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Experiments made on Stackyard Field, Woburn, 1876-1974

II. Effects of Treatments on Soil pH, P and K in the Continuous Wheat and Barley Experiments

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Introduction

The principal dates when the soils from all plots were sampled were 1888, 1927, 1932, 1954 and 1959; a sample representative of both sites was taken in 1876 and many plots were sampled between 1954 and 1959 to follow changes in soil pH after each dressing of chalk had been applied. In addition to the surface soils (0-9 in., 0-23 cm, depth) subsoils were sampled on a few occasions. At the start of the experiment only shallow cultivations were possible with horses but with the subsequent introduction of tractor ploughing in the late 1930s the ploughed surface soil has been gradually increased to about 9 in. deep (23 cm).

The 1876, 1888 and 1927 samples were taken with the Lawes and Gilbert steel box of $6 \times 6 \times 9$ in. capacity $(15 \times 15 \times 23 \text{ cm})$ (Johnston, 1969) and a composite sample was prepared from three sample holes per plot. Surface soils were sampled in 1927 by cutting out each sample with a spade; subsoil samples were taken from the bottom of the hole with a small steel cylinder. Four or five samples were taken from each plot and bulked. In 1932 and subsequently samples were taken with a semi-cylindrical sampling tool. During 1954–59 samples, usually a composite of 20 cores, were taken from quarter plots except on plots 10 and 11 which were divided into six sub-plots.

Most of the samples up to 1932 were analysed in the Chemistry Department at Rothamsted and the results are given in detail by Crowther (1936). We sub-sampled many of the stock samples of soils taken between 1876 and 1932, repeated some analyses and did some new ones. Methods of analysis are given in detail in the Appendix.

Soil reaction

Historical note. In 1881 Lawes and Gilbert knew from the analyses of drainage waters from Broadbalk at Rothamsted that the use of ammonium salts increased the loss of calcium from the soil. However, all the fields, except Park Grass, on which the Classical experiments were made, were on soil containing free CaCO₃ and no adverse effects from using ammonium sulphate had been noted at that time. (It was not until the 1950s that on both Broadbalk and the Hoosfield Continuous Barley experiments crop failures occurred where ammonium sulphate had been used for about 100 years. The acidity in these plots was corrected by chalk dressings and schemes for applying chalk at intervals were introduced, Johnston (1969), Warren and Johnston (1967).)

Although A. Voelcker (1865) had used litmus paper to test soils for 'something injurious to vegetation' we know of no record of the soils of Park Grass being tested in this way about this time. However, Clarke (1878, p. 625) discussing liming, considered two uses: (i) small dressings to replenish plant nutrients, (ii) large dressings to promote plant decomposition and 'sweeten the soil'. He also noted that the practice had extended to applying moderate dressings to old pastures with a considerable improvement in the herbage.

Lawes and Gilbert tried a simple test of liming on Park Grass in 1881 and a more detailed one in 1883, when half-plots were dressed with slaked lime. There was no immediate effect of this dressing but during 1885–87 small benefits 0.63-0.88 t/ha were recorded on those plots where NPK fertilisers were given (Hall, 1905). It was long after the introduction of a four-yearly cycle of lime dressings in 1903 that the effect of chalk on the yield, plant species and soil reaction on Park Grass became obvious (Warren & Johnston, 1964).

A. Voelcker (1865) had used litmus paper to test soil, noting that, 'if the blue colour of the test paper turns rapidly red, the soil is certain to contain something injurious to plant life'. However, Voelcker was at that time unable to decide whether the acid reaction was due to an excess of organic acids (humic acids) or the presence of small quantities of iron sulphate. Like Clarke he was well aware that many soils benefited from liming and in 1865 he was concerned with the need for lime as a plant nutrient.

By 1898 there had been a number of crop failures on the Continuous Wheat and Barley experiments at Woburn, J. A. Voelcker (1899) (son of A. Voelcker above) knew that the soil was deficient in lime, that there had been 'a drain on the land in respect of lime', but was still unable to decide 'whether the failure of plant was due to actual deficiencies of lime or to an acid or unhealthy condition of the soil'. The first field tests of liming at Woburn were made in 1898 on both the Wheat and Barley experiments. On these arable soils the lime dressings had immediate effects; in the first harvest after application the yields of grain and straw were increased where lime was given. The field experiments continued on sub-plots of the Wheat and Barley experiments until 1924, one problem studied being the duration of the effect of the dressing. In addition much work was done in pot experiments using soils from the Wheat and Barley experiments, the results were discussed by Voelcker (1903). The work was done in the glasshouse at Woburn to try to find how the lime worked; whether (i) by supplying a plant food; (ii) by neutralising acidity; (iii) or by affecting a change in the physical condition of the soil. Voelcker was able to conclude that the acidity of the soil was the cause of the failure to grow wheat and barley but could not decide what caused the acidity. Voelcker (1923) discussing the experiments at Woburn during 1876-1921 pointed out that the work at Woburn was the first to yield results on the effects of soil acidity and the use of lime as a remedy for this.

These relationships between the pH of the soils determined in water and 0.01_{M} -CaCl₂ suspensions. The pH of soil-water suspensions of samples taken up to 1932 were determined in the early 1930s using the quinhydrone electrode. For samples taken after 1954 the glass electrode was used and a 1 : 2.5 soil-solution suspension made either with water or 0.01_{M} -CaCl₂. For the 44 samples taken in 1956 both water and CaCl₂ were used and the following relationships were found:

soils from the Wheat experiment pH CaCl₂ = 0.89 (\pm 0.068) pH water-0.3 (\pm 0.38) soils from the Barley experiment pH CaCl₂ = 0.90 (\pm 0.047) pH water-0.2 (\pm 0.27)

These relationships were used to convert pH water values for the 1954 soils to pH CaCl₂ values. Other than for these soils, the pH CaCl₂ values have been determined for all the other soils taken from these experiments. We have had to assume that, since the soils were air-dried immediately after sampling and were then stored in air-tight containers, the pH has not changed in storage. Soil-water pH values determined by the quinhydrone electrode may differ systematically from those determined by the glass electrode. For the 46

1932 samples the following relationship was found between the soil-water pH using the quinhydrone electrode and the soil-CaCl₂ pH using the glass electrode:

pH CaCl₂ (glass electrode) = $0.97 (\pm 0.055)$ pH water (quinhydrone electrode)— $0.9 (\pm 0.3)$

Table 1 shows rates and years of application.

Effect of liming, 1898–1924. The gradual decrease in both barley and wheat yields after the first ten years of the experiment was in contrast to the Rothamsted results for continuous cereal growing and it was suspected that this was caused by increasing acidity especially on plots receiving ammonium sulphate. Between 1898 and 1921 various tests of liming were made on plots which had received ammonium sulphate and on plot 4 on the Barley experiment. Good quality burnt lime, slaked before use, was applied;

TABLE 1

Amounts and years of application of lime, expressed as CaO, Continuous Wheat and Barley experiments, Woburn, 1898–1924

	CaO, t/ha							
Plot	0.63	1.25	2.50	5.00				
		Wheat experimen	t					
2aa	1905, 1909		1. 17 1 20	In the second				
2b				1898				
2bb		1		1898, 1905				
5b			1905, 1924					
8aa, 8bb		1905, 1918	n Ult de Velson	Watth Latin Y				
		Barley experimen	t					
2aa	1905, 1909 1910, 1912	1923						
2b, 5b 8aa, 8bb	_	-		1898, 1912				
2bb				1898, 1905				
4b			1915	I				
5aa			1905, 1916					
3aa, 3bb			-	1921				

TABLE 2

Amounts of CaO applied between 1898 and 1924 and the soil pH in 1927, Continuous Wheat and Barley experiments, Woburn

	Wheat experi	iment	Barley experiment		
Plot	CaO applied t/ha	soil pH ^a	CaO applied t/ha	soil pH ^a	
2a	0	4.4	0	4.5	
2b	5	5.0	10	5.8	
222	2.5	4.8	3.8	5.1	
2bb	10	5.8	10	5.8	
5a	Õ	4.8	0	4.8	
5b	5	5.7	10	6.1	
8a	0	4.5	0	4.8	
8b	Ō	4.8	0	4.7	
8aa	2.5	4.9	10	5.9	
8bb	2.5	5.0	10	5.8	

(a) pH in water measured with a quinhydrone electrode.

The effects of the lime dressings on soil pH were clearly measurable. Table 2 shows the pH in water, using the quinhydrone electrode, of soils taken in 1927. The yields of both wheat and barley were increased where lime was given, see Tables 3 and 4 in Part I of this series of papers, pp. 36–37. Russell and Voelcker (1936) discussed the improvements in yield due to liming in greater detail.

Effect of liming, 1954–59. From 1943 to 1954 plots 2, 5 and 8 in both experiments were fallowed. By 1954 the crops on the other plots were very uneven in growth and, in August 1954, barley ranged from 3 to 33 in. (8-84 cm) in height. Soils growing poor and good barley had pH values in water ranging from $4 \cdot 2$ to $6 \cdot 2$. The Field Plots Committee decided on, and the Lawes Agricultural Trust Committee approved, a scheme whereby all the plots would have the pH of the surface soils increased to about 6 in water using ground chalk. It was also decided that nothing could be done to increase the pH of the subsoils, which in places were also quite acid, without applying very large dressings of chalk to the surface soils.

The 'lime requirement' of the soils was determined from titration curves with $Ca(OH)_2$ and the amounts of chalk needed to raise the pH values of the soils to 6 from 5.5, 5.0 and 4.5 were calculated. These dressings were applied in spring 1955 and the soils of all plots were sampled by quarter plots in March 1956 to check the pH values. Many of the soils were still not at pH 6 and further dressings of chalk were applied in August. The pH was again checked in July 1957 and a few plots received further dressings of chalk in August. Table 3 shows the pH of the soil, the amounts of chalk applied on each occasion and the final pH in August 1959.

TABLE 3

Amounts of chalk applied (t/ha) and the pH in water of the soils of the Continuous Wheat and Barley experiments, Woburn, 1954–59

Treatment	Plots	pH, Sept. 1954	Chalk, Spring 1955	pH, Mar. 1956	Chalk, Aug. 1956	pH, July 1957	Chalk, Aug. 1957	pH, Aug. 1959
		Conti	nuous Barle	ey experin	nent			
No nitrogen Ammonium N Nitrate N Nitrate N or rape cake Nitrate N or FYM	1, 4, 7 2, 5, 8 3, 6, 9 10a, 10b 11a, 11b	5·2 4·6 5·1 4·7 5·2	3·5 5·3 4·1 5·3 4·4	5.8 5.5 5.9 6.0 5.9	0.8 1.2 0.7 0.5 0.5	5·9 5·8 6·0 6·0 5·9	0·2 0·6 0·0 0·0 0·0	5·8 5·9 5·9 5·9 5·7
		Conti	nuous Whe	at experir	nent			
No nitrogen Ammonium N Nitrate N Nitrate N or rape cake Nitrate N or FYM	1, 4, 7 2, 5, 8 3, 6, 9 10a, 10b 11a, 11b	5.5 4.5 5.4 5.4 5.4	2.5 6.3 2.5 2.5 2.5	5.8 5.5 5.6 5.5 5.7	1.0 1.6 1.3 1.4 0.9	5·7 5·7 5·6 5·6	0.6 0.9 0.7 0.9 0.9	5·7 5·7 5·8 5·7

Fig. 1 shows the relationship between the change in pH from 1954 to 1959 and the total amount of chalk applied in both experiments, the soils being put into four groups according to their pH values in 1954. The groups had pH values $4\cdot0-4\cdot4$, $4\cdot5-4\cdot9$, $5\cdot0-5\cdot4$ and $5\cdot5-5\cdot9$. The average increase in pH by 1959 was calculated, as was the average chalk dressing to each group of soils. Fig. 1 shows that the relationships were not the same on both experiments but that they were approximately parallel. An increase of 1 pH unit required $37\cdot5$ cwt chalk/acre ($4\cdot7$ t/ha) on the Barley experiment and 34 cwt/acre ($4\cdot3$ t/ha) on the Wheat experiment (mean $35\cdot8$ cwt/acre ($4\cdot5$ t/ha)). These amounts can be compared with the laboratory determination of the lime requirement using titration curves of the soil with Ca(OH)₂. From the curves an increase of 1 pH unit (from $5\cdot0$ to $6\cdot0$) required 48





FIG. 1. Relationship between change in pH water and chalk applied.

the equivalent of 0.094 % CaCO3. Assuming 3440 t/ha of soil 0-23 cm depth, then this equals 3.2 t CaCO₃/ha. This is less than the dressing actually needed to achieve this increase in soil pH under field conditions. Many advisers have in the past used a 'field factor' to convert laboratory estimates of the CaCO3 needed to field dressings likely to have the same effect on soil pH. These results would suggest a factor not larger than about 1.4 should have been used. However, these experiments do not indicate whether the use of a field factor is necessary in liming to a given pH value or is a convenient way of allowing for losses of calcium whilst the lime dressings become mixed with the soil and raise the pH. In order not to over-lime the soils of these experiments the adjustment of soil pH took place during five years (1955-59) and more than one dressing of chalk was applied. During the five years there could have been some loss of calcium from the surface soil by leaching. Calcium equivalent to 250 kg CaCO₃/ha would need to have been lost each year for no field factor to have been required. This amount of chalk is within the range 135-270 kg CaCO₃/ha which can be calculated from figures postulated by Gasser (1973) as being the likely minimum and maximum losses of chalk from soil such as that at Woburn with a pH of about 5.8.

Changes in soil reaction during the whole period of the Classical experiments. We have recently determined the pH in 0.01M-CaCl₂ of soils taken in 1876, 1888, 1927, 1932, 1954, 1956 and 1959. Appendix Table 1 gives the results, Fig. 2 shows the change in pH with time for various groups of soils receiving contrasted treatments.

The unmanured soils. The pH of these soils decreased steadily from 5.3 in 1876 to about 4.6 in 1932. The pH then remained at about 4.6 and 4.5 on the Wheat and Barley





experiments respectively until 1954. Similarly, the pH of unmanured soils on Park Grass at Rothamsted decreased by about 0.5 unit between 1923 and 1959 (Warren & Johnston, 1964).

Soils receiving ammonium sulphate. Fig. 2 shows the effect of ammonium sulphate and the rapid acidification, a decrease of 0.6 pH unit, during the first 12 years of the experiment. Thereafter decrease in pH on these plots was less rapid and by 1927, at the end of the Classical manuring, the pH was 4.0 and 4.4 on the Wheat and Barley experiments. Although the soils then received no more fertiliser and were fallowed in most years between 1927 and 1954, soil pH continued to decrease becoming 3.7 and 3.9 on the Wheat and Barley experiments respectively. This is an unexpected result which contrasts with that on the unmanured plots where pH remained almost unchanged between 1927 and 1954 at about pH 4.5–4.6. Our results from plots receiving ammonium sulphate are averaged over the liming treatments made between 1898 and 1924. They show that these relatively small amounts of lime had little effect in preventing the decrease in soil pH over the whole period of the experiment.

Soils receiving sodium nitrate and organic manures. With all these manurial treatments Fig. 2 shows that pH fell steadily during the experiment. Appendix Table 1 shows that between 1876 and 1932 acidity increased in the surface soil of plots where nitrate N (sodium nitrate) was applied each year during 1877–1926. Appendix Table 1 also shows that in 1888 the plots receiving sodium nitrate were less acid than those without N. Between 1888 and 1932 this difference was maintained almost unchanged in the Wheat experiment and increased in the Barley experiment. The differences for the surface soils on the two dates are:

Increases in pH from sodium nit	rate	
Plots with sodium nitrate minus plots without N	1888	1932
Wheat experiment Barley experiment	0·19 0·16	0·15 0·32

Warren and Johnston (1964) reported similar results for the effect of sodium nitrate on soil pH for soils on Park Grass at Rothamsted. Their results showed that on the heavier soil at Rothamsted the effects of sodium nitrate were larger (between 0.5 and 1.1 pH unit, pH measured in water) than the increases reported here.

Additions of FYM on plot 11b during 1877–1926 did not prevent the soils becoming gradually more acid by 1932. But, as with sodium nitrate, the plots were less acid than those without N fertiliser. The increase in pH due to additions of FYM was slightly larger in 1932 than in 1888:

Increase in pH from F1	M	
Plots with FYM minus plots without N	1888	1932
Wheat experiment	0.24	0.32
Barley experiment	0.19	0.31

The results indicate the need for liming of this light soil if pH is not to decrease under any manurial treatment. Fig. 2 also shows that the liming treatments from 1954 to 1959 improved soil reaction, and that the soils of most treatments had much the same pH in each experiment in 1959.

Changes in soil reaction during 1959–72. After the plots were sampled in autumn 1959 they all received 11 cwt chalk/acre (1.4 t/ha) in September and a further dressing of

46 cwt chalk/acre (5·8 t/ha) in October 1963, with one small exception to be referred to later. Table 4 shows the amounts of chalk applied and the soil pH in water during 1959–65. Two dressings of chalk given in 1959 and 1963 and totalling 57 cwt/acre (7·2 t/ha) had increased soil pH by 1965 by about 0·4 unit to an average value of 6·2. After the site was divided in 1966 into Sections I, II and III to accommodate new experiments each section was limed as necessary. Table 4 shows the amounts of chalk given and soil pH after 1966.

т	A	RI	F	4
	-			-

Amounts of chalk (t/ha) applied and soil pH in water, Stackyard I, II and III^a, Woburn, 1959-72

	Stackyard					
	I		П		Ш	
Experiment 1877-1966	Wheat	Barley	Wheat	Barley	Wheat	Barley
pH 1959 Chalk applied 1959-63, t/ha	5.6	5·8 7·2	5·8 7·2	5·9 7·2	5.6 7.2	5·9 7·2
Chalk applied 1966-70, t/ha	0°	00	0	0.3	7·2b	0.3 7.9b
pH 1970 pH 1971	6.1	6.2	6.3	6.4	E	-
pH 1972					6.7	7.1

(a) Continuous Wheat and Barley experiments, 1877–1965, Stackyard I, II and III, 1966 and since (b) Includes dressings given in autumn 1970 and 1971

(c) 5 t/ha magnesian limestone was applied in October 1970 after soil sampling for pH in the spring

Stackyard I. In 1966 the Intensive Cereals experiment was started on this site; nitrogen was applied as 'Nitro-Chalk' containing 21% N and there was little change in pH from 1965 to May 1970 when the soils were again sampled. Magnesian limestone (5 t/ha) was applied in October 1970.

Stackyard II was fallowed from 1962 to 1971 except for a small fenced area containing a microplot experiment. Table 4 shows that when the soil was uncropped and not fertilised the pH changed little between 1965 and 1971 except for a small area adjacent to the microplot enclosure. On this area a grass-clover seeds mixture was sown in September 1971 but the clover failed to establish during 1972. Soil samples taken in August 1971 and analysed subsequently showed that the pH was 5.3. It was later established that this area did not receive the 5.8 t/ha dressing of chalk in 1963. Subsequently 5 t/ha chalk was applied in March 1973, the clover was resown and established well. Stackyard II received a further dressing of chalk (2.5 t/ha) in autumn 1973.

Stackyard III. The Long Term Phosphate experiment, which started in 1968, received dressings of chalk (usually 1 ton/acre (2.5 t/ha)) each year during 1967–71 except 1969. Table 4 gives the total amounts applied and shows that these dressings further increased soil pH by 0.7 unit by 1972.

These results show that dressings of chalk totalling 7.2 t/ha on Stackyard I and II increased pH from 5.8 to 6.2 during 1959–65 and further dressings totalling 7.5 t/ha further increased pH from 6.2 to 6.9 during 1965–72. From the laboratory determination of the lime requirement of Stackyard soil using titration curves of the soil with Ca(OH)₂ the increase in pH of 0.7 unit would require about 2.4 t CaCO₃/ha. Thus, of the 7.5 t/ha applied between 1965–71, 5.1 t/ha have been lost. The average annual loss (about 725 kg CaCO₃/ha) is larger than that calculated from Gasser's (1973) results (about 450 kg/ha). 52

Possibly this is because Gasser's results were derived from experiments where losses were measured over a number of years after a single dressing of liming material had been given whereas in this experiment chalk was applied in almost all years and nitrogen was also given, but as 'Nitro-Chalk' containing 21 % N. Similar large losses of chalk were reported by Johnston (1975). He estimated that in the Market Garden experiment, on similar light soil at Woburn, approximately 1000 kg CaCO₃/ha was lost each year from an average annual dressing of 1250 kg/ha while the soil was maintained at pH 6.9 and nitrogen fertilisers were given to the crops.

Soil phosphorus

The effect of the applied P on the P residues in the soil. Table 5 shows that in 1956 soils which had received P manuring between 1877 and 1926 generally contained more of both total and soluble P than did soils which received no P. Total P was determined by perchloric acid digestion of the soil and soluble P was measured in 0.5M-NaHCO₃, for details see Appendix.

TABLE 5

Total P and P soluble in 0.5M-NaHCO₃ in the surface soils of the Continuous Wheat and Barley experiments, Woburn, 1877–1956

	Surface	soils 0-23 cm	sampled March 1	956			
		P, mg/kg, a Barley e	ir-dry soil xperiment	Wheat e	Wheat experiment		
Plot	1877–1926ª	Total P	Soluble P	Total P	Soluble P		
No nitroge	en group						
1 7 4	Unmanured Unmanured PKNaMg	585 580 735	13 10 31	620 790 830	12 20 34		
Ammoniu	m N group						
2 5 8	N1 N1PKNaMg N2PKNaMg	645 805 795	18 42 40	595 840 965	19 51 68		
Nitrate N	group						
3 6 9 10a 11a	N1 N1PKNaMg N2PKNaMg N1P ^b N1K ^b	625 810 795 735 685	10 31 32 20 22	575 805 865 680 705	10 38 41 18 18		
Organic n	nanure group						
10b 11b	Rape cake FYM	750 760	17 26	695 750	15 21		

(a) Manures applied annually 1877–1926, for exceptions and further details see p. 32(b) Since 1907, for previous treatments see p. 32

There is more irregularity in the results than in many of the Classical experiments at Rothamsted, probably because the soil was more variable at the start of the experiments. The total P content of plots 1, 2 and 3 in both experiments without P manuring, illustrates this. In addition plots 7, 8 and 11a on the Wheat experiment contain anomalously large amounts of total P if the experimental site had been uniform at the start of the experiment. Throughout the period when fertilisers were applied the annual dressing of P, initially 30 lb/acre (34 kg/ha), later 25 lb/acre (28 kg/ha), was generous and quite large residues would have been left in the soil. After manuring ceased the crops were small and

removed little P so that measurable residues still exist in the soil. The value of the residues on plots 7, 8, 9 and 11 to arable crops, barley, potatoes and sugar beet, was tested in 1960-62, the results are discussed by Johnston, Warren and Penny (1970).

The relationship between P applied and P in the soil. In Part I estimates are given of the total P applied (Table 2) and the P removed in the crops (Table 7) and from these results the balance for P (additions *minus* losses) can be calculated. Table 6 shows the P balance

TABLE 6

Estimates of the P applied and P removed in the crops and the change in P in soil caused by the treatments of the Continuous Wheat and Barley experiments, Woburn, 1877–1961

				Pk	g/ha				
		Wheat experiment			Ba	Barley experiment			
Plot	Treatment ^a	Papplied	P removed in crops	P residue	Papplied	P removed in crops	P residue		
1	Unmanured	0	225	-225	0	226	-226		
2	Nb	0	240	-240	0	243	-243		
3	N*b	0	331	-331	0	322	-322		
4	PKNaMg	1457	271	1186	1457	257	1200		
5	NPKNaMg	1457	373	1084	1457	310	1147		
6	N*PKNaMg	1457	446	1011	1457	428	1029		
7	Unmanured	0	241	-241	0	215	-215		
8	NPKNaMg	1457	310	1147	1513	304	1209		
9	N*PKNaMg	1457	385	1072	1513	424	1089		
10a	N*P	504	308	196	560	291	269		
10b	Rape cake	504	381	123	504	318	186		
11a	N*K	95	311	-216	95	360	-265		
11b	FYM	908	459	449	908	471	437		

(a) For full details of treatments see Part I, Tables 1 and 2, pp. 32, 33
(b) N, nitrogen as ammonium sulphate; N*, nitrogen as sodium nitrate

for 1877-1961. Usually the P balance is best related to the *change* in total P content of soil but because individual plots were not sampled at the start of the experiments it is not possible to do this here. If soil is very uniform at the start of an experiment there is usually a good relationship between the P balance and the P content of the soil at the end of the experiment. Fig. 3 shows that there was a reasonable relationship between the P balance (1877-1961) and the total P content (in 1956) of groups of soils when the individual results for both experiments were averaged. Plot 4 (P without N) which in both experiments is on an outer edge of the experimental site fits the relationship poorly. If results for individual treatments are plotted there is some scatter but nothing to suggest that this was due to anything other than soil variability at the start of the experiments.

The relationship between methods of determining total P in soil. The perchloric acid method was used to determine total P in soil samples taken in 1956; subsequently the use of perchloric acid for this type of analysis was abandoned for safety reasons. Mattingly (1970) compared results got by the perchloric acid digestion with those from a fusion analysis with Na₂CO₃. Results by the perchloric acid method were slightly but consistently smaller. We determined the total P content of the soils sampled in 1959 using Na₂CO₃ fusion and compared the results with those by perchloric acid digestion on the 1956 samples. We found that although our samples were taken on two separate occasions, a straight line relationship between the results by perchloric acid digestion (Pp) and Na₂CO₃ fusion (Pf) accounted for 88% of the variance. The results by perchloric acid digestion were about 50 mg/kg smaller than those by Na2CO3 fusion. This result 54



FIG. 3. Relationship between P balance (additions minus losses) 1877-1961 and total P in soil in 1956.

compares favourably with that given by Mattingly (1970) for 37 soils taken from various experiments in central and southern England. His regression equation was:

 $Pf(mg/kg) = 38.8 (\pm 6.86) + 1.0021 Pp(\pm 0.01176)$

Soluble P as a fraction of the total P

The effect of acidity. The bicarbonate soluble P can be expressed as a percentage of the total P in these soils. For both experiments the values range from 1.6 to 7.0%. These values tend to be small but there is an interesting trend in the results. In both experiments those plots, including unmanured ones, which received ammonium sulphate and became most acid soonest have more bicarbonate soluble P:

Bicarbonate soluble P as a percentage of the total P

	Plots with							
		No N o nitrate N	r	Mean	Amm sulp	onium	Mean	
Barley experiment Soils without P Soils with P	2·2 4·2	1.6 3.8	1.7 4.0	1.8 4.0	2·8 5·2	5.0	2·8 5·1	
Wheat experiment Soils without P Soils with P	1·9 4·1	1·7 4·7	2·5 4·7	2·0 4·5	3·2 6·1	7.0	3·2 6·6	

The solubility of the P residues. More important than the solubility of the total soil P is the solubility of the residues of the applied P. Using the results in Table 5 we have

calculated the increase in total and bicarbonate soluble P due to residues of P applied in superphosphate and FYM, and expressed the increase in bicarbonate soluble P as a percentage of the increase in total P. The solubility of the residues is greater than that of the total soil P:

Increase in bicarbonate soluble P as a percentage of the increase in total soil P

P residues from	Barley experiment	Wheat experiment
Superphosphate	12	14
FYM	8	6

It must be remembered that these residues began to accumulate in the soil in 1877 and that no new P was added after 1926. Thus 10-15% of these old P residues from dressings of superphosphate have remained bicarbonate soluble.

Soil potassium

The effect of the applied K on the K residues in the soil. Table 7 shows the total K determined by digestion with HF and the K exchangeable with neutral 1N-ammonium acetate in samples taken in 1956. Although there was some relationship between total K in the

TABLE 7

Total and exchangeable K in the surface soils of the Continuous Wheat and Barley experiments, Woburn, 1877–1956

Surface soils, 0-23 cm sampled March 1956

	Treatment	K, mg Barle	kg, in air-dry soil y experiment	Wheat experiment		
Plot	1877-1926ª	Total K	Exchangeable K	Total K	Exchangeable K	
No nitro	gen group		an ann ann an ann an an ann an an an an	ICON DEL 10	Enteringenetic IX	
1 7 4	Unmanured Unmanured PKNaMg	664 820 659	64 54 74	712 694 778	74 57 119	
Ammoni	um N group					
2 5 8	N1 N1PKNaMg N2PKNaMg	684 704 805	60 79 87	682 686 685	60 102 64	
Nitrate N	group				Neurit audies	
3 6 9 10a 11a	N1 N1PKNaMg N2PKNaMg N1P ^b N1K ^b	680 790 846 717 812	48 78 85 68 101	688 668 704 634 731	54 99 85 65 88	
Organic r	nanure group					
10b 11b	Rape cake FYM	718 830	61 103	628 705	70 109	

(a) Manures applied annually 1877–1926, for exceptions and further details see p. 32
(b) Since 1907, for previous treatments see p. 32

soil and K manuring on the Barley experiment (plots 7 and 4 were exceptions) there was little relationship on the Wheat experiment. In part this was due to soil variability; results in Russell and Voelcker (1936) show that the clay content varies widely. Another reason lies in the fact that between 1907 and 1926 when the Classical N manuring was 56

TABLE 8

Estimates of the K applied and K removed in the crops and the change in K in the soil caused by the treatments of the Continuous Wheat and Barley experiments, Woburn, 1877-1961

	Treatment ^a	W	heat experim	ent	Barley experiment					
Plot		Kapplied	K removed in crops	K residue	Kapplied	K removed in crops	K residue			
1	Unmanured	0	487	-487	0	635	-635			
2	Nb	0	496	-496	0	662	-662			
3	N*b	0	713	-713	0	002	-002			
4	PKNaMg	3184	630	2554	3184	730	2454			
5	NPKNaMg	3184	834	2350	3184	977	2454			
6	N*PKNaMg	3184	979	2205	3184	1260	2307			
7	Unmanured	0	511	-511	5104	504	1924			
8	NPKNaMg	3184	688	2496	3320	394	- 394			
9	N*PKNaMg	3184	888	2296	3329	1261	24/3			
10a	N*P	146	611	-465	146	1201	2068			
10b	Rape cake	706	844	-138	706	021	-6/5			
11a	N*K	1267	728	530	1412	933	-221			
11b	FYM	2578	1059	1519	2578	1048	364 1191			

K. kg/ha

(a) For full details of treatments, see Part I, Tables 1 and 2, pp. 32, 33
(b) N, nitrogen as ammonium sulphate; N*, nitrogen as sodium nitrate

still given, the annual dressings of K were small (22 lb K/acre, 25 kg K/ha). On both experiments there was more exchangeable K where K fertilisers had been applied with only one exception, plot 8 on the Wheat experiment. Table 8 shows the K balance (additions minus removals) during 1877-1961. The relationship between K balance and exchangeable K in the soil is poor, partly because of the variable clay content of the soil, partly, no doubt, because only a few small dressings of K fertiliser were given after 1907.

The value of the K residues on plots 7, 8, 9 and 11 to arable crops, barley, potatoes and sugar beet was tested in 1960-62; the results are discussed by Johnston, Warren and Penny (1970). Soil from plots 1 and 4 on the Barley experiment sampled in 1967 was included in a pot experiment in the glasshouse which assessed the capacity of a range of soils to release K to ryegrass during intensive cropping. In the samples used there was a smaller difference in exchangeable K than shown in Table 7 and a negligible difference in total K uptake by ryegrass from the two soils (Johnston & Addiscott, 1971).

Summary

1. The reasons for and the historical background to the introduction of liming tests are given and comparison is made with the introduction of similar tests at Rothamsted.

2. The effects of the manurial treatments 1877-1926 and liming treatments in 1898-1924 and again in 1955-57 on soil pH, total and bicarbonate soluble P and total and exchangeable K are discussed.

3. The relationship between pH measured in water and in CaCl₂ using a glass electrode is given as is the relationship between pH CaCl₂ by glass electrode and pH water using a quinhydrone electrode.

4. All amounts of lime applied between 1898 and 1924 increased soil pH as determined in 1927; the larger amounts of lime increased soil pH most.

5. Chalk applied between 1955 and 1957 was intended to bring surface soil pH water to about 6. This pH value was attained by 1959 but amounts of chalk applied were larger

than those indicated by the laboratory determination of the lime requirements. The results suggested a field factor of 1.4. The need to use a field factor is discussed.

6. All soils became more acid during 1877-1954. Those treated with ammonium sulphate, 1877-1926, became most acid soonest but even unmanured soils and those which were fallowed became more acid during the course of the experiment. These results indicate the need for liming on this light soil if pH is not to decrease under any manurial treatment. Liming treatments during 1954-59 were successful in increasing the pH water of the surface soil to 6 without any overliming.

7. The P balance (additions minus losses) in the soil during 1877-1926 was related to the total P in the surface soil in 1956. Total P determined by fusion with Na₂CO₃ gave slightly larger values than those got by digestion with perchloric acid. The relationship between the results by the two methods on these soils compared favourably with that reported by Mattingly (1970).

8. When bicarbonate soluble P was expressed as a fraction of the total P it was shown that increasing acidity had increased soluble P.

9. For residues of P applied to soil the increase in bicarbonate soluble P can be expressed as a percentage of the increase in total soil P, the solubility of the P residues. When this was done for soils taken in 1956 the solubility of P dressings applied from 1877-1926 was found to be 12-14% for P residues from superphosphate and 6-8% for residues from FYM.

10. There is little information about K residues in this experiment. Soils which received most K during 1877-1926 had most exchangeable K in 1956.

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EXPERIMENTS ON STACKYARD FIELD. II

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APPENDIX

Total phosphorus

1956 samples: estimated colorimetrically after digestion with perchloric acid (Mattingly, 1970), as the vanado-molybdate complex (Hanson, 1950).

1959 samples: estimated after fusion with sodium carbonate (Mattingly, 1970) on the 'Technicon AutoAnalyzer' using the method described by Salt (1968).

Sodium bicarbonate-soluble P

Estimated colorimetrically using a 'Spekker' after extraction, using the method of Olsen et al. (1954).

Total potassium

Measured by flame photometry after digestion with hydrofluoric acid (Jackson, 1958).

Exchangeable potassium

Measured by flame photometry after successively extracting 6.25 g of soil with Nammonium acetate (250 ml).

Soil pH

Using quinhydrone electrode: determined by Miss S. G. Heintze using the technique of the Soil Reaction Committee of the International Society of Soil Science.

Using a glass electrode: measured in soil suspensions in water or 0.01M-CaCl₂ (1:2.5 soil : solution ratio). The mean of a quarter and two hour readings.

APPENDIX TABLE 1

Soil reaction. Continuous Wheat and Barley experiments, Woburn, 1876-1959

pH in 0.01M-CaCl₂ Site sample in 1876, pH 5.30

		Wheat experiment				Barley experiment						
Plot and treatment	1888	1927	1932	1954	1956	1959	1888	1927	1932	1954	1956	1959
No nitrogen group												
1 4 7	5·00 5·20 5·16	4.60 4.98 4.40	4·51 4·80 4·46	4.6 4.8 4.5	4·82 5·08 4·71	4·52 4·69 4·69	4·94 5·03 5·18	4·36 4·80 4·49	4·45 4·65 4·54	4·5 4·5 4·5	4·98 5·16 4·86	4.62 4.78 4.88
Ammonium N group												
2 5 8	4·56 4·70 4·76	4.00 4.20 3.86	4·00 4·24 3·94	3.7 3.8 3.5	4·51 4·72 4·49	4·49 4·64 4·65	4.69 4.66 4.60	4·32 4·48 4·50	4·32 4·35 4·39	4.0 3.9 3.8	4·72 4·78 4·58	4·73 4·96 4·82
Nitrate N group												
3 6 9	5·32 5·16 5·46	4·94 4·88 4·95	4·70 4·75 4·78	4·5 4·5 4·6	4·64 4·70 4·71	4·63 4·67 4·76	5·14 5·22 5·26	5·11 4·80 4·92	4·96 4·83 4·81	4·5 4·3 4·3	5·14 4·96 5·08	4·90 4·84 5·10
FYM 11b	5.36	5.19	4 ∙91	4.5	4.82	4•68	5.24	4.99	4.86	4.6	5.18	4.70
Variousa												
10a 10b 11a	$5 \cdot 17$ $5 \cdot 31$ $5 \cdot 32$	4·58 4·30 4·81	4·54 4·40 4·70	4·4 4·5 4·4	4·59 4·74 4·80	4.64 4.59 4.59	5.01 5.10 5.24	4·38 4·24 4·72	4·46 4·10 4·66	4·2 3·9 4·4	5.04 5.40 5.00	4.58 4.76 4.68
(a) For details see	Tables	1 and 2	, Part	I, pp	32, 33							

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