was in use even in 1944 and comparisons with earlier results are not possible. All three methods place the soils in appropriate order from their known histories of manuring and cropping. For each method of analysis, all the plots not given P contain about the same amount, and the small additions of P in castor meal have slightly increased the soluble P. Where P fertiliser has been applied annually, all methods extract much more P and the ratio between manured and unmanured soils was greater with these reagents than with citric acid. This is because improved analytical techniques now allow smaller amounts of P to be determined accurately, so weaker extractants can be used. Compared with plots receiving superphosphate annually, P added in alternate years on plots 17 and 18 has given about half the increase in bicarbonate-soluble P but only about a quarter of the increase in $CaCl_2$-soluble P or acetic acid-ammonium acetate-soluble P. The effect of different extractants in measuring soluble P when P was added in FYM and as superphosphate can be compared. The FYM plot (2B) has slightly more total P than the N_2PKNaMg plot (7) and the ratio of the bicarbonate-soluble P on the two plots was the same as for the total P, but there was more $CaCl_2$ soluble P on the FYM plot than would be expected from the ratio of the total P. This effect of FYM enhancing the

TABLE 5·14

Readily soluble phosphorus in Broadbalk soils, 1966

Surface soil, 0–9 in. (mean of all sections)

		P soluble in:		
Plot	Treatment	0·01 M-$CaCl_2$ g mols/litre × 10^{-6}	0·5 M-$NaHCO_3$ mg/100 g	Acetic acid-ammonium acetate at pH 4·8, mg/100g
3	None	0·2	0·8	0·4
2A	FYM since 1885	13·5	7·5	12·8
2B	FYM	19·5	9·7	15·3
19	Castor meal	1·9	4·4	1·5
5	P K Na Mg	7·2	8·0	11·7
6	N_1 P K Na Mg	10·8	8·8	9·7
7	N_2 P K Na Mg	8·2	8·8	7·4
8	N_3 P K Na Mg	6·6	8·1	3·6
15	N_2†P K Na Mg	8·3	8·8	6·9
17	N_2	1·6	4·3	2·2
18	P K Na Mg	2·7	5·2	2·8
9	N_1*P K Na Mg	6·8	8·4	5·1
16	N_2*P K Na Mg	4·7	6·7	4·6
10	N_2	0·2	0·7	0·2
11	N_2 P	5·9	8·0	7·7
12	N_2 P Na	7·1	8·3	8·6
13	N_2 P K	5·9	8·0	6·8
14	N_2 P Mg	8·0	8·4	6·9
20	N_2 K Na Mg	0·2	0·4	0·4

N Nitrogen as ammonium salts.
N* Nitrogen as sodium nitrate.
N† All nitrogen as ammonium sulphate in autumn.

solubility of that fraction of the total soil P soluble in $CaCl_2$ was also noted on Barnfield (Warren & Johnston, 1962b) and on Hoosfield (Warren & Johnston, 1967).

The P soluble in 1% citric acid was determined in the 1944 samples and Table 5·15 shows how citric acid soluble P on plots 2B (FYM) and 13 (N_2PK) increased between 1865 and 1944. The increase in citric-soluble P (and also K, see Table 5·18) on the unmanured plot between Dyer's results and those of 1944 probably reflects 'analyst variation' because the amounts of P and K in the extracts were very small. Ignoring the obviously poor sample from plot 2B in 1881, there is a linear relation between 1% citric acid soluble P and time for both FYM and superphosphate plots.

TABLE 5·15

Effect of superphosphate and FYM on the P soluble in 1% citric acid, Broadbalk

Surface soil 0–9 in., mg P/100 g soil

Plot	Treatment	1865	1881	1893	1944
3	None	4	3	3	6
2B	FYM	15	16	24	47
13	N_2PK	11	16	18	35

1865, 1881, 1893 results from Dyer (1901)

At Rothamsted during the 1950s total P in soils was determined colorimetrically, as the vanado-molybdate complex after digesting the soil with perchloric acid. Soil taken from 6 plots sampled in 1893 was analysed this way and the results compared with those obtained by Dyer with his 48-hour digestion with HCl. Table 5·16 shows that the agreement in all but one comparison (plot 7) was very good. Total P was determined in samples of the surface soils taken from the same plots in 1944, and the change from 1893 to 1944 was calculated, (Table 5·16). That there is no consistent pattern probably reflects differences in sampling at different times because the different analytical methods agree.

TABLE 5·16

Change in the total P in the soil with method of analysis and year of sampling, Broadbalk

Surface soils, 0–9 in., mg P/100 g soil

		1893			
Plot	Treatment	HCl[1]	$HClO_4$	1944 $HClO_4$	1944 minus 1893
3	None	49·8	51·9	58·0	+6·1
2B	FYM	93·8	92·5	121·4	+28·9
5	P K Na Mg	95·6	93·9	108·4	+14·5
7	N_2P K Na Mg	85·1	78·3	107·9	+29·6
11	N_2P	86·0	86·8	105·2	+18·4
13	N_2P K	89·5	89·0	111·9	+22·9

[1] Dyer (1901).

Potassium. The Broadbalk soil contains more than 1% total K and any residues of K manuring are much smaller than this, so they cannot be estimated precisely as total K. Table 5·17 shows the K soluble in 1*N*-

ammonium acetate, 0·01M-$CaCl_2$ and acetic acid-ammonium acetate at pH 4·8, in the soils sampled in 1966. Both reagents containing ammonium ions extracted about the same amount of K and the ratio of the K extracted from the manured and unmanured soils was about 4:1. The $CaCl_2$ extracted only about one-third as much K from the soils with residues.

TABLE 5·17

Readily soluble potassium in Broadbalk soils, 1966

Surface soil 0–9 in. (mean of all sections)

		K mg/100 g		
Plot	Treatment	1N-Ammonium acetate	0·01M-$CaCl_2$	Acetic acid-ammonium acetate at pH 4·8
3	None	10·2	1·6	9·7
2A	FYM since 1885	63·4	24·2	58·8
2B	FYM	65·5	24·4	61·0
19	Castor meal	11·8	1·9	10·7
5	P K Na Mg	36·4	12·0	35·4
6	N_1 P K Na Mg	36·8	11·1	35·6
7	N_2 P K Na Mg	34·1	10·1	32·7
8	N_3 P K Na Mg	29·5	9·0	28·3
15	N_2†P K Na Mg	35·8	11·7	35·0
17	N_2	25·2	5·5	23·4
18	P K Na Mg	26·5	6·9	26·3
9	N_1*P K Na Mg	32·0	9·3	31·3
16	N_2*P K Na Mg	31·9	8·7	31·5
10	N_2	8·9	1·0	7·8
11	N_2 P	8·2	1·0	7·2
12	N_2 P Na	8·1	0·9	7·2
13	N_2 P K	32·2	9·0	31·1
14	N_2 P Mg	8·9	1·1	8·1
20	N_2 K Na Mg	30·0	6·9	28·7

N Nitrogen as ammonium salts.
N* Nitrogen as sodium nitrate.
N† All nitrogen as ammonium sulphate in autumn.

The ratio between the amounts of K extracted by the $CaCl_2$ from the manured and unmanured soils was 10:1.

K soluble in 1% citric acid was determined by Dyer (1901) in the soils from some plots sampled in 1865, 1881 and 1893 and this method was also used on the 1944 samples. Table 5·18 shows the change with time in the citric soluble-K in soils, unmanured (plot 3), given N_2PK (plot 13) and FYM (plot 2B). Before 1865 soluble K increased rapidly in the soils given

TABLE 5·18

Effect of potassium sulphate and FYM on the K soluble in 1% citric acid, Broadbalk

Surface soil 0–9 in., mg K/100 g soil

Plot	Treatment	1865	1881	1893	1944
3	None	3	3	3	7[1]
2B	FYM	25	24	32	40
13	N_2PK	17	19	16	18

1865, 1881, 1893 results from Dyer (1901).

[1] See comment in first paragraph on page 104 opposite.

FYM and fertiliser K. Since 1865 the citric soluble K in the unmanured soil has remained unchanged; in the FYM plot it has increased, except for the 1881 sampling which was also anomalous for P, and, surprisingly, in the N_2PK plot it has apparently remained unchanged.

The fact that residues of K seemed not to increase the citric soluble K on plot 13 (N_2PK) was further investigated. Warren & Johnston (1962a) showed that for Rothamsted soil, K soluble in 0·3*N*-HCl is directly related to the K soluble in 1*N*-ammonium acetate. For the 1944 samples the same type of relationship can be shown between the citric-soluble K and the exchangeable K calculated from figures given by Chambers (1953) and recently checked by re-analysing the 1944 samples. Using this relationship, Dyer's values for the citric-soluble K in the early samples have been converted to exchangeable K, and for the 1893 samples the values were recently checked by analysing for exchangeable K. Page and Williams (1925) gave values for exchangeable K (by Hissink's method) in soils from some plots sampled in 1923. Figure 5·5 shows the change in exchangeable K with time for plot 3 (unmanured), 10 (N_2), 7 ($N_2PKNaMg$), 13 (N_2PK) and 2B (FYM). Where K was given, the exchangeable K was always more than where it was withheld. When K was added, either as K_2SO_4 or in FYM, the exchangeable K in the soil continued to increase as the residues accumulated up to 1923. Since 1925 tractors have been used to plough Broadbalk and the depth of cultivated soil has gradually increased. 'Old' cultivated surface soil (about 0–5 in.) with a large amount of exchangeable K and established equilibrium between exchangeable and fixed K became mixed with the next 2 or 3 in. of soil with less exchangeable K. After mixing, cation exchange took place, K ions migrated to exchange sites in the 'new' cultivated soil and from these sites became fixed in non-exchangeable form. Thus the exchangeable K of the 0–9 in. soil decreased by 1944, more with fertiliser than with FYM. Since 1944 comparatively less K has been fixed and the exchangeable K has increased again.

A K balance sheet for plots 2, 3, 5, 7, 10, 11, 12, 13 and 14 was prepared by Chambers (1953) for the period 1844–1944. Dyer, with Lawes and Gilbert's help, prepared a balance sheet for the same plots for the period 1844–93 and, contrary to Chambers' statement, this was published (Dyer, 1901). A balance sheet has now been prepared for all plots other than 9, 16, 19, 20; these four plots were omitted because they had major changes in manuring. To do this it was necessary to calculate from the manure sheets for 1844 to 1851 the amount of K applied to each plot. For those plots for which comparisons were possible, these new calculations of the amounts of K applied were found to agree closely with those of Dyer (Chambers' figures do not agree with these). For the period 1852–58 the K applied was taken as 120 lb K/acre/year, and for 1859–1967 as 80 lb K/acre/year, both of which are slightly less than the theoretical value for fertiliser potassium sulphate but make some allowance for the cruder materials used in the early years. The K content of the FYM was calculated from values given by Warren & Johnston (1962b). Table 5·19 shows the K applied to each plot during the three periods 1844–93, 1844–1944, 1844–1967; for the last two periods allowance was made for the fallow years (a correction not made by Chambers).

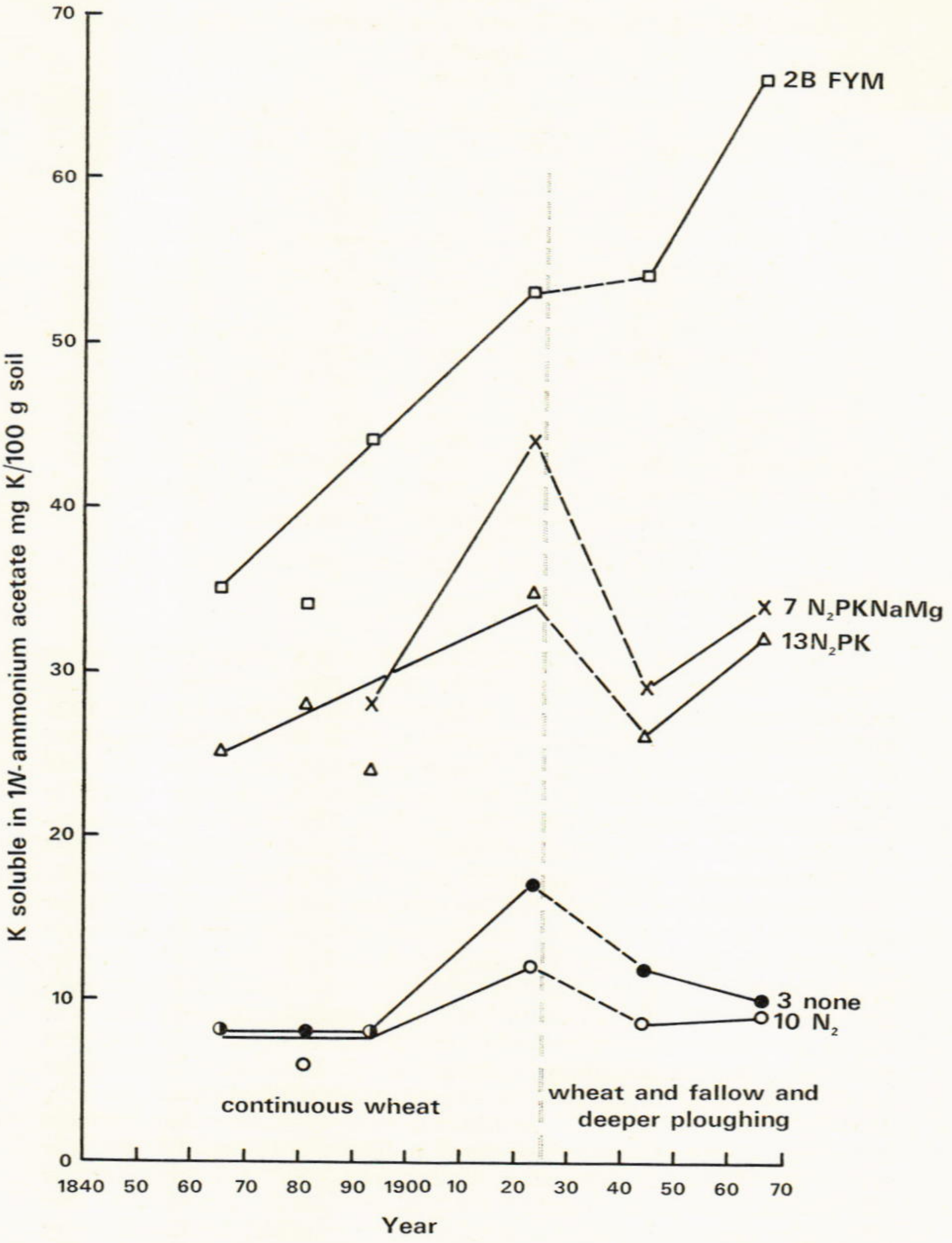

FIG. 5·5. Effect of added K and change in cultivation on amount of K soluble in 1*N*-ammonium acetate, Broadbalk soils.

TABLE 5·19

Total K applied to and K removed in the winter wheat crops on Broadbalk

lb K/acre

Plot	Treatment	Total K applied			Total K removed in the crop		
		1844–1893	1844–1944	1844–1967	1844–1893	1844–1944	1844–1967
3	None	0	0	0	632	980	1306
2A	FYM since 1885	1260	8320	9840	n.d.	n.d.	4522
2B	FYM	8100	14160	16680	2057	4281	5310
5	P K Na Mg	4180	7540	8980	943	1479	1904
6	N_1 P K Na Mg	4060	7420	8860	n.d.	n.d.	3047
7	N_2 P K Na Mg	4080	7440	8880	2116	3754	4502
8	N_3 P K Na Mg	3960	7320	8760	n.d.	n.d.	5386
15	N_2†P K Na Mg	4220	7580	9020	n.d.	n.d.	3980
10	N_2	190[1]	190	190	953	1413	1790
11	N_2 P	10[1]	10	10	988	1403	1741
12	N_2 P Na	490[1]	490	490	1447	2122	2554
13	N_2 P K	4250	7610	9050	2000	3634	4348
14	N_2 P Mg	470[1]	470	470	1521	2229	2668
17/18	$\frac{1}{2}$P K Na Mg[2]	2310	3990	4710	n.d.	n.d.	2894

n.d. not determined separately for this period.

[1] K applied between 1844 and 1851.

[2] $\frac{1}{2}$ PKNaMg full amount to each plot in alternate years.

N Nitrogen as ammonium salts.
N† All nitrogen as ammonium sulphate in autumn.

For plots 2B, 3, 5, 7, 10, 11, 12, 13 and 14 the K content of the crop between 1844 and 1893 was given by Dyer (1901). Chambers (1953) analysed samples of the crops grown on these plots between 1902 and 1921 and calculated the K uptakes. For the period 1922–44 he then extrapolated the K uptakes from his observed trends in K uptake between 1852 and 1921. However, this extrapolation did not allow for the improvement in yields after 1925 when the fallow cycle began. Therefore I have recalculated K uptakes. Dyer's values for 1844–93 were used. For the period 1894 to 1944 Chambers' analytical results and the 10-year mean yields were used, except that for 1935–44 uptakes were based on Gilbert's figures for 1882–91 because yields in these two decades were very similar; allowance was made for fallow years. For the period 1945 to 1967 allowance was made for the fallow years, the effects of fallow on the yields of the succeeding crops, and the effect after 1957 of later harvest by combine harvester on the K contents of the straw when calculating K uptakes. To compare with these detailed calculations, a shorter calculation of the total K uptake between 1844 and 1967 was made by summing the uptakes for three periods, 1844–1921 (no fallow), 1922–56 (fallow) 1957–67 (fallow and combine harvester). Yields used are those given in Tables 3·16 and 3·17 and the proportion of K in the dry matter was taken as 0·50% K in grain (except plot 3, 0·52% and plots 10 and 11, 0·48%K) and for the straw as in Table 4·10. For those plots where comparisons are possible, the K uptake by the detailed calculation was 89–91% of that by the shorter calculation, so 90% of the K uptake by the short calculation was used for those plots, 2A, 6, 8, 15, 17/18 for which detailed calculations were not possible. Table 5·19 shows the cumulative K uptakes for 3 periods 1844–93, 1844–1944, 1844–1967.

During each period the uptakes on plots 10 and 11 (N_2 and N_2P) are so close that the mean value was used to calculate the extra uptake on those plots given K. The uptakes on these 2 plots were used to compare with those on plots given PKNaMg rather than the uptakes on plots 12 (N_2PNa) and 14 (N_2PMg) because the amount of Na (51 lb) and Mg (28 lb) given on plots 12 and 14 were much more than the 14 lb Na and 10 lb Mg given in the PKNaMg treatment and Chambers (1953) concluded that the extra Na and Mg on plots 12 and 14 released soil K which was taken up by the crop (see p. 61). The extra K applied on plots given K was compared with that on plots 10 and 11. Thus the applied K remaining in the soil was calculated, as was the extra exchangeable K, as lb K/acre over that on plots 10 and 11. Table 5·20 shows that only a small proportion, 10%, of the extra K remaining in the soil stayed in an exchangeable form in the 0–9-in. depth in the two periods 1844–1944 and 1844–1966. A rather larger proportion remained exchangeable in the first period, 1844–93, when the shallow ploughing did not mix the applied K through so large a mass of soil.

TABLE 5·20

Proportion of applied K remaining in the soil which is exchangeable in the 0–9 in. depth, Broadbalk

Plot	Treatment	% of K remaining in the soil which is exchangeable in the 0–9 in. depth		
		1844–93	1844–1944	1844–1966
2A	FYM since 1885	n.d.	n.d.	20
2B	FYM	13	10	10
5	P K Na Mg	18	9	8
6	N_1 P K Na Mg	n.d.	n.d.	10
7	N_2 P K Na Mg	19	11	11
8	N_3 P K Na Mg	n.d.	n.d.	11
15	N_2†P K Na Mg	n.d.	n.d.	11
13	N_2 P K	13	9	10
17/18	½P K Na Mg[1]	n.d.	n.d.	13

n.d. not determined separately for this period.

[1] ½ PKNaMg full amount to each plot in alternate years.

N Nitrogen as ammonium salts.
N† All nitrogen as ammonium sulphate in autumn.

Chambers (1953) plotted his estimates of the K remaining in the soil, (negative values on plots not receiving K), against the K extracted by 1*N*-ammonium acetate. Extrapolating the straight line obtained, he calculated that there would be no exchangeable K after 38·5 cwt K/acre had been removed and this he called the 'potential K reserve'. Fig. 5·6 shows my estimates of the K remaining in the soil plotted against the K extracted by 1*N*-ammonium acetate for the three periods. The remarkable feature is that Chambers 'potential K reserve' has apparently increased between 1893 and 1944/1967, possibly because the cultivated soil has been deepened. However, it is not likely that this measurement is a fundamental soil

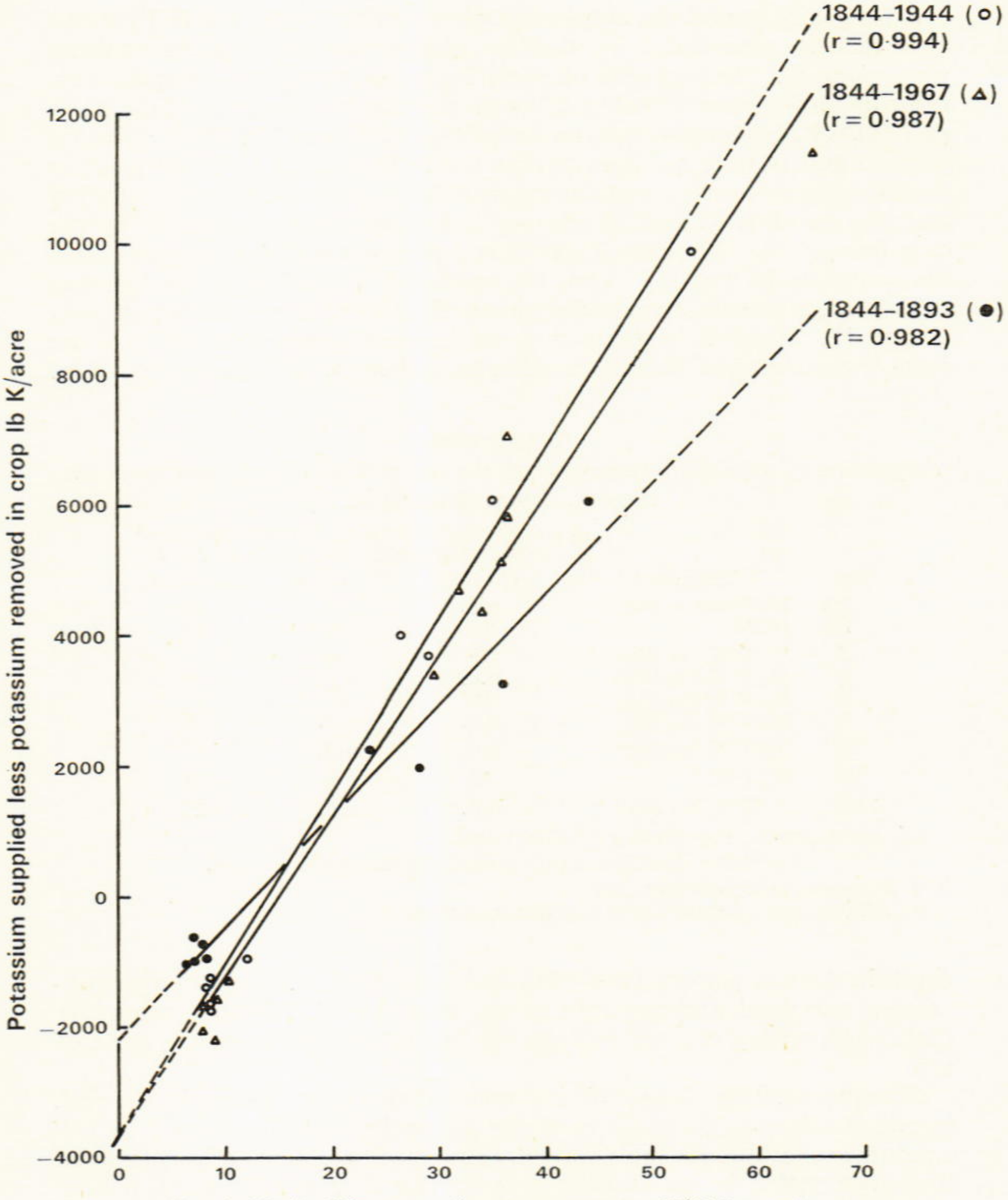

Fig 5·6 Relationship between K supplied to, and K removed in crop and soluble K in soil on Broadbalk between 1844 and 1893, 1844 and 1944. and 1844 and 1966.

property. 1790 lb K was removed by the crop given N but not K between 1844 and 1967 without apparently altering the exchangeable K content of the soil; also we now know, from exhaustive cropping studies made under glass, that plants can die of K starvation in soils that still have a chemically measurable exchangeable K content of 40–50 ppm. Also we now know that the exchange complex in soils can become saturated so that the exchangeable K content as measured by extraction with 1*N*-ammonium acetate does not increase, though the amount of K remaining in the soil from applications of manure, does continue to increase. Both these factors, increase in total uptake without decrease in exchangeable K, and increase in K added without change in exchangeable K, will tend to lower the point of intersection on the vertical axis and thus increase the 'potential K reserve'. However, these measurements clearly show that the balance between the K applied and the K removed from a soil is related to the exchangeable K content of the soil; it is the interpretation of any extrapolation of the curves that may be misleading.

Other work

Besides Lawes' and Gilbert's own studies, H. von Liebig and Dyer were the first to appreciate and use the Broadbalk soils to advance the study of soil chemistry, but others in addition to many already mentioned, have used them.

Soil organic matter including studies on nitrogen and carbon. Soils from Broadbalk, particularly from plots 2B (FYM), 3 (unmanured) and 7 ($N_2PKNaMg$) were used for much of the work done at Rothamsted on the chemistry and biochemistry of soil organic matter. Page used alkali to extract organic carbon (Arnold & Page, 1930) and organic nitrogen (Hobson & Page, 1932a). Subsequently the separation of the humic (Hobson & Page, 1932b) and the non-humic (Hobson & Page, 1932c) fractions from such extracts was made. Bremner used soil from plot 2B (together with other soils) to determine the usefulness of neutral extractants in dissolving soil organic nitrogen (Bremner & Lees, 1949) and organic carbon (Bremner, 1949a). He also studied acid hydrolysis of soil organic matter Bremner, 1949b) and examined the α-amino acids in the hydrolysate (Bremner, 1950). Bremner & Shaw, (1954) used the soil given FYM in work on amino sugars and subsequently the humic acids isolated from this soil were hydrolysed and the α-amino acids and amino sugars in the hydrolysate were examined (Bremner, 1955 and 1957). Reagents including hydrofluoric acid were used by Bremner (1959) to study fixed ammonium in soils from plots 2B, 3, 7 and 13; this work was extended to the effects of HF pretreatment on the subsequent extraction of organic matter by alkaline and neutral reagents (Bremner, & Harada, 1959). Gasser (1962) measured the mineralisation of organic nitrogen in soil from plots 2B, 3, 5, 7, 15 and 16. Jenkinson (1965) used soils from plots 2B and 3 when measuring the rate of decomposition of added carbon-14 labelled plant material; subsequently he followed (1966, 1968) the residual radioactivity throughout the soil organic matter.

Soil phosphorus. There have been studies by:

1. Dean (1938) who used the Broadbalk soils for his pioneering work on the fractionation of soil phosphorus.
2. Aslyng (1954) illustrated his ideas on phosphate potentials in soils by analyses of the Broadbalk soils.
3. Nagelschmidt and Nixon (1944) used an X-ray diffraction technique to show that superphosphate applied as fertiliser reverted to apatite in soil.

Soil potassium. K studies on Broadbalk soils are more recent. They include work by Talibudeen & Dey (1968) on activity ratios, by Addiscott (in press) on quantity/intensity curves and the relationship of buffer capacity to K saturation of the cation exchange complex, and by Arnold (1962) on potassium potentials.

Other elements. Rickson's unpublished work done in 1948 on the fluorine content of the Broadbalk soils showed that, though plots treated with superphosphate contained slightly more F (mean 0·022% F) than the untreated plots (mean 0·017% F), the individual figures fluctuated considerably. However, much of the added F had been lost from the 0–9-in. layers. Though there was no relation between F content and pH of the soil, there was an indication that F content was related to $CaCO_3$ content.

Little (1953) used some of the soils in his study on readily soluble sulphates in soils.

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