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Effects of atmospheric deposition, soil pH and acidification on heavy metal contents in soils and vegetation of semi-natural ecosystems at Rothamsted Experimental Station, UK

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Abstract

The effects of acidification on the soil chemistry and plant availability of the metals Pb, Cd, Zn, Cu, Mn and Ni in new and archived soil and plant samples taken from the $>$100-year-old experiments on natural woodland regeneration (Geescroft and Broadbalk Wildernesses) and a hay meadow (Park Grass) at Rothamsted Experimental Station are examined. We measured a significant input of metals from atmospheric deposition, enhanced under woodland by 33% (Ni) to 259% (Zn); Pb deposition was greatly influenced by vehicle emissions and the introduction of Pb in petrol. The build up of metals by long-term deposition was influenced by acidification, mobilization and leaching, but leaching, generally, only occurred in soils at pH$<$4. Mn and Cd were most sensitive to soil acidity with effective mobilization occurring at pH 6.0–5.5 (0.01 M $CaCl_2$), followed by Zn, Ni and Cu at pH 5.5–5.0. Pb was not mobilized until pH$<$4.5. Acidification to pH 4 mobilized 60–90% of total soil Cd but this was adsorbed onto ion exchange surfaces and/or complexed with soil organic matter. This buffering effect of ion exchange surfaces and organic matter in soils down to pH 4 was generally reflected by all the metals investigated. For grassland the maximum accumulation of metals in herbage generally corresponded to a soil pH of 4.0. For woodland the concentration of Pb, Mn and Cd in oak saplings (*Quercus robur)* was 3-, 4- and 6-fold larger at pH 4 than at pH 7. Mature Oak trees contained 10 times more Mn, 4 times more Ni and 3 times more Cd in their leaves at pH 4 than at pH 7. At pH values $<$4.0 on grassland the metal content in herbage declined. Only for Mn and Zn did this reflect a decline in the plant available soil content attributed to long-term acid weathering and leaching. The chief cause was a long-term decline in plant species richness and the increased dominance of two acid-tolerant, metal-excluder species

Introduction

Soil acidification has important consequences for chemical and biological processes in soils. Long-term acidification of woodland and grassland through atmospheric deposition causes an irreversible reduction in cation exchange capacity (CEC) and the mobilization, to potentially toxic concentrations, of Al, Fe and Mn (Billett et al., 1990; Blake et al., 1999; Johnson et al., 1991). Soil acidification decreases the number of plant species in natural grassland (Goulding et al., 1998; Tilman et al., 1994). Atmospheric deposition is a major cause of acidification on all unfertilized agricultural, natural and semi-natural land (Blake et al., 1999; van Breeman et al., 1984). However, the cause of acidification on most agricultural land is the application of ammonium-based fertilizers (Goulding and Blake, 1998; Goulding and Annis, 1998).

Soil minerals contain varying quantities of the potentially toxic ‘heavy’ metals (density $>$6 g cm^{-3}) Mn, Pb, Cd, Zn, Cu and Ni, depending on the mineralogical composition. Such metals are also deposited from the atmosphere (Jones et al., 1987a, b). Until recently it was thought that the accumulation of metals

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in the surface horizons of soil led to only minimal mobilization and subsequent movement through the soil profile; leaching and plant uptake were also assumed to be small (Bowen, 1977; Weber, 1981). However, soil acidification changes the equilibrium, partitioning and speciation of metals in the different soil phases. In general the solubility, and hence mobility and potential plant availability, of most heavy metals increases with decreasing pH (Harter, 1983; McKenzie, 1980). Natural and polluted soils can, therefore, be both sources and sinks for toxic metals (Stigliani et al., 1991).

Most experiments to date have used areas of different pH to study the impacts of acidity on metal mobilization. Substituting ‘space for time’ in this way confounds comparisons because of differences in soils and climate. There is little published literature showing changes with time in soil pH and heavy metal distribution in soils and these tend to cover only the short-term (Kreutzer et al., 1989; Martin and Coughtry, 1987; Tyler et al., 1987). The long-term experiments and soil and plant archive at Rothamsted Experimental Station permit studies of the impacts of acid deposition on soils and plants at a single site over a period of >150 years (Blake et al., 1999, 2000). In this paper we report the use of these resources to study the relationship between soil acidification and its impacts on metal mobilization. New and archived soil samples from Park Grass and the Geescroft and Broadbalk Wilderness Experiments were used to study and compare changes in the potentially toxic heavy metals—Pb, Cd, Zn, Cu, Mn and Ni—under grassland and regenerating woodland, subject to acidifying inputs from atmospheric deposition and fertilizer. Comparisons between limed and unlimed soils provide a wide range of pH values. Archived herbage samples from Park Grass, and recent samples of oak (*Quercus robur)* vegetation taken from both Geescroft and Broadbalk Wildernesses, also show how the changes in soil pH and chemistry influence the plant uptake of metals. The archived samples allow changes in pH and metal chemistry to be viewed in the light of long-term metal inputs from the atmosphere, which have been quantified using the data from the soil and vegetation analyses.

Materials and methods

Site descriptions

Rothamsted Experimental Station is ca. 50 km north of London. The two long-term experiments called Geescroft Wilderness and Broadbalk Wilderness are areas of what was arable land that were fenced off in 1881 and 1883, respectively, and allowed to revert to deciduous woodland by natural regeneration. The soil under Broadbalk Wilderness was heavily limed in the 19th century and so has been buffered against acidifying inputs; its pH has only decreased by 0.3 units since 1883; by contrast, the soil under Geescroft Wilderness was not limed and has acidified by 2.5 pH units over the same period (see Figure 1 in Blake et al., 1999). The Park Grass Experiment examines the effect of various types and amounts of fertilizers and lime on the yield and composition of grass cut for hay. This study focuses on (i) those plots which represent a semi-natural grassland ecosystem receiving no fertilizers or manures, only atmospheric deposition—Plot 3a is limed and Plot 3d is unlimed, and (ii) a plot receiving ammonium sulphate fertilizer (144 kg N ha^{-1} $year^{-1}$) which causes rapid and severe acidification when no lime is applied—Plot 11/1d (Blake et al., 1999).

Soil samples have been collected from the Wildernesses and Park Grass on average every 25 years, beginning in 1883 on the Wildernesses and 1876 on Park Grass. They were air-dried and stored in sealed glass jars. This investigation examined only soils from the 0–23-cm layer, where maximum metal accumulation and soil acidification have occurred. In addition, herbage samples from Park Grass have been taken annually and stored air dry since 1856, whilst the botanic diversity has been measured periodically since the 1860s.

Soils description and sampling

The dominant soil type at Rothamsted farm is described as Batcombe Series, a Chromic Luvisol according to the FAO classification (Avery and Catt, 1995). A full description was given by Blake et al. (1999). The surface mat of undecomposed litter found on the most acid plots was not included in the 0-23 cm soil samples. Samples were collected from the Wildernesses in 1883, 1904, 1964 and 1991 and from Park Grass Plots 3d and 11/1d in 1876, 1906, 1923, 1959, 1966 (not 11/1d), 1976 (11/1d only) 1984 (not 11/1d) and 1991. Liming on Plot 3a did not start until 1903.

Samples from this plot were collected in 1959, 1966, 1984 and 1991.

The earliest samplings were taken with a 23 cm deep, 15 × 15 cm metal box from four separate sampling positions, i.e., four large replicates. The four samples from each layer were then bulked when air-dry. Jenkinson (1971) and Blake et al. (1999) record the details of the method of sampling and positions of the sample holes. This method was continued for 0–23-cm soils on both Wildernesses until 1991. From 1959, Park Grass soils were sampled in a 'W' pattern, taking eight cores to 23 cm with a 3-cm semi-cylindrical auger; the cores were bulked to give a representative sample. In 1991, additional samples were taken from the 0–7.5-cm layer at each site (not 11/1d) to study the accumulation and acid mobilization of Pb in the most contaminated soil layer.

Soil pH

Soil pH was measured in a 5 g soil:12.5 ml 0.01 M calcium chloride ($CaCl_2$) suspension. Full details were given by Blake et al. (1999). In all, 25 archived 0–23-cm Rothamsted soil samples were used, covering the period 1876–1991 and having an overall pH range of 7.3–3.1.

Heavy metal weathering and 'availability'

To study the changes in metal contents in different soil pools in response to increasing soil acidity the following extractions were used:

Total metal content

Total soil metal content was determined by digesting 0.25 g of ground (<1 μm) air-dried soil in aqua-regia following the method of McGrath and Cunliffe (1985). Changes in total metal content reflect the effect of acid weathering in low pH soils (Blake et al., 1999) or, in limed, or not strongly acidified soils, reflect the accumulation of metals from anthropogenic inputs (Jones et al., 1987a,b)

'Available' metal content

An estimate of the amount of metal available for plant uptake was made by shaking 5 g of <2 mm sieved, air-dried soil with 10 cm^3 of 0.05 M diammonium ethyldiaminetetraacetic acid (EDTA), adjusted to pH 7.0, in a polypropylene centrifuge tube for 2 h. The mixture was centrifuged and the supernatant drawn off and passed through a 0.2-μm membrane filter. This method extracts ion exchangeable, sorbed and organically bound metals which can be released to the soil solution, although the dissolution of metals and their extractability with EDTA is partially pH dependent. The method relates closely to uptake for a range of plants (Ure, 1990).

Exchangeable metals

A measure of exchangeable metals was made by leaching 5 g of <2 mm sieved, air-dried soil with 75 cm^3 of 1 M ammonium acetate (NH_4OAc) (Metson, 1956). This extracts metal cations adsorbed on charged surfaces which are released to the soil solution through the process of ion exchange. This reversible process buffers the most readily plant available pool in soils.

The methods for available and exchangeable metals analyze a 'labile' pool that relates closely to plant uptake and can be compared over time and space for changes. However, metals, as with other soil components, move dynamically between a number of pools and associated chemical fractions. To provide a better idea of the dynamics of metal chemistry, a detailed sequential analysis of selected samples from Park Grass was made using the method of McGrath et al. (1993). The extractants used and the fractions extracted were: (1) 0.1 M $CaCl_2$ to measure an 'exchangeable' fraction; (2) 0.5 M NaOH to measure an 'organically-bound' fraction; (3) 0.05 M EDTA to measure those metals bound to oxides and carbonates; (4) aqua-regia to measure the residual metal content of the soils. All soil extractions were made on duplicate sub–samples.

Vegetation sampling and analysis

Herbage from Park Grass has been harvested twice-yearly since 1873 (Warren and Johnston, 1964). The herbage, usually cut in June and October, is not washed but merely chopped into short lengths for dry matter determination and archived. For each period selected for analysis, samples from both harvests in each year were bulked in proportion to the dry-weight yield to give a representative sample, and the yields of four consecutive years bulked (e.g., 1920–23) to minimize variation.

Samples of oak vegetation were taken from both Wildernesses in 1991. These included leaves from mature trees and wood cortex samples taken by boring to a depth of approximately 5 cm in the trunks. An equal number of saplings of roughly equal biomass were also sampled. The samples were washed repeatedly in distilled water to remove all visible traces of adhered soil, and as much surface contamination as possible, and oven dried.

For analysis for total metal content, all plant material was bulked, ground in a Glen Creston mill to pass a 0.5-mm grating, and sub-samples of 0.25 g were digested using a nitric–perchloric acid mixture following the method of Zarcinas (1987). All analyses were made on four replicate sub-samples.

Determination of long-term heavy metal inputs from the atmosphere

Atmospheric inputs of Pb, Cd, Zn, Cu and Ni to the woodland and grassland at Rothamsted were estimated from the increases in total metal content of the surface (0–23 cm) layer of soils not strongly acidified since the 19th Century. For Park Grass the annual increase in metal content was determined by regression analysis of the more complete data set from the unlimed Plot 3d. (Regression equation: $y = a + bx$ where b, the regression coefficient, equals the annual change and x the time in years). On Plot 3a metal concentrations were found to fluctuate following lime application. The use of Plot 3d is justified by the data given in Nicholson et al. (1994) which shows that no Cd had, up to 1992, moved down the soil profile below 23 cm. Thus, it is likely that no net leaching of atmospherically deposited metals had occurred from this depth.

The metal content in herbage cut and removed from Park Grass was calculated from the metal content of the herbage multiplied by the mean herbage yield. This value was used to compensate for metal uptake and removal on Park Grass.

Spectroscopic analysis. Metal cations in soil extracts were initially measured by inductively coupled plasma emission spectroscopy (ICPAES), following acidification to 5% with HCl. For all extractants, Cd concentrations were found to be below the ‘Safe Detection Limits’ (SDL) for the Applied Research Laboratories (ARL 34000) ICPAES (see McGrath and Loveland, 1992). In addition, the lower values for total Pb, EDTA-extractable Ni and NH_4OAc-exchangable Pb, Cu, and Ni were also below the SDL. These metals were therefore re-determined by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) using a Perkin-Elmer 372 spectrophotometer with deuterium arc background correction. Prior to analysis, the total and EDTA extracts were evaporated to dryness and made up to 0.2% HNO_3. Using NH_4OAc to determine exchangeable metal cations further complicates analysis by GFAAS because of severe background absorption by the NH_4OAc. To overcome this, the metals were extracted from the NH_4OAc by chelation with diphenylthiocarbazone and extraction into chloroform, following the method of Iu et al. (1979). For the sequential analyses, only the Cd concentrations were too small to be measured by ICPAES and were determined by GFAAS. All GFAAS measurements were made against matrix matched standards.

All metals in samples of vegetation were analyzed by ICPAES, apart from Cd extracts which were analyzed by GFAAS (suppression from $HClO_4$ did not occur on samples with >0.1 mg Cd kg^{-1}). For all soil and vegetation samples, spectroscopic analyses were made in duplicate.

Quality assurance data

Quality Control for soil analyses was maintained by the use of BCR Certified Reference Material 142 and an internal reference soil (Sample HRM 1). For vegetation, certified reference material NBS 1573 (Tomato leaves) and an internal standard (ryegrass) was used. The analysis of the internal standards was repeated every 10 samples. The averaged determinations gave good agreement with the certified reference and internal values (Table 1). An approximate guide to the presence of soil and dust contamination on the herbage was obtained from the Ti content (Williams, 1974).

Soil storage effects

For the metals studied here, only extractable Mn has been shown to increase significantly following air-dry storage (Smith, 1990). Blake et al. (2000) discussed the temporal changes in some of the chemical properties of air-dried, stored, Rothamsted soils used in this investigation. Exchangeable Mn was the only cation which showed a comparatively large increase following storage, but the increase was systematic: amounts of NH_4OAc-exchangeable Mn increased by 100% over a 32-year period. Values of Mn were accordingly adjusted for the effect of long-term storage.

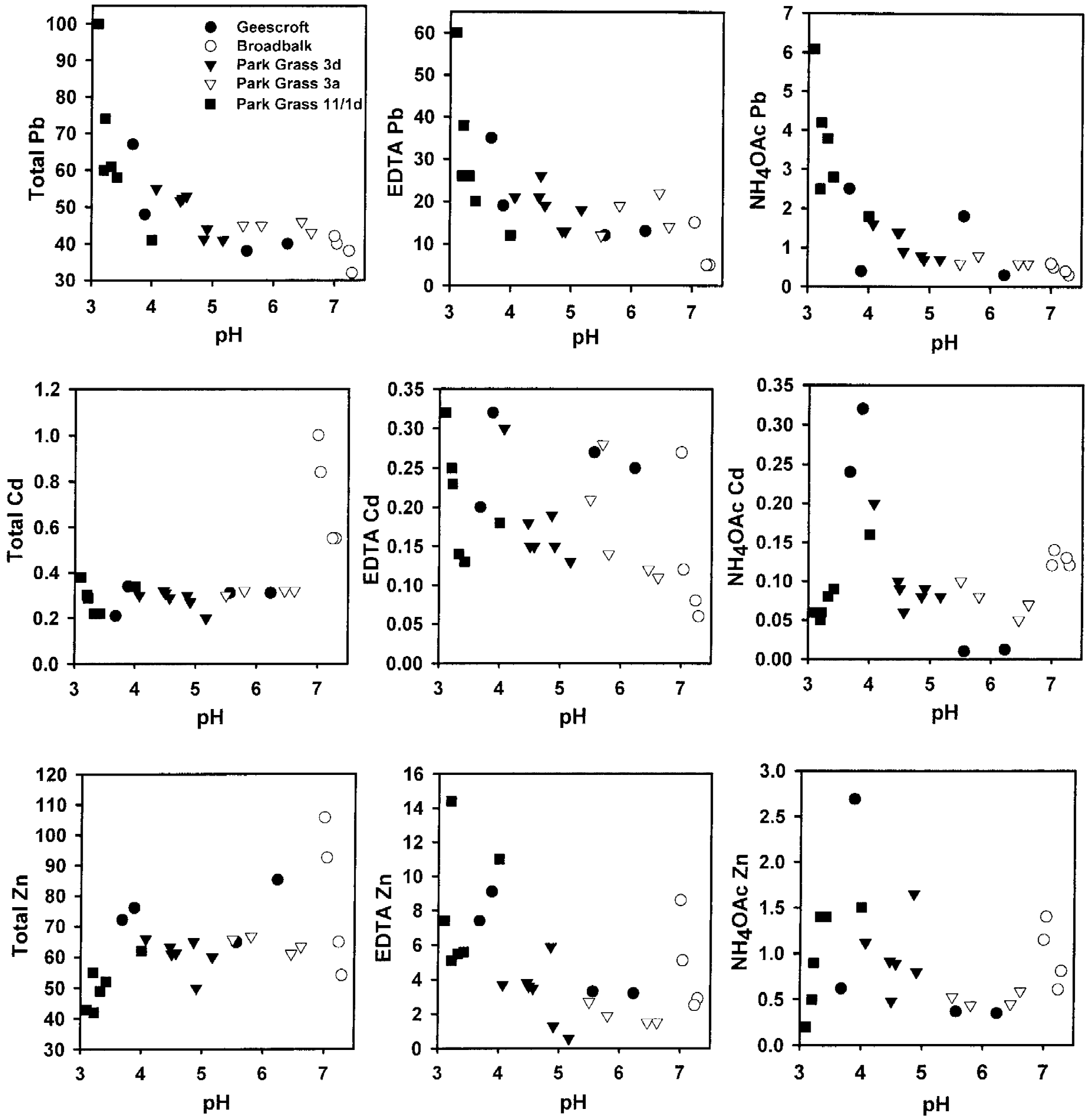

Figure 1.

Results and discussion

The effect of pH and acidification on the 'availability' of soil heavy metals

The total, EDTA-extractable and NH_4OAc-exchangeable metal contents in the soils are graphed against pH in Figure 1. This shows changes with pH (and, therefore, time) on metal availability across the whole site.

Lead

The relationships between EDTA-extractable and NH_4OAc-exchangeable Pb and pH closely followed that for total Pb, increasing below ca. pH 4.5. Figure 2a shows that there is a significant correlation ($p < 0.001$) between NH_4OAc-exchangeable Pb and total Pb, suggesting that the increase in exchangeable Pb was the result of the increase in total Pb (i.e., deposited Pb), rather than Pb mobilization because of soil acidification. No other available or exchangeable

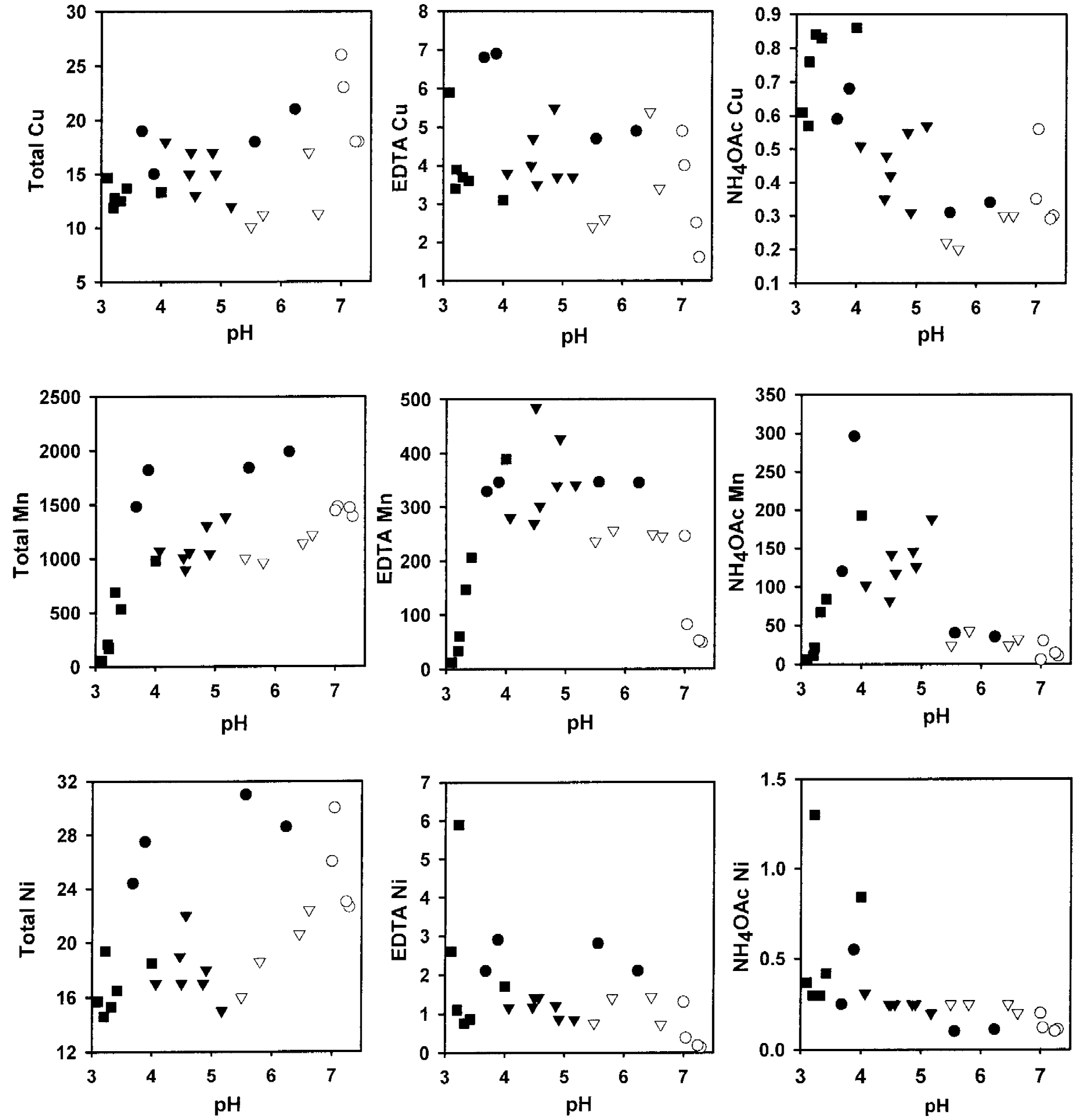

Figure 1. Continued. The relationship between total, 0.05 M EDTA-extractable and 1 M NH_4OAc-exchangeable metal content ($\mu g\ g^{-1}$) and pH, for 0–23-cm Rothamsted soils from the Geescroft and Broadbalk Wildernesses (woodland) and Park Grass (hay meadow) Plot 3a (unfertilized, limed), Plot 3d (unfertilized, unlimed) and Plot 11/1d (fertilized -$(NH_4)_2SO_4$, unlimed).

metal contents were so closely related to their total content in soil. However, for soils more acid than pH 5, the proportion of NH_4OAc-exchangeable Pb increases linearly with decreasing pH (Figure. 2b). Thus Pb has been mobilized in acidified soil.

Between 1876 and 1906 the total Pb content of Plot 11/1d increased by 17 $\mu g\ g^{-1}$ compared to 3 $\mu g\ g^{-1}$ on Plot 3d (Figures 1 and 3). Apart from atmospheric deposition the only other possible source of this Pb on 11/1d was contaminated fertilizer. The ammonium sulphate used in agriculture at this time was largely unrefined and was manufactured from sulphuric acid produced by the lead chamber process. The latter contained a number of impurities, but especially lead

Table 1. Measured, certified and standard values (μg g^{-1}) for soil and plant standard materials used in this investigation

Standard/measured	Pb	Cd[a]	Zn	Cu	Mn	Ni
Soils						
BCR Standard CRM 142						
Certified value:	37.8	0.25	92.4	27.5	569	28.9
Measured:	36.5	0.24	91.0	26.5	567	28.1
Rothamsted Internal HRM 1						
Standard value:	93.0	8.5	301	92.0	346	29.0
Measured:	92.0	7.4	290	96.0	343	29.0
Plant material						
NBS Standard, Ref. 1573-						
(Tomato leaf). Certified value:	6.3	3.0	62.0	11.0	238	n.a
Measured:	7.0	2.9	59.8	11.2	236	–
Rothamsted Internal (Ryegrass)						
Standard value:	3.5[a]	0.2	28.0	6.4	241	4.3
Measured:	3.5[a]	0.2	27.3	6.8	240	4.5

[a] determined by GFAAS; n.a, not available.

sulphate derived from the action of the acid upon the lead chamber (Newth, 1909). Thus, we conclude that the fertilizer was the most likely source of Pb on this Plot. In addition, Plot 11/1d is about half (approximately 100 m) the distance of Plot 3d from the B467 road from Harpenden to Redbourn. This compounds the long-term effect of atmospherically deposited Pb derived from vehicle emissions.

Results of the sequential analysis of metal contents in archived soils from the Park Grass experiment are shown in Figure 3. For Pb, the amounts of all the fractions, apart from residual Pb, increased with the increase in the total content of Pb that occurred over the period 1876–1991. The percentages of the total that comprised Pb in the 0.05 M $CaCl_2$-exchangeable fraction, increased from 3 to 15% with time and acidification. A similar trend was also seen in the NaOH-extractable fraction, indicating that the Pb associated with organic matter increased from 2 to 12.0% of the total as pH decreased from 4.5 to 3.1.

Cadmium

The total Cd concentration in soil sampled in the 19th Century soil was greater on Broadbalk Wilderness (0.55 μg g^{-1}) than on Park Grass and Geescroft Wilderness soils (0.31 and 0.20 μg g^{-1}, respectively), but similar to that determined by Jones et al. (1987b) for unfertilized soil on the adjacent Broadbalk arable field (0.51 μg g^{-1}). The most likely cause of this variation was the slightly acidic nature of Geescroft and Park Grass at the start of the experiments, which resulted in some Cd offtake occurring in crops and hay. This was not so on the heavily limed Broadbalk experiments.

Apart from Broadbalk Wilderness the total Cd content did not vary with pH. The increase in the Cd content of soil from Broadbalk Wilderness is attributed to its deposition from the atmosphere between 1883 and 1991 and the enhanced scavenging effect of the developing woodland canopy. This trend was repeated for the other metals studied because no acid mobilization has occurred in this soil.

The EDTA-extractable Cd contents varied with pH within each site but not across the sites (Figure 1). NH_4OAc-exchangeable Cd was up to four times greater at pH 4 than at other pH values. At this pH 60–90% of the total Cd content of the soils had been mobilized and was exchangeable. The decrease in NH_4OAc-exchangeable Cd below pH 4 cannot have been solely caused by ion exchange and leaching of Cd from the 0–23-cm soils because EDTA extractable Cd was increased. Sequential analysis (Figure 3) shows that more Cd was associated with the NaOH-extractable fraction at very acid pH values, suggesting

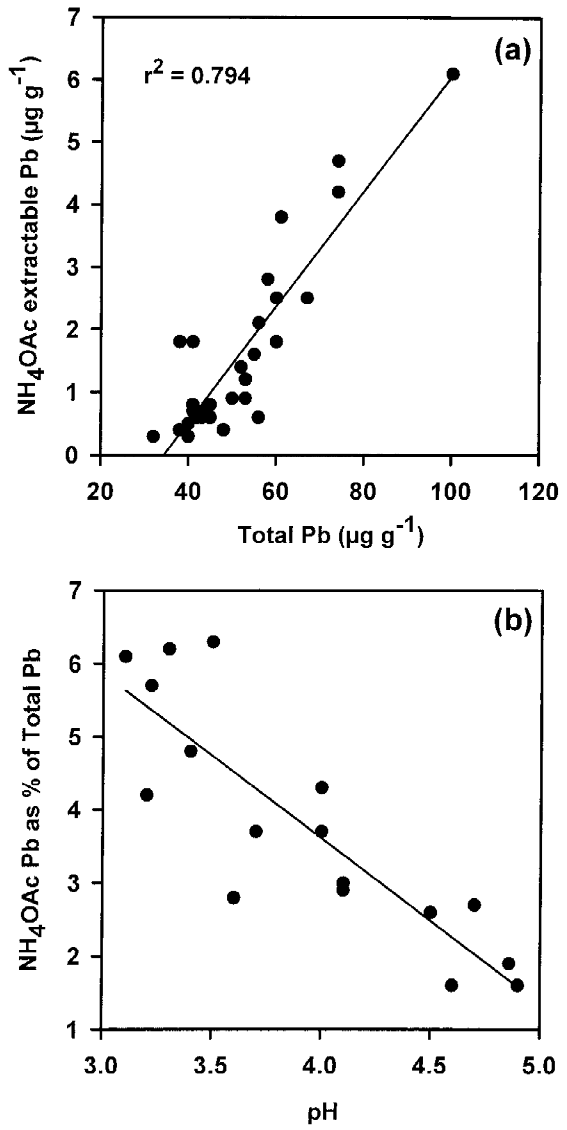

Figure 2. (a) The relationship between total Pb and 1 M NH_4OAc-exchangeable Pb for 0–23-cm Rothamsted soils (includes 0–7.5-cm soils for 1991) from the Geescroft and Broadbalk Wildernesses (woodland) and Park Grass (hay meadow) Plot 3a (unfertilized, limed), Plot 3d (unfertilized, unlimed) and Plot 11/1d (fertilized, $(NH_4)_2SO_4$; unlimed). (b) The relationship between pH (<5.0) and NH_4OAc exchangeable Pb expressed as the percentage of total Pb for the most strongly acidified soils at these locations.

that a greater proportion of acid mobilized Cd has become complexed with organic matter.

Zinc and copper

The very acid soils at pH <3.5 on Park Grass Plot 11/1d contained less total Zn than the others, suggesting that acid weathering and leaching had occurred in excess of the rate of atmospheric deposition. The effect of acidification on Zn content of the soils from Geescroft Wilderness appears to have been partly offset by enhanced Zn inputs to the woodland canopy. The average total Zn content of the samples from Broadbalk Wilderness was a little larger than those of the other sites, but the content was as variable as that of Cd (Figure 1).

The effect of increasing soil acidity was most clearly reflected by a progressive increase in EDTA-extractable Zn. NH_4OAc-exchangeable Zn changed with pH in a similar way to Cd but much more variably. Sequential analysis (Figure 3) showed that all the Zn fractions in soils from Park Grass Plot 3d increased between 1906 and 1991, the result of Zn deposited from the atmosphere and increasing soil acidity.

Copper contents of the soils were very variable, although the graph (Figure 1) gives some indication that total Cu decreased at low pH similarly to Zn. NH_4OAc-exchangeable Cu generally increased at pH <5.5 but sequential analysis also shows a much larger increase in NaOH extracted Cu below this pH (Figure 3), suggesting that a large proportion of acid mobilized Cu has been complexed by soil organic matter. EDTA-extractable Cu was greatest in the acid soils of Geescroft Wilderness, but this may partly reflect the higher total Cu content found in these soils.

Manganese and nickel

The Mn and Ni contents of soil at Rothamsted were very variable. Generally total Mn content decreased with pH, very rapidly at pH values <4, from an average site value in the 19th Century of 1250 to 12.6 μg Mn g^{-1} in the most acid soil of Park Grass Plot 11/1d in 1991. Measures of available and exchangeable forms of Mn show a steady but variable increase as pH decreases from 7 to 4 (Figures 1 and 3) and then a rapid decrease at more acid pH values, corresponding to the decline in total Mn. Blake et al. (1999) have described the effect of acidic deposition and soil acidification on mineral weathering and subsequent leaching of Mn on Geescroft Wilderness.

There is some suggestion of a decrease in total Ni with declining pH at each site. Measures of NH_4OAc-exchangeable Ni show an increase with acidity; most was extracted from soils from Park Grass Plot 11/1d. Sequential analysis of Park Grass soils also showed an overall increase in exchangeable Ni with declining soil pH, although the content extracted with $CaCl_2$was greater than extracted with NH_4OAc. This increase

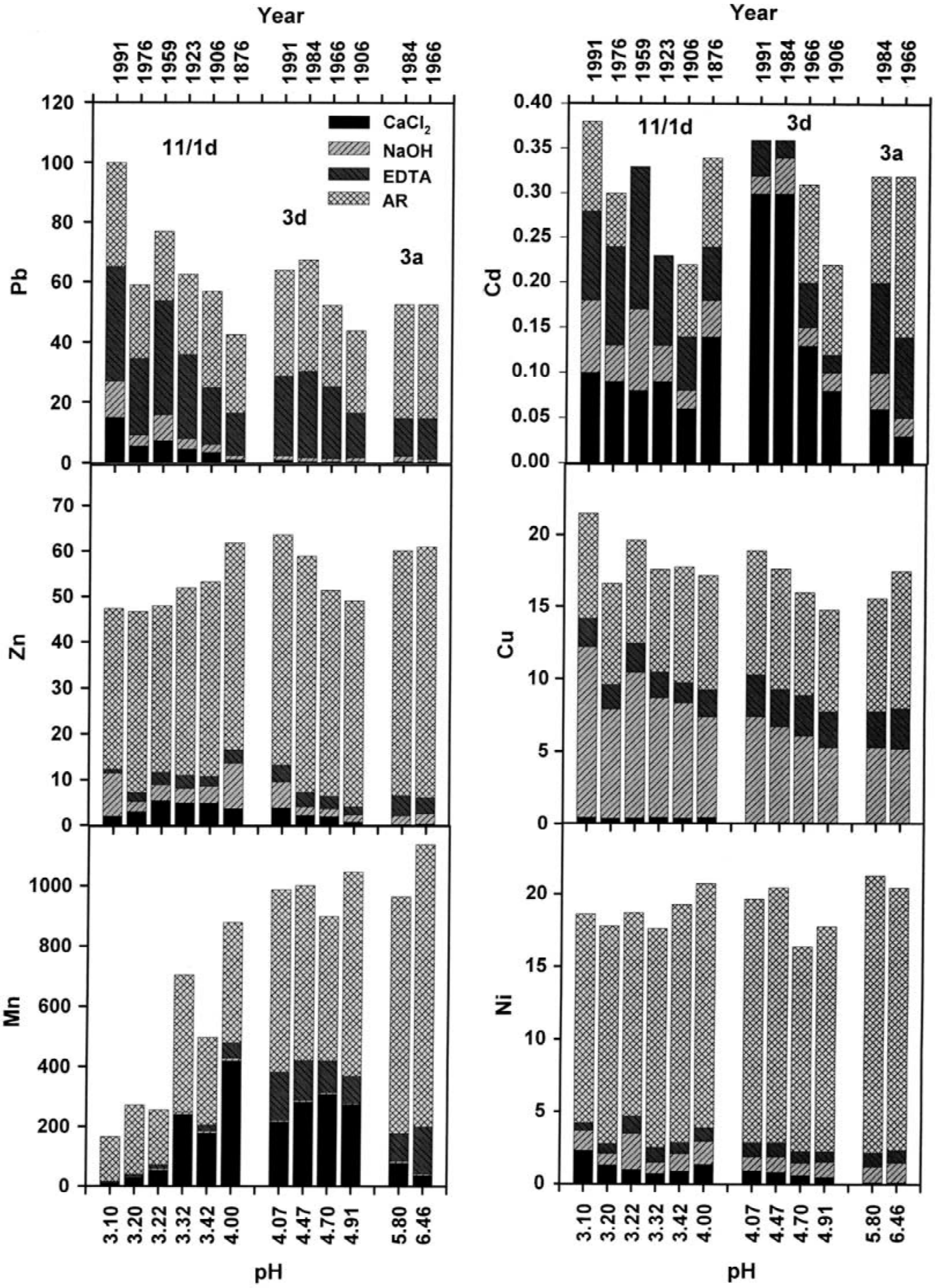

Figure 3. Sequential analysis (μg g^{-1}) of selected 0–23-cm soils from Park Grass (hay meadow) for Plot 3a (unfertilized, limed), Plot 3d (unfertilized, unlimed) and Plot 11/1d (fertilized, $(NH_4)_2SO_4$; unlimed) showing changes in metal fractions in relation to soil pH (acid) and the year sampled.

is consistent with the acid mobilization of soil Ni deposits.

The accumulation of heavy metals by vegetation

The pH of soil samples from the three Park Grass plots range over almost 4 units from just above 3 to almost 7. In Figure 4, the data have been arranged to show the changes in metal contents with those of pH, and with time for each plot, making an almost continuous pH curve. The irregular time steps and the discontinuity between plots must be noted, however, especially the 'increase' in pH moving from Plot 3d in 1990 to Plot 11/1d in 1864. The first one or two sets of data from Plot 11/1d should be disregarded in the context of this pH: time course.

Sample contamination

Samples contaminated with soil should contain anomalously large amounts of other soil-derived metals as well as Ti. Figure 4 shows the Ti contents of herbage samples from Park Grass. Only one herbage sample contains an abnormally large concentration of Ti, that from Park Grass Plot 3d, collected between 1988 and 1991. The sample taken in 1990 from Plot 3d has a large Standard Error for the Ti analysis and also contains the largest amount of Pb, Zn, Mn and Ni, but the contents of Pb, Mn and Ni and, especially Zn, are not anomalous, neither does this sample contain the most Cd or Cu. We therefore conclude that this is the only sample that could be contaminated by soil.

Lead contents in herbage samples from Plot 3a were very similar to those determined by Williams (1974) which are shown in parenthesis in Figure 4. The decline in Pb in the most recent sample mirrors the removal of Pb from petrol, but there was not a concurrent decline in the total soil Pb content of this Plot. Comparing the changes in Pb content with soil pH, the concentration increases from 5–10 to ca. 20 μg g^{-1}as the pH decreases from 7 to 4, and then decreases as the pH continues to decrease. This is despite a general increase in Pb, and the availability of Pb in the most acid soils (Figures 2b and 3). Manganese, Cd and Ni follow similar trends, Zn shows some similarities, but Cu exhibits few clear trends.

Nicholson et al. (1994) made a detailed survey of the Cd content in herbage from Park Grass Plot 3, and these data are also shown, in parentheses, in Figure 4. These are a little smaller than our measurements but follow the same trends, which Nicholson et al. attributed to soil acidification. The slightly smaller Cd content may be attributed to different sampling strategies: Nicholson et al. used only the June herbage samples; we used combined June and October samples

Increases in the herbage content of Cd and Zn on Plot 3d are consistent with the increases in total, NH_4OAc- and $CaCl_2$-exchangeable Cd and Zn measured (Figures 1 and 3). Comparing the data from Plots 3a and 3d for the same sampling periods, shows that there was, on average, 20-30% more Zn, Cu and Cd in the herbage from Plot 3d compared to Plot 3a. The overall trend for these metals in herbage from Plot 3a (limed) was to increase. This implies that one-quarter to one-third of these metals came from acid mobilized soil sources and the remainder was the result of increasing total soil metal content through deposition. Although direct foliar absortion of these metals cannot be ruled out, the effect should be similar on both plots because the area of interceptive canopy appears, visibly, to be the same.

On plot 11/1d the Zn and Cu contents were very variable but approximately decreased with pH and were less than those on Plot 3d, despite having larger NH_4OAc- and $CaCl_2$-exchangeable soil Zn and Cu contents.

The Mn content of herbage closely followed the trend for $CaCl_2$-exchangeable Mn in soil (Figure 3). Mn is very sensitive to soil acidity, with mobilization and uptake occurring even on the limed soils of Plot 3a in response to the recent, small increase in acidity. The Mn content in herbage more than doubled between 1856 and 1972 on Plot 3d, reaching a maximum at a pH of about 4.0. The Mn content then declined as pH continued to decrease.

There was no increase in Ni in herbage from Plot 3a, suggesting that any increase in total soil Ni was not reflected by increased uptake, and that no foliar adsorption of atmospherically derived Ni had occurred. By contrast, the Ni content in herbage from Plot 3d increased as pH decreased, consistent with the increase in NH_4OAc- and $CaCl_2$-exchangeable Ni.

Heavy metal content of vegetation from acidified and limed woodland

The heavy metal contents of oak saplings (*Quercus robur)* growing on the acid soil from Geescroft Wilderness were much larger than those in saplings growing on the neutral soil in Broadbalk Wilderness (Figure 5). The Pb, Mn and Cd contents were increased 3-, 4- and 6-fold, respectively, by soil acidification. The metal contents of mature oak leaves taken from trees grow-

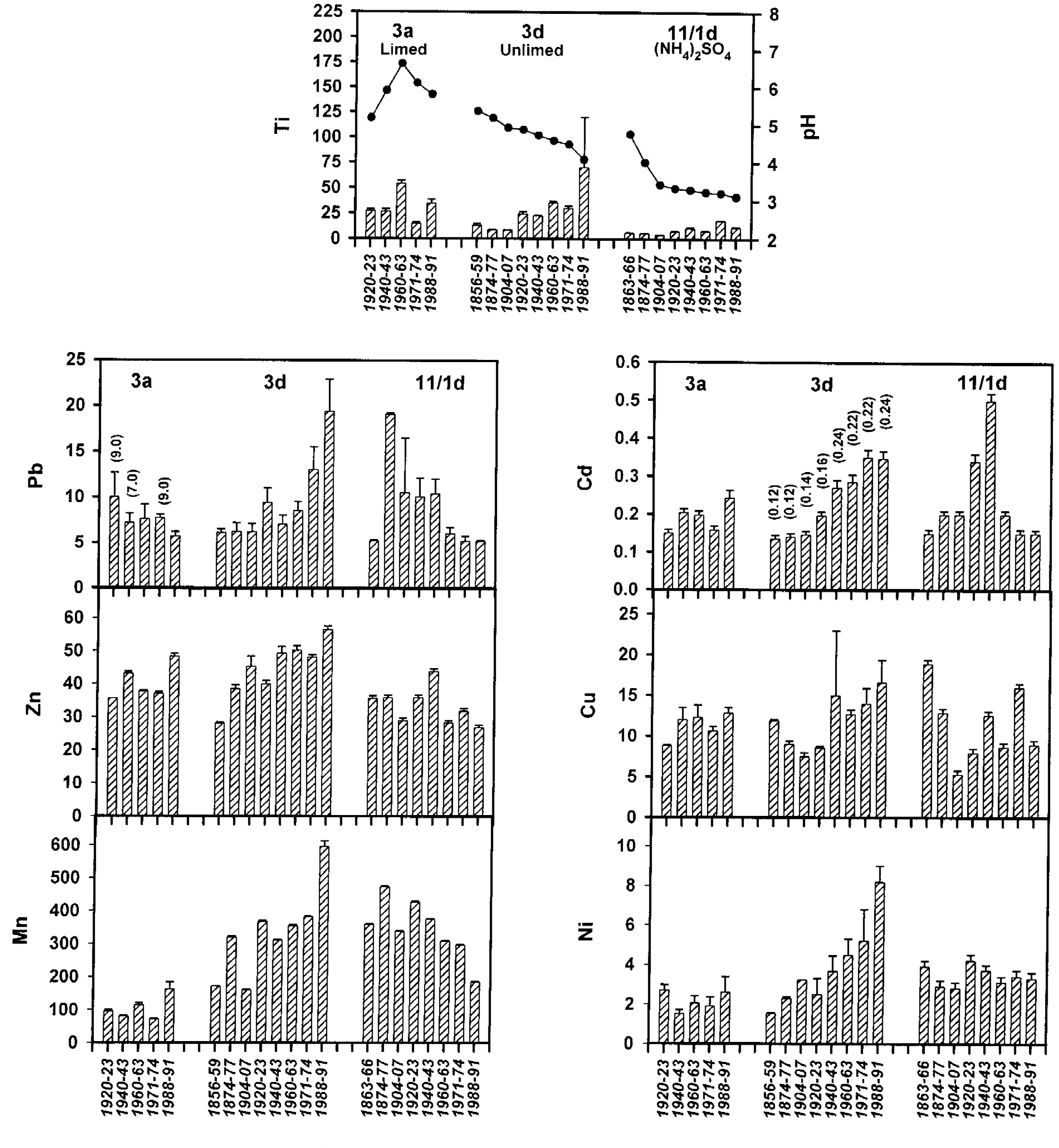

Figure 4. Changes in metal content (μg g^{-1}) with time and soil pH in Park Grass (hay meadow) herbage from Plot 3a (unfertilized, limed), Plot 3d (unfertilized, unlimed) and Plot11/1d (fertilized, $(NH_4)_2SO_4$; unlimed). [Values in parenthesis are those determined on equivalent samples by Williams (1974) for Pb, and Nicholson et al. (1994) for Cd; Error bars represent sampling and analytical variation on four sub-samples].

ing on acid soil (Table 2) were also consistently larger, although large differences were observed only for Mn (10 times larger), Ni (four times larger) and Cd (three times larger). Metal contents in mature oak timber (cortex sample) taken from trees growing on acid soil were also larger for Cd, Cu, Mn and Ni, but the only large difference occurred with Mn. No increase in Pb and Zn was determined.

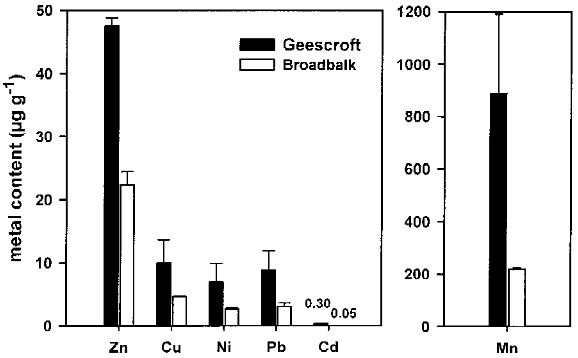

Figure 5. Total metal content of oak saplings *Quercus robur* taken from woodland of the acid Geescroft Wilderness (pH 3.8) and the limed Broadbalk Wilderness (pH 7.0) in 1991. [Error bars represent sampling and analytical variation on four sub-samples].

Table 2. Metal uptake into mature oak leaves and timber (cortex), for acidified and limed woodland of the Geescroft and Broadbalk Wildernesses

	Metal (μg g^{-1})					
	Pb	Cd	Zn	Cu	Mn	Ni
Geescroft						
Content in leaves	2	0.13	61	11.2	2292	10
Content in timber	1.4	0.03	4.0	2.3	140	1.1
Broadbalk						
Content in leaves	1.6	0.05	38	10.9	283	2.5
Content in timber	1.6	0.01	4.0	1.9	18	0.5

Estimating atmospheric inputs of heavy metals to woodland and grassland since the 19th century from soil and vegetation data

Table 3 shows the increases in metal contents in the 0–23 cm soil from Broadbalk Wilderness for the period 1883–1991. These reflect total deposition because, at near neutral pH values, little soil mobilization and uptake occurs and metals translocated into leaves are recycled back into the soil through litter-fall. Only a relatively small quantity of metals was measured in the timber cortex of the mature trees (Table 2). An estimate of the total quantity accumulated, following 108 years of woodland development, was made by calculating the present day, accumulated, tree weights (kg ha^{-1}) following the method of Jenkinson (1971). These values were used to compensate for metal accumulation in the timber stand (Table 3). Because of the nearness of Geescroft Wilderness to the B467 road from Harpenden to Redbourn the inputs of Pb to this woodland are also discussed.

Jones et al. (1987a,b) determined metal inputs from deposition for the limed, arable part of the Broadbalk Experiment adjacent to the Broadbalk Wilderness; a negligible amount (ca. 1%) was taken up by crops from this calcareous soil (pH 7.9). The data for the 1881 and 1980 samples that they used, and the calculated annual metal inputs are included in Table 3 for comparison with our woodland data.

Table 4 shows the annual metal inputs to Park Grass between 1876 and 1991 based on increases in metal content in soil and corrected for metal offtake in herbage (apart from Mn there is no evidence of leaching of heavy metals from 0–23-cm soils of plot 3d). Inputs calculated from the data of Jones et al. (1987a,b) based on archived soil samples taken in 1876, 1959 and 1984, but not corrected for hay offtake, are also included for comparison.

Lead

The amounts of Pb deposited to soils have been greatly influenced by vehicle emissions from leaded petrol and the proximity of sites to the B467 road from Harpenden to Redbourne. Concentrations of Pb in soils from Geescroft Wilderness, adjacent to the road (the middle of the wood is ca. 50 m from the road), were 39.9, 38.1, 48.0 and 67.2 μg g^{-1} for the years 1883, 1904, 1964 and 1991, respectively; an increase of 27.4 μg g^{-1} over the 110 years, with an annual input of 0.25 μg Pb g^{-1}. There was no increase pre-1900, i.e., before the widespread use of motor vehicles. The post-motor vehicle rate of increase was 0.31 μg Pb g^{-1} year^{-1}. Assuming that the soil weight in the 0–23 cm layer of Geescroft Wilderness is 2870 t ha^{-1} (Jenkinson, 1971), and allowing for an accumulation of 4.1 g ha^{-1}year^{-1} in the timber, this approximates to an input of 718 g Pb ha^{-1} year^{-1}.

On Broadbalk Wilderness, about 1 km from the road, amounts of Pb in the soil increased by 225 g ha^{-1} year^{-1} for the period 1883–1991; corrected for Pb accumulation in the timber, this gives an input of 229 g ha^{-1} year^{-1} (Table 3). On Park Grass Plot 3, situated approximately 200 m from the road, Pb inputs were a little larger at 311 g ha^{-1} year^{-1} (Table 4) suggesting that nearness to the road overrides any enhanced scavenging by the canopy of the woodland.

Table 3. Changes in soil metal content and estimated metal inputs attributed to atmospheric deposition on limed woodland of the Broadbalk Wilderness 1883–1991

Year sampled	Metal content ($\mu g\ g^{-1}$)				
	Pb	Cd	Zn	Cu	Ni
1883	32 [38]	0.55 [0.51]	54 [65]	18 [23]	23 [23]
1904	38	0.55	65	18	–
1964	40	0.84	93	23	–
1991	42 [46]	1.00 [0.77]	98 [80]	26 [25]	26 [25]
Average yearly increase in soil ($\mu g\ g^{-1}$)	0.093		0.41	0.074	0.028
(Cd = ng g^{-1})		(4.20)			
(g ha^{-1} $year^{-1}$)[a]	225 [234][b]	10.1 [7.6]	991 [439]	179 [59]	67 [59]
Accumulated in timber[c] (g ha^{-1} $year^{-1}$)	4.1	0.03	10.1	4.8	1.3
Total intercepted by woodland (g ha^{-1} $year^{-1}$)	229	10.13	1001	184	68

[ ] 1881 and 1980 soil samples measured on adjacent Broadbalk arable field, Plot 3 (no fertilizer inputs since 1843) by Jones et al. (1987a,b) using XRF (Cd by GFAAS).

[a] g $ha^{-1}year^{-1}$ calculated from yearly increase data ($\mu g\ g^{-1}$). Average weight of fine soil to 23 cm over study period beneath developing woodland was 2418 kg ha^{-1}.

[b] [ ] Assumes average weight of fine soil to 23 cm on Broadbalk arable field is 2870 kg ha^{-1} (Jenkinson, 1971).

[c] Calculated from Broadbalk Wilderness data in Table 3. Tree weight accumulated over 108 years is 274 000 kg ha^{-1}.

Table 4. Annual inputs of metals to semi-natural grassland attributed to atmospheric deposition; as represented by unfertilized Park Grass Plot 3d

	Metal input (g $ha^{-1}y^{-1}$)				
	Pb	Cd	Zn	Cu	Ni
Based on soil data from Jones et al.(1987a,b)[a] for period 1876–1984	248	1.98 (2.7)[b]	248	0	50
This study; 1876–1991 Average yearly increase in soil (b)[c] ($\mu g\ g^{-1}$)	0.128		0.067	0.024	0.015
(Cd = ng g^{-1})		(0.873)			
(g $ha^{-1}year^{-1}$)	286	2.34	179	63	41
Offtake in hay (g $ha^{-1}year^{-1}$)[d]	25	0.6	100	30	10
Total input to Park Grass	311	2.94	279	93	51

[a] Based on metal increase in 0-23 cm soils; analysed by XRF spectroscopy (Cd by GFAAS). Average weight of fine soil to 23 cm over study period was 2676 kg ha^{-1}.

[b] Value from Rathbaum et al. (1986).

[c] Regression Coefficient (b) for total metal contents of Plot 3d shown in Figure 1.

[d] Calculated from metal contents in herbage given in Figure 4 multiplied by mean herbage yields.

Cadmium

By 1991 the amount of Cd in soil under Broadbalk Wilderness had increased by 0.45 μg g^{-1}, giving an input of 10.13 g Cd ha^{-1} year^{-1} when corrected for Cd accumulated in the timber. On the adjacent arable field, data from Jones et al. (1987b) indicate that the input between 1881 and 1980 was 7.6 g Cd ha^{-1}year^{-1}.

Table 4 shows that 2.94 g Cd ha^{-1}year^{-1} was deposited onto Park Grass during the period 1876–1991. Measurements by and Jones et al. (1987a) and Rothbaum et al. (1986) gave an annual input of 1.98–2.70 g Cd ha^{-1}year^{-1}, respectively, up to 1984, when based solely on increases in soil Cd. Corrected for Cd offtake in hay over this period, Cd input was 2.54–3.26 g ha^{-1}year^{-1}, values in good agreement with those from this study.

Zinc, copper and nickel

The content of Zn in soil from Broadbalk Wilderness increased from 54 to 98 μg g^{-1} between 1883 and 1991 (Table 3), giving an input of 1001 g Zn ha^{-1}year^{-1}. On the adjacent arable field the data of Jones et al. (1987a) gave an input of 439 g Zn ha^{-1}year^{-1} between 1881 and 1980. Our data suggest that the input to grassland was 279 g Zn ha^{-1}year^{-1}.

Copper increased from 18 to 26 μg g^{-1} between 1883 and 1991 on Broadbalk Wilderness, giving an input of 184 g Cu ha^{-1}year^{-1}. The data from Jones et al. (1987a) indicate an input of 59 g Cu ha^{-1}year^{-1}to the adjacent arable field. Our data suggest an input to grassland of 93 g Cu ha^{-1} year^{-1}.

Nickel increased from 23 to 26 μg g^{-1} between 1883 and 1991 on Broadbalk Wilderness, giving an input of 68 g Ni ha^{-1} year^{-1}. The data from Jones et al. (1987a) indicate an input of 59 g Ni ha^{-1}year^{-1} to the adjacent arable field. Our data suggest that inputs to the grassland were slightly less at 51 g Ni ha^{-1} y^{1}.

Based on the changes in metal contents of the three sites, the woodland of Broadbalk Wilderness intercepted 15 and 33% more Ni, 35 and 250% more Cd, 128 and 259% more Zn and 212 and 98% more Cu than the adjacent arable part of the Broadbalk Experiment and Park Grass, respectively. This reflects the effect of the developing woodland canopy on the interception of these atmospherically deposited metals, with no local confounding influences such as there were for Pb.

Factors affecting the content of acid mobilized, plant available heavy metals in Rothamsted soils

To correctly assess the effects of soil acidification on metal availability it must be separated from changes in total soil metal contents caused by the input of metals from the atmosphere and other anthropogenic sources. The impact of atmospheric deposition of metals and acidifying pollutants is greatly influenced by the interception capacity of vegetation, most especially woodland which, at Rothamsted, has enhanced the input of metals by up to 2.5-times.

Soil acidification has a very significant impact on the availability of some metals. A combination of weathering rate, individual sensitivity to soil acidity and the depletion of the total soil metal content ($<$ pH 4) influences heavy metal mobilization and accumulation in the available pool in these soils. Mn and Cd were most sensitive to increased soil acidity with effective mobilization occurring at pH 6.0–5.5, followed by Zn, Ni and Cu at pH 5.5–5.0. Pb was not readily mobilized until pH$<$4.5. The maximum concentrations of exchangeable Cd, Zn and Mn were found at about pH 4, Pb Cu and Ni at pH$<$4. However, complexing with organic matter reduces the quantity of labile Cu$>$Cd$>$Pb. This effect increases as organic matter accumulates in acid soils.

Factors affecting the accumulation of heavy metals in vegetation on acid soils at Rothamsted

The progressive acidification of soils resulted in the accumulation of metals in vegetation above that attributed to increased total soil content (and possible foliar absorption) resulting from the deposition of these metals from the atmosphere. The lack of clear evidence for the mobilization and uptake of Cu on grassland was probably because acid mobilized Cu readily complexes with organic matter (Baker, 1990), reducing the plant available fraction in the rooting zone.

The reduction of the pH of soil to $<$4 on some of the plots of Park Grass resulted in a concomitant reduction in the content of all metals except Cu in the herbage (Figure 4). However, only Mn and Cd showed a concurrent decline in the NH_4OAc- and $CaCl_2$-exchangeable fractions in soil. The decline in soil pH has been accompanied by a decline in the numbers of plant species in the plots (Goulding et al., 1998: Tilman et al., 1994): on Plot 3d the decline was from ca. 50 to ca. 25 species as pH decreased from ca. 6 to ca. 4; on Plot 11/1d the number of species declined from ca. 50 to ca. 2 as pH decreased from ca. 6 to ca. 3. The two remaining acid-tolerant plant species on Plot 11/1d are *Holcus latanus,* which dominates, and *Athoxanthum odoratum,* of which only a few plants are found. Both species display metal tolerance through physiological adaptations for the exclusion of metal ions from the cytoplasm (Baker and Walker, 1990; Cummings and Taylor, 1990). Thus, the decline in the metal content of herbage from the most strongly acidified soils appears to be the result of the loss of acid sensitive species that take up the metals and the survival of 'tolerant' species that can restrict metal uptake. Analyzing plant material from soil having a pH<4.0 can, therefore, give a misleading view of metal availability.

Consequences of soil acidification and heavy metal mobilization

A likely future change in land use in Europe is towards the removal of some land currently used for arable agriculture and conversion to extensive grassland or woodland. Although desirable in terms of biodiversity, conservation and regeneration of the natural environment, such a policy could increase the rate and extent of soil acidification, especially on soils where the acid neutralizing capacity has already been reduced through acid deposition and the use of acidifying fertilizers such as ammonium salts with no or too little lime. The risk of acidification and metal mobilization will be increased for new woodland because the developing aerial canopy increases the deposition of both acidifying and metal pollutants. Even on soils thought to be well buffered against acidity, natural and regenerating ecosystems can rapidly acidify through the deposition of acidifying pollutants (Blake et al., 1999).

The renewed use of ammonium sulphate as a source of S as well as N in agriculture could have serious consequences for soil acidity if liming is not maintained (Goulding and Blake, 1998). There is good evidence that lime applications have decreased, especially in upland areas and other areas where agriculture is no longer prosperous or even economic (Goulding and Annis, 1998). Soil acidification in such circumstances will result in metal mobilization, leaching and enhanced plant uptake.

Herbage at Rothamsted growing on soils that have a pH of ca. 4 can accumulate Mn, Cd and Pb approaching the maximum concentrations tolerated by cattle; the Mn concentrations exceed the minimum phytotoxic concentrations of some plant species (Blake et al.,1994; Chaney, 1989; Goulding and Blake, 1998). For woodland and grassland developed on similar soils but not contaminated by anthropogenic metal inputs from, e.g., industry, roads and fertilizers, Mn and Al are the most likely contaminants through acidification, mobilization and accumulation in herbage (Blake et al., 1999). The most long-term effect of acid weathering in such ecosystems is, however, likely to result in deficiencies of the essential trace elements such as Zn, Cu and Mn. This was clearly indicated by the data for the Mn content of soils and plants in this study, which over the wide pH range encountered displayed a sufficiency–toxicity–deficiency relationship (Marschner, 1986) with declining pH.

The practice of disposing of metal-contaminated sewage sludge on agricultural soils (McGrath, 1984) will result in large concentrations of labile metal ions if soils are allowed to acidify. Soils given regular applications of superphosphate fertilizers have been shown to accumulate Cd over and above that deposited from the atmosphere, because small quantities of Cd occur in phosphate-bearing deposits (Jones et al., 1987b; Nicholson et al., 1994). Because Cd from anthropogenic inputs appears to be relatively sensitive to soil acidification, increases in soil acidity could have serious consequences for the availability of this highly toxic metal. This could have direct implications for human health if cereal crops are grown on poorly buffered soils in regions of high acid deposition or receiving acidifying N fertilizer inputs.

Any liming policy to directly ameliorate the effects of severe soil acidification will need to take into account the temporary effect of increased concentrations of soluble, potentially toxic metals displaced from the exchange surface by Ca^{2+} (Kreutzer et al., 1989, Marschner et al., 1989). Where the accumulation of organic matter on acid soils has resulted in imobile organo–metal complexes, the application of lime and the resulting increase in mineralization will also release complexed metals into the available pool.

Conclusions

Changes in 'available' heavy metal content must be assessed in light of the changes in total metal content, with deposition, acidification and mobilization accounted for. In the late 1980s, 25% of the UK had a soil pH<5 (McGrath and Loveland, 1992); this was mainly in the wetter upland grassland areas where liming is uneconomic. Agricultural policies and market competition have caused farmers to look for ways to cut costs—omitting lime is an easy option. In areas with already acid soils, where liming is uneconomic in the short-term, or where extensification, afforestation, the use of acidifying fertilizers or metal contaminated sewage sludges increases acid or metal inputs or both, metal mobilization and uptake could become an increasing problem. Complexation on organic matter could reduce the risk of uptake into the food chain, but ameliorative liming, increasing pH too quickly, could exacerbate the problem. Preventing soil acidification through pH monitoring and liming is a better policy.

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