LONG-TERM CHANGES IN THE Cu, Pb, AND Zn CONTENT OF FOREST SOIL ORGANIC HORIZONS FROM NORTH-EAST SCOTLAND

M. F. BILLETT, E. A. FITZPATRICK, and M. S. CRESSER
Department of Plant and Soil Science, University of Aberdeen, Meston Walk, Aberdeen , AB9 2UE, Scotland

(Received June 4, 1990; revised February 5, 1991)

Abstract. Forest soil organic horizons from old and young plantations in the Alltcailleach Forest, N.E. Scotland were first sampled in 1949/50 and resampled in 1987. Copper, Pb and Zn in the soils were determined simultaneously on the original (stored) and the resampled soils. Overall mean Cu and Pb concentrations increased from 12.7 to 15.3 and 49.5 to 60.8 mg kg^{-1} between 1949/50 and 1987. Zinc concentrations decreased from 76.4 to 60.7 mg kg^{-1}. Amounts of all 3 heavy metals increased because of increases in the thickness of organic horizons. Mean accumulation rates for Cu, Pb and Zn were 39.1, 186 and 114 g ha^{-1} yr^{-1}, respectively. The rate of accumulation of Pb was significantly related to the rate of accumulation of organic matter. Copper and Zn concentrations were directly correlated with pH and inversely correlated with C/N ratio, whereas Pb was inversely correlated with pH and directly correlated with % C and C/N ratio. The more acidic soil organic horizons therefore contained higher concentrations of Pb and lower concentrations of Cu and Zn.

1. Introduction

The accumulation of heavy metals in soil organic horizons is well-documented both from areas in the vicinity of pollution point sources (eg. Tyler, 1975; Martin *et al.*, 1982; Zoltai, 1988) and from more remote areas such as the northeastern United States (Andresen *et al.*, 1980; Johnson *et al.*, 1982). Atmospheric deposition is an important source of heavy metals in forest soil organic horizons in many parts of the world.

Copper, Pb and Zn complex to varying degrees with organic matter in soils, with Cu and Pb being the most tightly held (Heinrichs and Mayer, 1980). Elevated concentrations of heavy metals in humic horizons have been shown to decrease organic matter decomposition rates (Ruhling and Tyler, 1973; Tyler, 1975), although toxicity of individual heavy metals is known to be influenced by soil acidity (Bergkvist *et al.*, 1989).

Long-term changes in the chemistry of soil profiles from the Alltcailleach Forest have been studied using stored soils. Chemical changes are characterized by decreases in pH (Billett *et al.*, 1988), base cations and cation exchange capacity, and increases in extractable Al and sulphate (Billett *et al.*, 1990a). Concentrations of organic C and N have decreased with time (Billett *et al.*, 1990b).

The use of stored soil samples in long-term studies effectively solves the problem of the reproduction of analytical methodology, which is important if realistic comparisons are to be made. Doubts have been expressed about the stability of soil samples during storage (Bartlett and James, 1980). Although the problems

Water, Air, and Soil Pollution **59**: 179–191, 1991.

of storage have been extensively discussed elsewhere (Billett *et al.* 1988, 1990a, b), the possibility of changes in soil chemistry during storage cannot be totally discounted. Where direct comparisons can be made between old and modern data, (eg. % N and loss-on-ignition), no significant changes occurred during storage (Billett *et al.*, 1990b). Although it has been shown that extractable amounts of Fe, Cu, Mn and Zn change during air-drying and storage of soils (Shuman, 1980), it is unlikely that the total heavy metal content of stored soils will change with time.

The purpose of this paper is to document changes in both the concentration and amount of Cu, Pb and Zn in the upper organic horizons of 15 forest soil profiles in the Alltcailleach Forest, N.E. Scotland between 1949/50 and 1987. Changes in the pools of each of the 3 elements are used to estimate long-term accumulation rates. Additional data from the sites are used to investigate the relationship of heavy metal concentration with soil pH, % C content and C/N ratio.

2. Field Sites

Forest soil organic horizons were collected from 15 sites in the Alltcailleach Forest, N.E. Scotland. The sites, originally sampled in 1949 and 1950 by one of the authors (E.A.F.), were never infilled so they could be precisely relocated.

The Alltcailleach Forest is situated in the upper Deeside valley and lies 55 km west of Aberdeen, the nearest major city. The sites are located in a remote upland area, approximately 120 km NNE of the Midland Valley, the most important industrial region in Scotland. Prevailing wind direction is from the west and south-west. The forest comprises a mixture of older plantations established in the 1880's and younger stands planted between 1938 and 1961, either directly from *Calluna* moorland or after the clearfelling of an earlier plantation. The sites are divided accordingly into Group 1 sites (19th century plantations) and Group 2 sites (20th century plantations). The most commmon species are Scots Pine (*Pinus sylvestris*), Sitka and Norway Spruce (*Picea sitchensis* and *Picea abies*), with less common European Larch (*Larix decidua*), Douglas Fir (*Pseudotsuga menziesii*) and Lodgepole Pine (*Pinus contorta*). The soils comprise both well-drained podzols and cambisols and poorly drained gleysols and histosols. These are developed on glacial, fluvio-glacial and alluvial drift deposits, which in turn overlie a variety of granitic, ultra-basic and metamorphic rocks. A detailed description of all the soil sites, including the history of forestry and changes in ground vegetation, is given in Billett *et al.* (1988).

The Alltcailleach Forest sites are situated between elevations of 200 and 350 m. The annual precipitation is 880 mm and the mean daily temperature in the region 6 °C (Meteorological Office, 1952).

3. Methodology

Forest soil organic horizons were sampled from the combined L, F and H (O) horizon of mineral soils and the Hl horizon of histosols. At each of the 15 sites a new 1 m-wide face was cut 75 cm from the original face sampled in 1949/50, and ca. 1 kg of soil collected from various points along the organic horizon to provide a single representative sample. All large roots were subsequently removed and the soils air-dried at room temperature. The original soils were treated in a similar way and stored in air-tight bags between 1949/50 and 1987. Dry bulk density measurements were made at each of the sites using a 5.6-cm diameter corer. Forest soil organic horizons were sampled in triplicate and the dry bulk density determined by dividing the mass of ovendry soil by the volume of field-moist soil.

Heavy metal concentrations were determined following the digestion of 200 mg of 1-mm sieved oven-dry organic material using a concentrated $H_2SO_4/HClO_4$ acid mixture (Cresser and Parsons, 1979). All digestions were duplicated and blank digestions performed at intervals throughout the experiment. Copper and Pb determinations were carried out using graphite furnace atomic absorption spectrometry, with di-ammonium hydrogen phosphate as a matrix modifier. Zinc was determined using flame atomic absorption spectrometry. Standards for Cu, Pb and Zn were prepared using Spectrosol solutions and analysed routinely with the samples. Results of Pb and Zn determinations on duplicate soil digests were in good agreement, with 95% of the samples showing variation about the mean of less than 15% for Pb and 7% for Zn. Duplicate Cu analyses were more variable with 70% of the samples exhibiting variation about the mean of less than 25%. The same acid digests were used for the determination of organic N by Hoskins distillation followed by titration with 0.2 M HCl. Organic C was measured by the 'wet oxidation' method of Tinsley (1950) using 0.0667 M sodium dichromate solution. Soil pH was determined using a soil:0.01 M $CaCl_2$ solution ratio of 1:4. All analyses were duplicated and details of the methodology and variability of duplicate analyses for C, N and soil pH are given in Billett *et al.* (1990b).

4. Results

4.1. Cu, Pb AND Zn CONCENTRATIONS

Table I lists the overall differences in Cu, Pb and Zn concentration between the older (Group 1) and younger (Group 2) soils and shows how concentrations have changed between 1949/50 and 1987.

4.1.1. *Differences Between Old and Young Plantations*

The average ratio of Cu:Pb:Zn in both groups of soils was 1:3.9:4.8. In the 1949/50 samples there was no significant difference between Cu concentrations of the Group 1 sites (mean 14 mg kg^{-1}) and the Group 2 sites (mean 12 mg kg^{-1}). In

TABLE I

Copper, Pb and Zn concentrations (mg kg^{-1}) of Group 1 and Group 2 soil organic horizons sampled in 1949/50 and 1987. The Mann-Whitney U-Test was used to show where significant differences occurred between the Group 1 and 2 soils

	Cu		Pb		Zn	
	1949/50	1987	1949/50	1987	1949/50	1987
Group 1 (19th century plantations)						
Mean	14	13	58	81	80	53
95% S.E.	2	2	12	16	8	8
Median	15	13	62	88	79	53
n=	6	6	6	6	6	6
Group 2 (20th century plantations)						
Mean	12	17	42	47	73	66
95% S.E.	6	2	14	12	10	22
Median	12	18	38	43	69	57
n=	7	9	7	9	7	9
U=	18.5	9.5[a]	17.5	5.5[a]	14	22

[a] $p<0.05$.

1987, however, there was a significant difference between Cu concentrations in the Group 1 (mean 13 mg kg^{-1}) and the Group 2 sites (mean 17 mg kg^{-1}). Mean Pb concentrations in 1949/50 were 58 mg kg^{-1} in the Group 1 sites and 42 mg kg^{-1} in the Group 2 sites. In 1987 mean Pb concentrations were 81 and 47 mg kg^{-1} in the Group 1 and 2 sites, respectively. Median values for the 2 Groups were only significantly different in 1987 ($U=5.5$, $p<0.05$, Mann-Whitney U-test).

Zinc concentrations in the soil organic horizons were higher than Pb concentrations, particularly when the soils were first sampled. In 1949/50 mean Zn concentrations were 80 and 73 mg kg^{-1} in the Group 1 and Group 2 sites respectively. Mean Zn concentrations in 1987 were different (53 and 66 mg kg^{-1}). None of the differences in Zn concentrations between the old and young plantations in either 1949/50 or 1987 were statistically significant.

4.1.2. *Changes Between* 1949/50 *and* 1987

Between 1949/50 and 1987 there were no statistically significant changes in the Cu concentration in the Group 1 and 2 sites. Mean Pb concentration increased from 58 to 81 mg kg^{-1} for the Group 1 sites and from 42 to 47 mg kg^{-1} for the Group 2 sites. These changes correspond to increases of 40 and 12%, respectively. Neither of these changes were statistically significant when the data were considered individually in Groups. However, if all the sites were considered collectively there was a significant increase in Pb concentration between 1949/50 and 1987 ($T=10.5$, $p<0.05$, Wilcoxen Signed Rank Test).

At most sites Zn concentrations decreased between 1949/50 and 1987. Group

TABLE II

A comparison of Cu, Pb and Zn concentrations (mg kg^{-1}) at sites with single species stands of Scots Pine and Spruce (Norway or Sitka). The Mann-Whitney U-Test was used to show where significant differences occurred

	Scots Pine (n=12)			Spruce (n=9)			
	Mean	95% S.E.	Median	Mean	95% S.E.	Median	U
Cu	10.4	1.48	13.0	19.2	1.14	20.0	7.5[b]
Pb	67.3	6.19	67.0	36.8	2.76	35.0	10.5[a]
Zn	60.5	5.78	57.5	82.1	10.97	79.0	32.5

[a] $p<0.01$.
[b] $p<0.001$.

1 sites showed a mean change from 80 to 53 mg kg^{-1} and Group 2 sites a mean change from 73 to 66 mg kg^{-1}, with only the changes in the Group 1 sites being statistically significant ($T=10$, $p<0.05$). These changes correspond to decreases of 34 and 10%, respectively. If all the data were considered collectively there was a significant decrease in Zn concentration between 1949/50 and 1987 ($T=10$, $p<0.05$).

The concentration data was also used to investigate broad species effects on heavy metal concentration in forest soil organic horizons. Single species stands with Scots Pine had statistically significantly lower Cu concentrations and higher Pb concentrations than sites on which Sitka or Norway Spruce had been grown (Table II). No significant difference existed in Zn concentration between the 2 types of stand.

4.2. TOTAL Cu, Pb AND Zn CONTENTS

Estimates of forest soil organic horizon heavy metal pools in both 1949/50 and 1987 were made using dry bulk density measurements determined in 1987. As the soils had a higher % C content in 1949/50 and therefore a lower bulk density, this may lead to an overestimate of element pools. Calculations suggest that heavy metal pools of soil organic horizons in 1949/50 could have been up to 13% lower than estimates made assuming no change in dry bulk density over the sampling period (Billett *et al.*, 1990b).

Measurements made of O and Hl horizon thickness when the soils were first sampled showed that there was an increase in depth at 13 out of 15 sites (Billett *et al.*, 1988, 1990b). The overall mean organic horizon thickness in 1949/50 was 4 cm compared to 9 cm in 1987, with the Group 1 plantations having much thicker organic horizons that the Group 2 plantations. Two of the Group 2 sites did not have an upper organic horizon in 1949/50.

Total Cu, Pb and Zn contents of the forest soil organic horizons are shown in Figures 1 and 2 for the Group 1 and Group 2 sites, respectively. The amounts of Cu, Pb and Zn stored in the upper organic horizons of the older (Group 1)

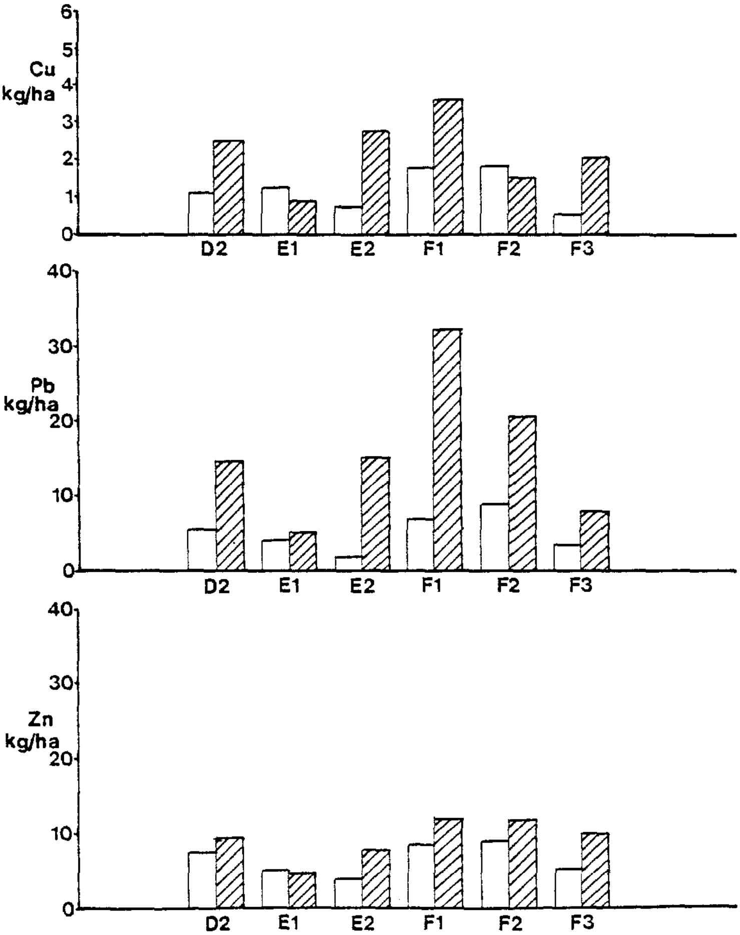

Fig. 1. Total Cu, Pb and Zn contents (kg ha^{-1}) of forest soil organic horizons at the Group 1 sites (horizontal axis). Opens bars represent the soils in 1949/50 and diagonal shaded bars the soils in 1987.

forest sites increased in most cases, with Pb showing the most consistent and largest increases between 1949/50 and 1987 (Figure 1). The mean Cu, Pb and Zn contents of the Group 1 sites increased by 83% (1.2 to 2.2 kg ha^{-1}), 212% (5.1 to 15.9 kg ha^{-1}) and 39% (6.7 to 9.3 kg ha^{-1}), respectively. At the Group 2 sites (Figure 2) the mean Cu, Pb and Zn contents increased by 140% (1.18 to 2.83 kg ha^{-1}), 72% (4.89 to 8.42 kg ha^{-1}) and 45% (8.14 to 11.8 kg ha^{-1}), respectively. When the soils were first sampled Cu and Pb contents of the 2 Groups of soils were broadly similar, with Zn contents of the younger sites being slightly higher. In 1987 both Cu and Zn contents were higher at the Group 2 sites.

Estimations of mean accumulation rates of Cu, Pb and Zn are subject to large standard errors principally because of large differences in organic horizon thickness at the individual sites. However, the results show some large differences between

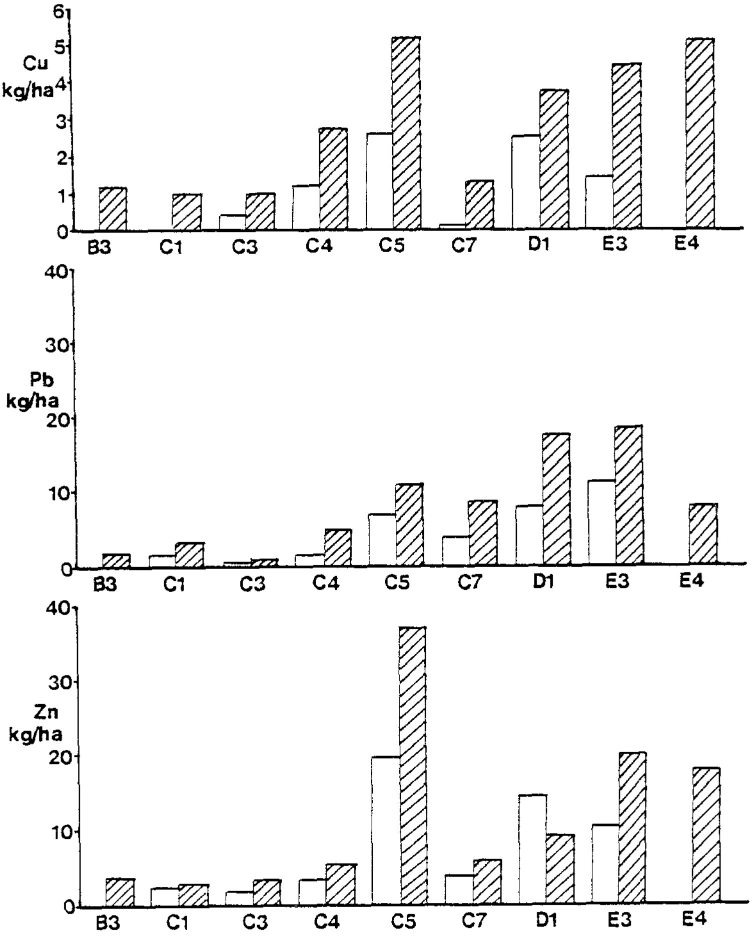

Fig. 2. Total Cu, Pb and Zn contents (kg ha^{-1}) of forest soil organic horizons at the Group 2 sites (horizontal axis). Open bars represent the soils in 1949/50 and diagonal shaded bars the soils in 1987.

old and young plantations and between different heavy metals. Mean accumulation rates for Cu and Zn for the Group 2 sites (50.1 and 144 g ha^{-1} yr^{-1}) were more than twice those for the Group 1 sites (22.4 and 68.2 g ha^{-1} yr^{-1}). In contrast the mean accumulation rate for Pb in the Group 1 sites was 282 g ha^{-1} yr^{-1}, compared to 121 g ha^{-1} yr^{-1} in the Group 2 sites. The overall accumulation rates for Cu, Pb and Zn were 39.1, 186 and 114 g ha^{-} yr^{-1}, so heavy metals were accumulating in the order Cu$<$Zn$<$Pb.

Figure 3 shows that the accumulation rates of organic matter (% C) and Pb were significantly related. If the 2 outlying points, with the extremely high and low C accumulation rates are excluded, the statistical relationship was much stronger (r_s = +0.75, p$<$0.01). Copper and Zn accumulation rates were not significantly correlated with organic matter accumulation rates (r_s=+0.37 and +0.50, respectively).

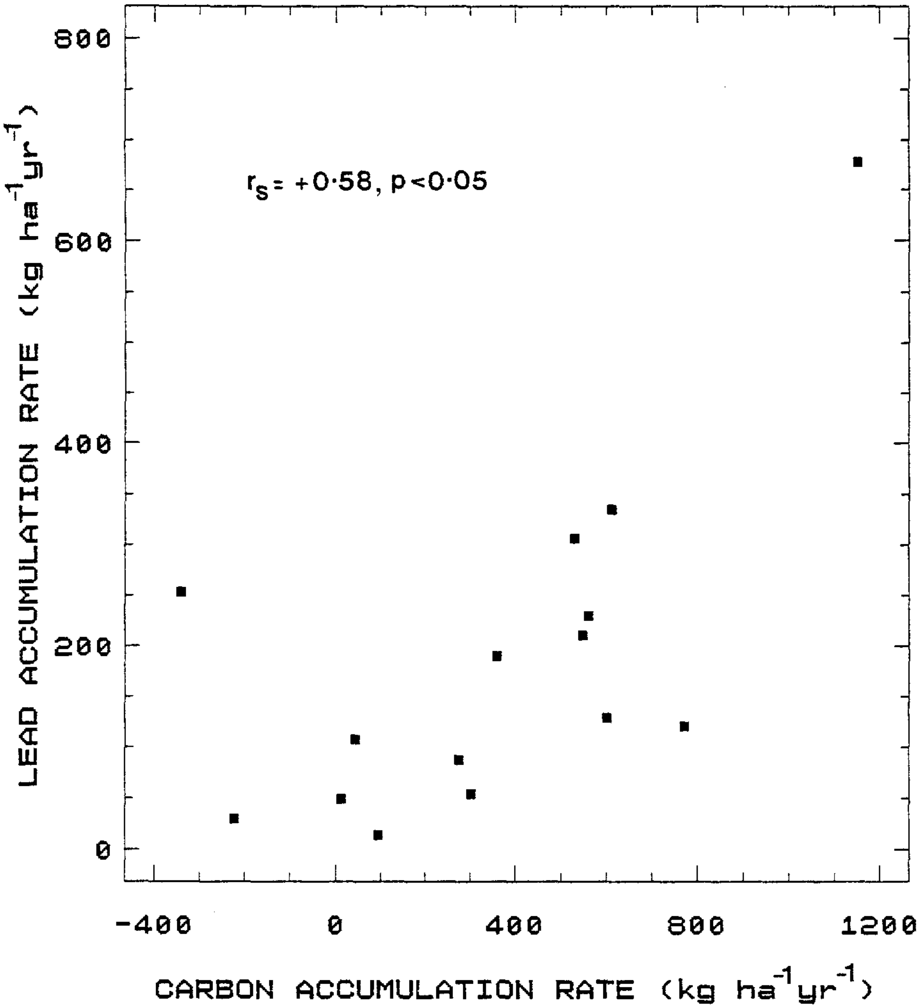

Fig. 3. The relationship between Pb accumulation rates (kg ha^{-1} yr^{-1}) and C accumulation rates (kg ha^{-1} yr^{-1}) in the 15 soil sites (r_s= Spearman Rank Correlation Coefficient).

4.3. RELATIONSHIPS WITH pH, % CARBON AND C/N RATIO

Figure 4 shows that a number of significant statistical relationships exist between Cu, Pb and Zn concentration and pH, % C and C/N ratio. Copper and Zn are directly correlated with pH and inversely correlated with C/N ratio, whereas Pb is directly related to % C and C/N ratio and inversely related to pH. In addition soil pH was related to % C (r_s= –0.55, $p<0.01$) and C/N ratio (r_s= –0.73, $p<0.001$). Individual heavy metals were less closely related to each other. Lead was negatively correlated with both Cu (r_s= –0.44, $p<0.05$) and Zn (r_s= –0.28), whereas Cu and Zn were not significantly correlated (r_s= 0.34).

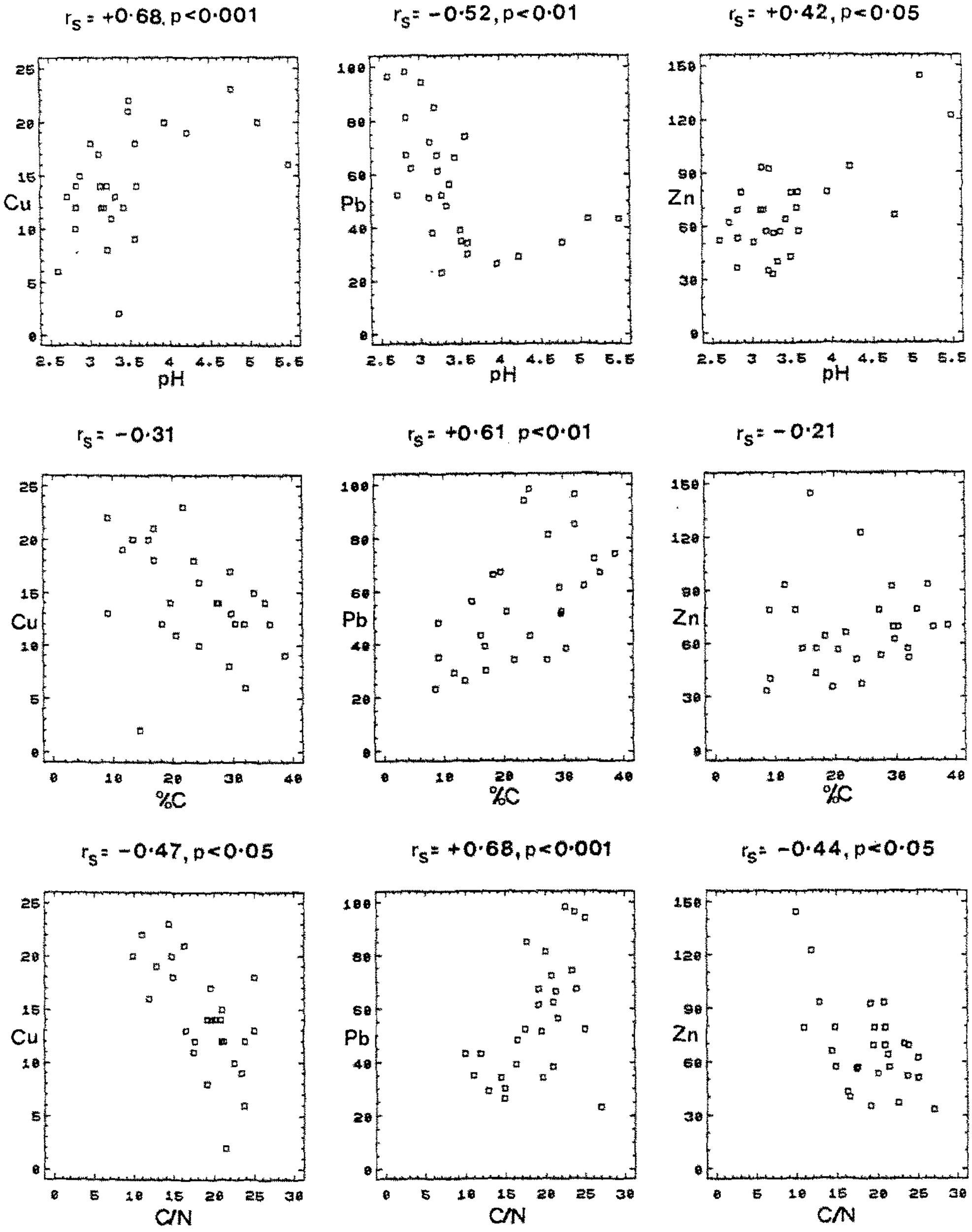

Fig. 4. The relationships between heavy metal concentration, soil pH, % C, and C/N ratio (r_s = Spearman Rank Correlation Coefficient).

5. Discussion

Mean Cu and Zn concentrations of soil organic horizons from the Alltcailleach Forest were similar to those from remote areas in the northeastern U.S. (Andresen *et al.*, 1980; Friedland *et al.*, 1984), whereas mean Pb concentrations were a half to a third lower. This may be a result of the lower Pb deposition rate in N.E. Scotland (Flower, 1987) compared to the northeastern U.S. (Groet, 1976).

Mean heavy metal amounts in the Alltcailleach Forest sites in 1987 were 2.59, 11.4 and 10.8 kg ha^{-1} for Cu, Pb and Zn and compare well with estimates from other remote sites (Gosz *et al.*, 1973; Andresen *et al.*, 1980; Smith and Siccama, 1981; Friedland *et al.*, 1984). Lead and Zn contents of the Alltcailleach Forest sites were also similar to those measured at a number of inland sites in S. Norway (Steinnes *et al.*, 1989).

Comparison of the older (Group 1) and the younger (Group 2) forest sites showed that when the soils were first sampled in 1949/50, there was no significant difference in heavy metal concentration. In 1987, however, the older forest sites had a significantly higher concentration of Pb than the younger forest sites. These results underline the importance of foliar interception of Pb in terms of its concentration in the soil. The Group 1 site plantations, with their continuous canopy cover between 1949/50 and 1987, would have had a much greater capacity to trap atmospheric Pb than the younger Group 2 plantations. An increase in Pb concentration in soil organic horizons with increasing stand age has also been reported by Johnson *et al.* (1982) and Jones *et al.* (1988).

Copper concentration was significantly higher in the Group 2 sites in 1987 compared to the Group 1 sites. This may reflect a greater dilution of Cu at the older forested sites, where organic matter accumulation rates were higher.

Long-term changes in heavy metal concentration over the period 1949/50 to 1987 were characterized by a statistically significant increase in Pb and a decrease in Zn concentration. Changes in the Group 1 sites were much larger than those at the Group 2 sites. None of the changes in Cu concentration between 1949/50 and 1987 were statistically significant.

Increases in Pb concentration with time in the Alltcailleach Forest sites were consistent if somewhat lower than results from a number of other studies (Siccama *et al.*, 1980; Johnson *et al.*, 1982; Friedland *et al.*, 1984). Long-term increases in Cu and Zn concentration were reported by Friedland *et al.* (1984), with increases in Cu being much lower than for Zn. Siccama *et al.* (1980), however, found that both Cu and Zn decreased in concentration in the forest floor over a 14-yr period and the authors ascribed the changes to a dilution effect due to organic matter accumulation with time. Although this may be part of the cause of the decrease in Zn concentration in the Scottish sites, it is well-known that Zn is mobilized and lost from acidified forest soils whereas Cu and Pb are retained (Andersson and Nilsson, 1974; Bergkvist *et al.*, 1989).

High concentrations of Pb occurred in the more acidic, highly organic, less decomposed soils. The solubility of heavy metals is known to be closely related to soil solution pH (Bergkvist, 1987a) and the concept of a critical soil solution pH has been discussed in this context (Bergkvist *et al.*, 1989). The concept can be applied to the Alltcailleach Forest soils which showed a large increase in Pb concentration at pH values less than 4. The importance of organic matter in complexing and retaining Pb is well known and Bergkvist (1987a, b) has shown that a close relationship exists between the vertical transport of Pb and organic matter in the soil profile. This explains the direct correlation between Pb and % C in soils from the Alltcailleach Forest which has also been observed in other studies (Coughtrey *et al.*, 1979; Andresen *et al.*, 1980).

The behavior of Zn in these soils is consistent with increased Zn mobility and availability for plant uptake at low soil pH (Bergkvist, 1986, 1987c; Andersson and Nilsson, 1974). Copper behaved in a similar way to Zn and in all cases the statistical relationship of Cu with pH and C/N ratio was stronger. These results were in apparent disagreement with a number of studies which suggest that Cu complexes strongly with organic matter (eg. Bergkvist *et al.*, 1989). However, if Cu is held strongly by organic matter it will not be available for uptake by plants and not be returned to the soil in litter. Soils which exhibit a large increase in O horizon thickness with time (in particular the Group 1 sites) will therefore not show an increase in Cu concentration, particularly if atmospheric deposition of Cu is low.

Significant differences occurred in Cu and Pb concentration between single species stands of Scots Pine and Norway and Sitka Spruce. Although these differences could be attributed to a direct species effect, the relationships need to be treated with caution, because other factors may be influencing these data.

Copper, Pb and Zn were accumulating in the forest floor in the Alltcailleach Forest largely because of an increase in organic matter thickness since 1949/50. Heavy metals contents were increasing in the order $Cu < Zn < Pb$. The mean Cu accumulation rate was 39.1 g ha^{-1} yr^{-1} and this compared with mean estimates of between 21.4 and 65.2 g ha^{-1} yr^{-1} for different forest types in the northeastern U.S. (Friedland *et al.*, 1984). Lead was accumulating in the Alltcailleach Forest at a rate of 186 g ha^{-1} yr^{-1} and this compared to estimates of 350 g ha^{-1} yr^{-1} for a polluted site in N.W. England (Jones *et al.*, 1988) and 175 to 599 g ha^{-1} yr^{-1} for sites in the northeastern U.S. (Friedland *et al.*, 1984).

The mean accumulation rate for Zn of 113.5 g ha^{-1} yr^{-1} was much lower than other published rates of Zn accumulation in forest soils (Jones *et al.*, 1988; Friedland *et al.*, 1984).

Heavy metal deposition rates measured between 1972–75 at a number of rural sites in the U.K. ranged from 98 to 480, 160 to 450 and 490 to 1200 g ha^{-1} yr^{-1} for Cu, Pb and Zn, respectively (Cawse, 1980). A Pb deposition rate of 125 g ha^{-1} yr^{-1} was measured in 1985 at a heathland site ca. 12 km W of the Alltcailleach Forest (Flower, 1987). This value is similar to the Pb accumulation rate estimated for the younger (Group 2) plantations but significantly lower than that for the older (Group 1) forest sites. Overall mean accumulation rates for Cu and Zn in the Alltcailleach Forest were significantly lower than atmospheric deposition rates recorded at U.K. rural sites.

6. Conclusions

Statistically significant differences in heavy metal concentration between the older (Group 1) sites and the younger (Group 2) sites were confined to Cu and Pb in 1987. There were no statistically significant changes in Cu concentration between 1949/50 and 1987, whereas Pb exhibited a significant increase and Zn a significant decrease in concentration.

The results showed that the low pH (2.8 to 3.5) soil organic horizons with high % C and high C/N ratios contained higher concentrations of Pb and lower concentrations of Cu and Zn than the higher pH (>3.5) soils. The factors controlling the behavior of Cu and Zn appeared therefore to be different from Pb.

Long-term studies of forest soil organic horizons from N.E. Scotland demonstrate that although Cu, Pb and Zn concentrations showed increases and decreases with time, all 3 heavy metals are accumulating because of an increase in forest floor thickness.

Both our results and those of other workers confirm the importance of soil acidification in directly or indirectly influencing heavy metal concentrations in acid forest soils. Long-term acidification, associated with increases in organic matter thickness is likely to lead to Pb accumulation. Although current Pb concentrations have not reached levels thought to cause a decline in soil organic matter decomposition rates (Ruhling and Tyler, 1984), increases in Pb concentration at the rates measured between 1949/50 and 1987 may lead to deleterious effects on organic matter decomposition in 70 to 80 yr time. Recently, however, significant reductions in Pb concentrations in the atmosphere have been recorded in the U.K. (Page *et al.*, 1988) and it is likely that these reductions will be reflected in decreases in Pb accumulation rates in U.K. soils.

Acknowledgments

The authors would like to thank the Balmoral Estate for granting permission to work in the area and the Department of the Environment and the Natural Environment Research Council for providing financial support. We also acknowledge A. Kindness and B. Sharpe for their help with the determination of heavy metals.

References

Andersson, A. and Nilsson, K. O.: 1974, *Ambio* **3**, 198.
Andresen, A. M., Johnson, A. H., and Siccama. T. G.: 1980, *J. Environ. Qual.* **9**, 292.
Bartlett, R. and James, B.: 1980, *Soil Sci. Soc. Am. J.* **44**, 721.
Bergkvist, B.: 1986, *Water, Air, and Soil Pollut.* **31**, 901.
Bergkvist, B.: 1987a, *Forest Ecol. and Manage.* **22**, 29.
Bergkvist, B.: 1987b, 'Leaching of Metals in the Upper C Horizons of Spruce and Beech Forest Soils', in S. E. Lindberg and T. C. Hutchinson (eds.), *International Conference, Heavy Metals in the Environment*. New Orleans, September 1987, CEP Consultants Ltd., Edinburgh, Vol. 2, pp. 479–481.

Bergkvist, B.: 1987c, *Water, Air, and Soil Pollut.* **33**, 131.
Bergkvist, B. Folkeson, L., and Berggren, D.: 1989, *Water, Air, and Soil Pollut.* **47**, 217.
Billett, M. F., FitzPatrick, E. A. F., and Cresser, M. S.: 1988, *Soil Use and Manage.* **4**, 102.
Billett, M. F., Parker-Jerris, F., FitzPatrick, E. A. F., and Cresser, M. S.: 1990a, *J. Soil Sci.* **41**, 133.
Billett, M. F., FitzPatrick, E. A. F., and Cresser, M. S.: 1990b, *Environ. Pollut.* **66**, 67.
Cawse, P. A.: 1980, 'Deposition of trace elements from the atmosphere in the UK'. in Inorganic Pollution and Agriculture. *Her Majesty's Stationary Office*, London, pp. 22–46.
Coughtrey, P. J., Jones, C. H., Martin, M. H., and Shales, S. W.: 1979, *Oecologia* **39**, 51.
Cresser, M. S. and Parsons, J. W.: 1979, *Anal. Chim. Acta* **109**, 431.
Flower, C. A.: 1987, 'Atmospheric Inputs of Nutrients and Pollutants to Uplands in North-East Scotland', Unpublished Ph.D. Thesis, University of Aberdeen.
Friedland, A. J., Johnson, A. H., and Siccama, T. G.: 1984, *Water, Air, and Soil Pollut.* **21**, 161.
Gosz, J. R., Likens, G. E., and Bormann, F. H.: 1973, *Ecol. Monogr.* **43**, 173.
Groet, S. S.: 1976, *Oikos* **27**, 445.
Heinrichs, H. and Mayer, R.: 1980, *J. Environ. Qual,* **9**, 111.
Johnson, A. H., Siccama, T. G., and Friedland, A. J.: 1982, *J. Environ. Qual.* **11**, 577.
Jones, K. C., Watts, S. A., Hanson, A. F., and Dighton, V.: 1988, *Environ. Pollut.* **51**, 31.
Martin, M. H., Duncan, E. M., and Coughtrey, P. J.: 1982, *Environ. Pollut.* **B3**, 147.
Meteorological Office.: 1952, 'Climatological Atlas of Britain', *Her Majesty's Stationary Office*, London.
Page, R. A., Cawse, P. A., and Baker, S. T.: 1988, *Sci. Total Environ.* **68**, 71.
Ruhling, A. and Tyler, G.: 1973, *Oikos* **24**, 402.
Ruhling, A. and Tyler, G.: 1984, *Water, Air, and Soil Pollut.* **22**, 173.
Shuman, L. M.: 1980, *Soil Sci.* **130**, 336.
Siccama, T. G., Smith, W. H., and Mader, D. L.: 1980, *Environ. Sci. Technol.* **14**, 54.
Smith, W. H. and Siccama, T. G.: 1981, *J. Environ. Qual.* **10**, 323.
Steinnes, E., Solberg, W., Petersen, H. M., and Wren, C. D.: 1989, *Water, Air, and Soil Pollut.* **45**, 207.
Tinsley, J.: 1950, *Transactions of the 4th International Meeting of the Society of Soil Science* **1**, 161.
Tyler, G.: 1975, *Nature* **255**, 701.
Zoltai, S. C.: 1988, *Water, Air, and Soil Pollut.* **37**, 217.