Soil Analyses in the Rothamsted Park Grass Experiment

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Introduction

Soil and plant analyses of long-term field experiments provide a unique opportunity to observe large scale changes in nature and agro-ecosystems. Changes in the soil have been accelerated due to human activity, e.g. the development of agriculture, industry and transportation. In the middle of the last century, in 1856, the Park Grass experiment was established in Rothamsted (LEWIS, 1991). The original aim of the experiment was the observation of changes in the botanical composition of grass as a result of different types and amounts of fertilizer (LEWIS, 1980), but it also provided the opportunity to study numerous environmental effects (JOHNSTON et al., 1986, GOULDING et al., 1985). After 135 years the boundaries of the plots are clearly defined. The overlapping between plots treated in different ways is less than 30 cm.

Material and Methods

Measurements were carried out on a selection of old and new samples collected over the duration of the Park Grass experiment (LEWIS, 1991). Those studied were taken from the unlimed control plot (labelled 3d), a plot limed but not fertilized since 1903 (labelled 3b), and an unlimed plot exposed to the strongest acidifying effects: fertilization with ammonium sulphate (labelled 11/1d). Regarding liming, from 1903 and every fourth year until 1964, lime (originally lime, more recently calcium carbonate) was applied to the southern halves of most of the plots. From 1965 each half plot was further subdivided and only sub-plots "d" remained unlimed. From 1965 subplots "a", "b" and "c" were limed to maintain pH 7, 6 and 5, respectively. Plot 11/1d is given 144 kg N/ha every spring in the form of ammonium sulphate, and 35 kg P, 225 kg K, 15 kg Na, 10 kg Mg and 550 kg sodium silicate per ha in winter. The soil is well drained or moderately well drained flinty loams on clay or chalk. The samples offered the possibility to examine the effect of atmospheric deposition, fertilizer and liming on the chemistry of surface soil and plants. To study these three topics examinations were made on the following:

1. The pH in water and in 0.01 *M* $CaCl_2$.
2. The exchangeable element content using an ammonium acetate extract.
3. The elements extractable with 0.05 *M* ammonium-EDTA.
4. Sequential extraction. The four extracts employed were $CaCl_2$, NaOH, EDTA and aqua regia, as described by McGrath & Lane (1989), McGrath & Cegarra (1992), and McGrath et al. (1993) to study the metals attached to different phases of soil.

Extraction with 0.1 *M* calcium chloride gave an estimate of the water soluble and exchangeable fractions of metals; extraction with 0.5 *M* sodium hydroxide estimated the organically bound elements; extraction with sodium - EDTA estimated oxides and carbonates. After digestion with aqua regia the "residual" (aqua regia-soluble) amounts of elements were determined.

Nineteen elements were determined by inductively coupled plasma emission spectrometry. Plant analyses were made after total digestion with aqua regia.

Results

Changes in the pH of the soil are the most likely cause of the changes in the composition of the soil and herbage (Figure 1). The pH of the soil on all plots was approximately 5.7 when the experiment began. On the control plot the pH was reduced to 4.7 by 1991. The main reason for this was atmospheric acidification and deposition, with some input from crop uptake and mineralization. Data from the limed plot show that soil acidification can be prevented by liming. Fertilization with ammonium sulphate caused severe soil acidification. The pH of the fertilized plot decreased to 3.5 by 1991, which induced numerous other changes. To summarize the effects, in the control plot the ammonium-EDTA extractable Ca content decreased, due to the leaching of $CaCO_3$. Extractable iron and magnesium became more available, while the concentration of extractable manganese increased only slightly. On the limed plot these changes were not observed, indeed extractable Ca increased. The effect of the severe acidification on the fertilizer plot is shown in the large reduction in available Ca, Mg and Mn and the increase in available Fe (Figure 2).

The connection between the element content of the herbage and the availability of that element in the soil can be seen by comparing the element contents obtained with different soil extracting agents with the total element content of the plant. A relationship can be seen between the ammonium EDTA extracted calcium content of the control and the fertilizer plots and the calcium content of hay in those plots. The changes in the plant were smaller than those in the soil. When analyzing the results attention should also be drawn to changes in the botanical composition. It is interesting to compare the calcium

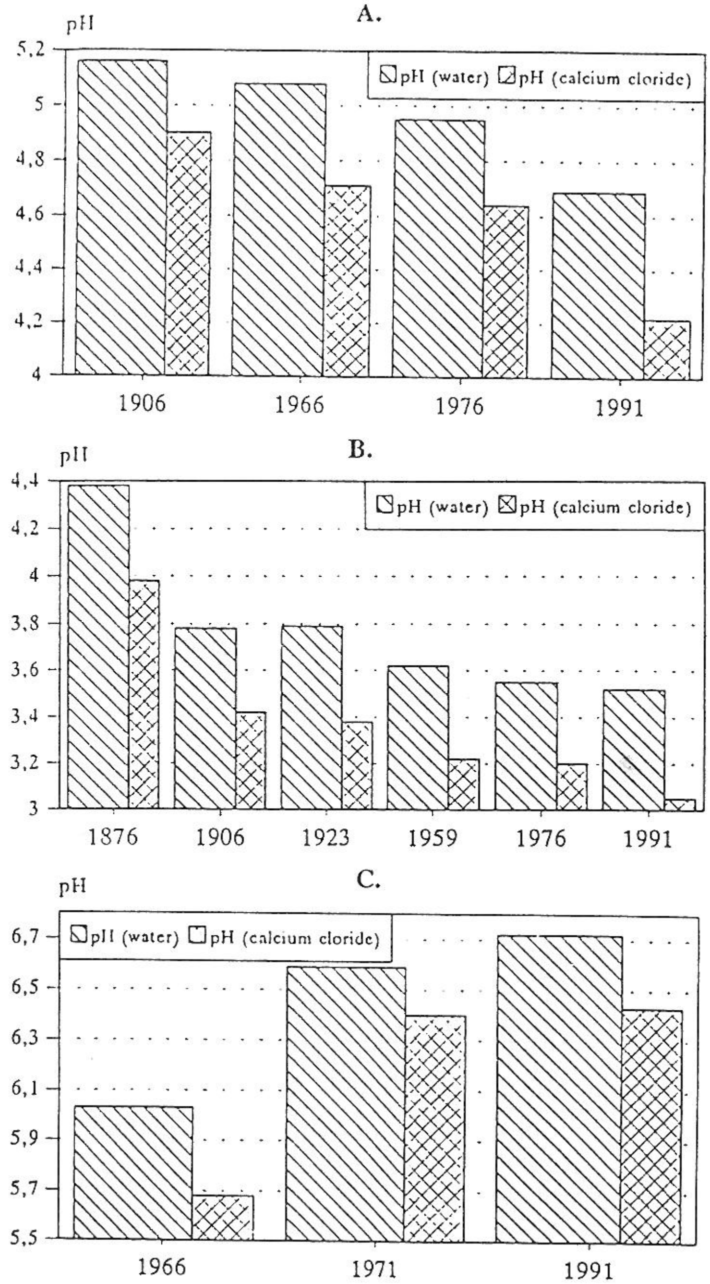

Figure 1

pH changes in soil over 100 years (Park Grass Experiment). pH changes in: A. Control plot; B. Plot fertilized with ammonium sulphate; C. Limed plot.

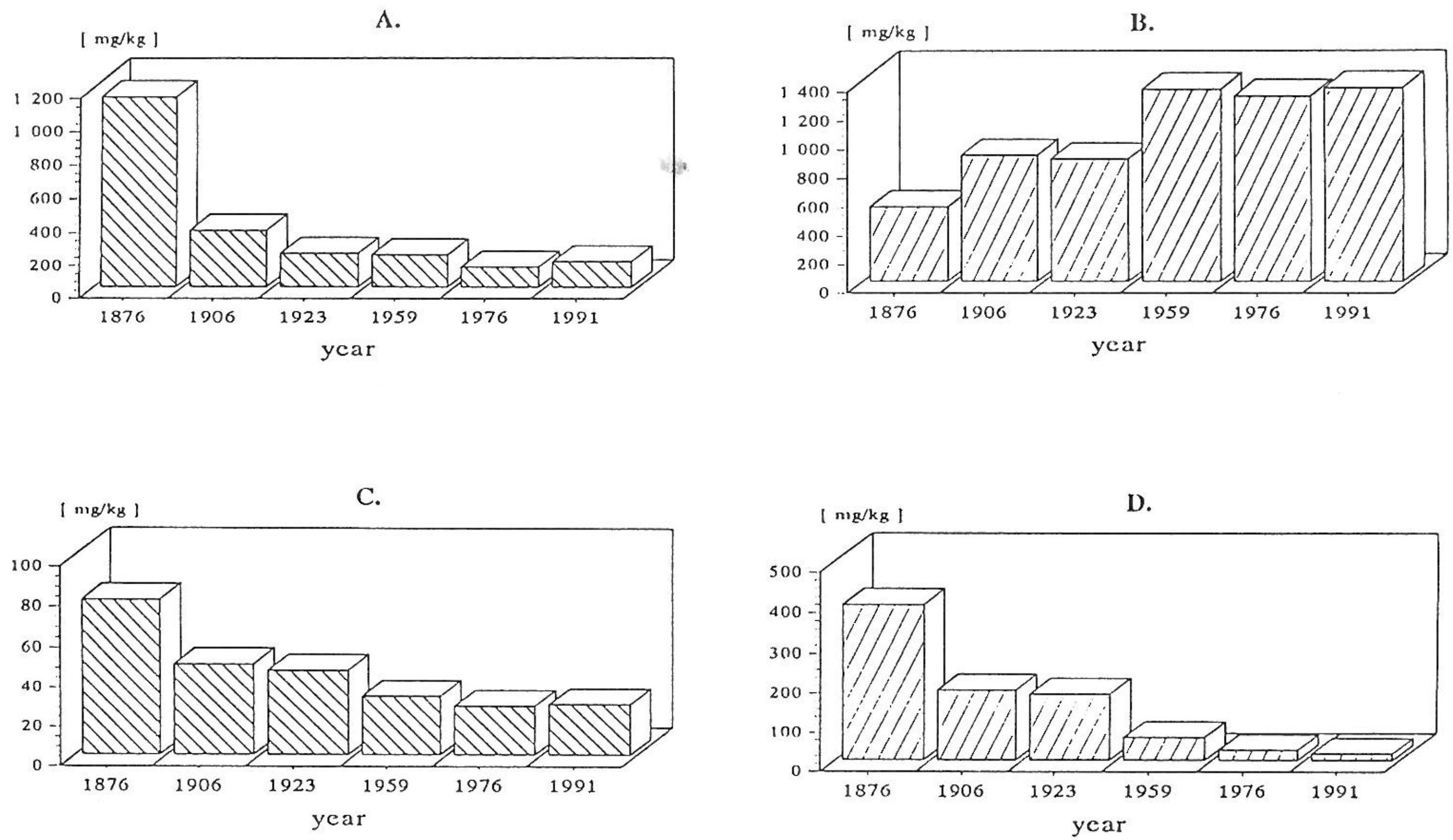

Figure 2
Ammonium-EDTA extracted element content of fertilizer plot. A. Calcium. B. Iron. C. Magnesium. D. Manganese.

content of the soil with that of the hay in the 1970s. There was an order of magnitude difference between the calcium content of plants produced on the control and the limed plot and those on the fertilizer plot. The calcium content was 1.5% in the dry material of grass from the limed plot while the control contained 1.2% and the fertilizer plot only 0.2% calcium. This very low Ca content might cause Ca deficiency in grazing cows.

Soil acidification and atmospheric deposition have also had a major effect on the mobilization of heavy metals. In the control plot it can be seen that the content of available heavy metals (Zn, Cd, Pb and Ni) increased as a result of deposition from the air and acidification. This increase could also be observed on the fertilized soil for Pb and Cd, but the concentration of Zn slightly decreased, and that of Ni remained constant because losses by leaching became important. Heavy metal mobility can be evaluated by comparing all soil analysis methods (Figure 3). In the case of Cd one sees an increase in all fractions on the control plot, because of the atmospheric deposition of Cd and limited mobilization from acidification. On the fertilized plot the exchangeable part decreased. And finally there was a slight increase in the percentage of $CaCl_2$ extractable Cd while the total Cd content of the 0-20 cm layer decreased. At the same time, in the control plot the total amount of Cd increased, as did the 0.1 *M* $CaCl_2$ extractable content. This effect can also be seen for the element content of grass. Similar results were observed for Zn. The Zn content of the control plot increased while the opposite effect was exhibited by the fertilized plot, because of leaching. This change had an effect on the Zn concentration of the hay, which decreased in a similar manner. The concentration of strongly adsorbed heavy metals, such as lead, increased due to industrial and traffic emissions. As with Cd and Zn, Pb has moved into the available fractions of the soil. Lead does not appear to have been lost from the fertilized plot in spite of strong acidification, presumably because deposition more than offset loss. Comparing the lead in the control with that in the fertilized plot it can be seen that the lead level is higher in the case of fertilization (Figure 4). While in 1991 the control plot contained 60 ppm lead, the lead concentration in the fertilized plot was 100 ppm. This was because of the lead accumulation from the fertilizer. The origin of the fertilizer lead content may be the sulphuric acid, which was produced by lead chamber processing. Attention is drawn to the percentage extraction of Pb in four sequential extracts. In 1876 the largest was the residual fraction, while in 1991 it was the EDTA extractable fraction. In addition, the $CaCl_2$ extractable Pb quantity was 5 times higher than in 1876.

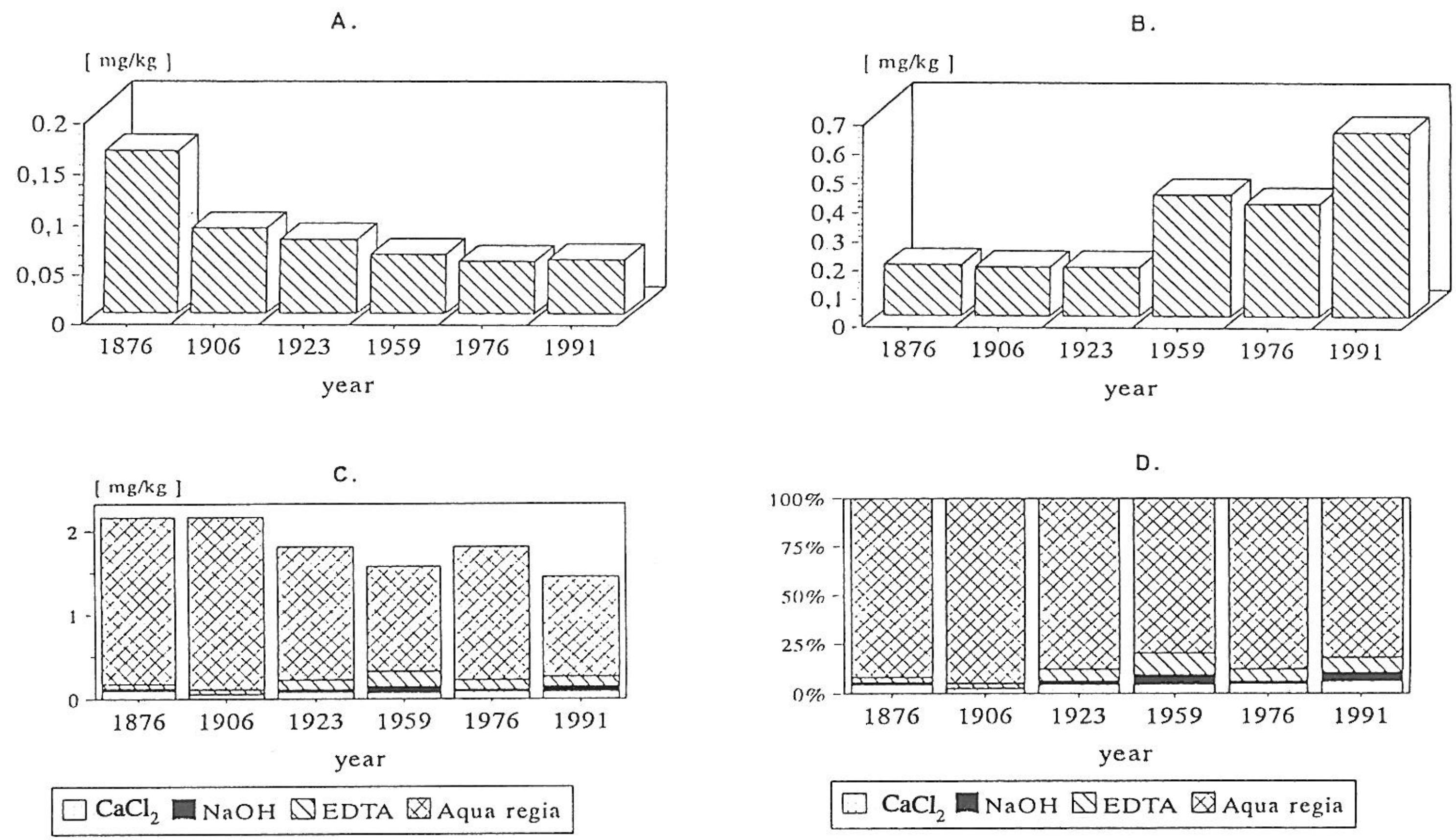

Figure 3
Cd extraction data from the fertilized plot (Park Grass Experiment). A. Ammonium acetate extracted Cd content. B. Ammonium-EDTA extracted Cd content. C. Cd in different parts of the soil, mg/kg. D. Cd in different parts of the soil, in %.

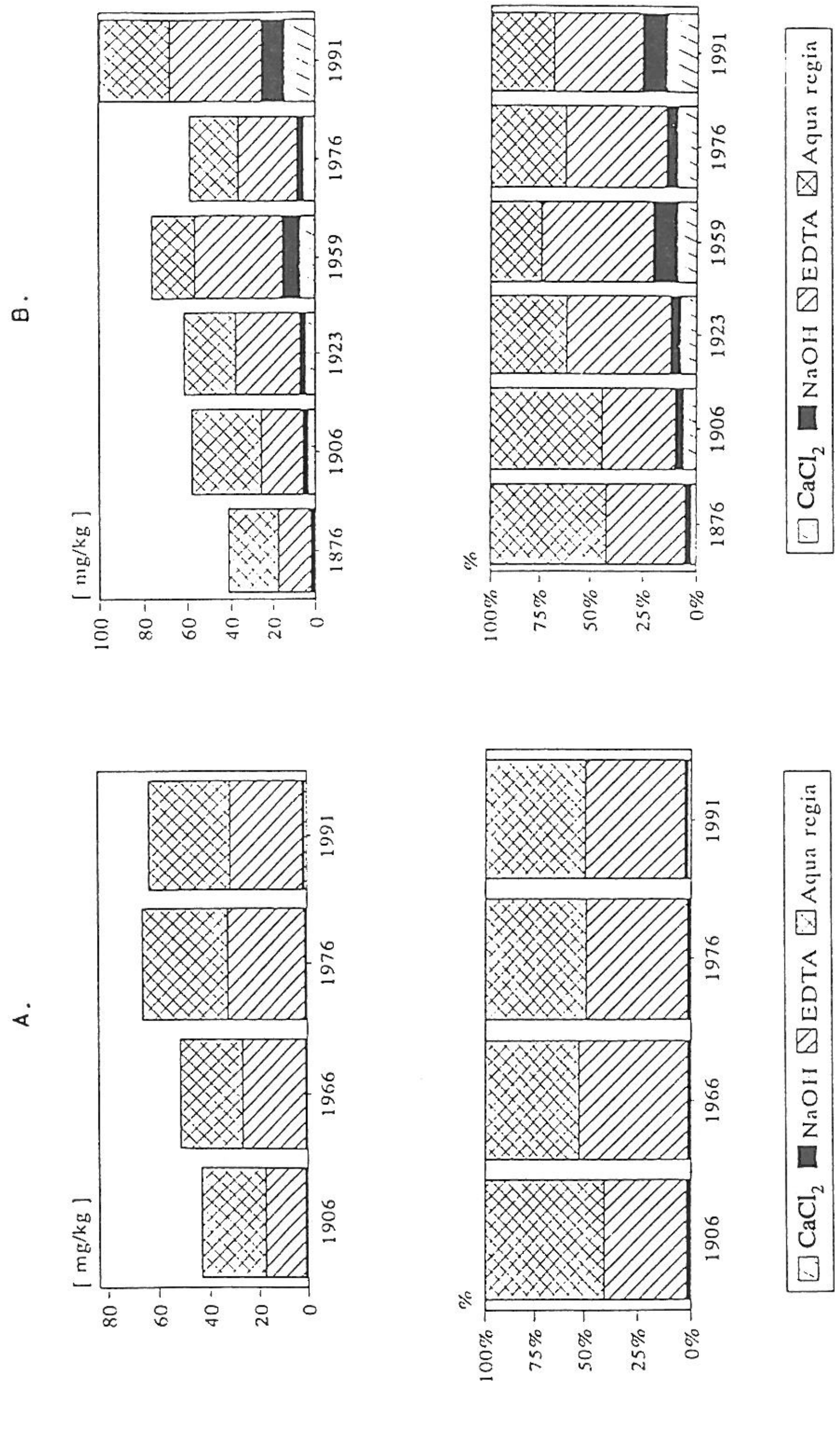

Figure 4
Comparison of the lead content of the control (A) and fertilized (B) plots (Park Grass Experiment).

Conclusions

The following conclusions can be drawn:

1. The main reason for the changes in the control plot are natural acidification and acidic deposition.

2. The heavy metal (Pb, Cd, Ni, Zn) content of the control plot has increased because of industrial emission; this is also seen in other European long-term experiments (Halle, Askow).

3. Ammonium sulphate fertilizer has increased the mobility of many of the heavy metals in the soil (Cd, Zn) by decreasing the pH.

4. The lead content of the ammonium sulphate fertilized plot has increased because of atmospheric deposition and because the fertilizer contains lead. The reason for the higher lead content is that the sulphur acid was produced by the lead chamber process.

5. The McGrath soil sequential extraction method is useful for examining the changes in the heavy metal content of the soil in long-term experiments.

Summary

In the last century the Rothamsted Classical Experiments were of fundamental importance in the understanding of plant nutrition by inorganic and organic manure. In this century, almost 150 years later, the unique continuity of the experiments, together with their veritable treasure trove of stored crop and soil samples and data, allows them to contribute to current research on many topics ranging from nitrate leaching to pesticide residues. The heavy metal contents were measured in soil and hay samples from a control, a fertilized and a limed plot in the Park Grass Experiment. Today there is a 1.2 pH difference between the control and the fertilized plot, resulting from a pH change of 1.0 in the control plot and 2.2 in the fertilized plot over 150 years due to acidic deposition and fertilization. The pH change has caused many changes in the heavy metal content in the top layer of soil. Different extraction methods (e.g. with ammonium acetate, EDTA, and sequential analysis) were used to estimate the heavy metal content in different fractions. In the control plot the contents of Ca and Mg decreased, while the Zn, Cd and Pb contents increased. In the fertilized plot the higher leaching effect caused lower Ca, Mg and Zn contents while the Pb content increased, because it is strongly adsorbed on the soil and the fertilizer contained a small amount of lead.

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