

# Ombrotrophic peat as a medium for historical monitoring of heavy metal pollution

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## Abstract

Knowledge of historical trends in heavy metal deposition can aid the study and impact prediction of contemporary pollution. For this purpose, analysis of ombrotrophic peat cores has proved a valuable complement to other sedimentary analyses. However, doubts still remain concerning the mobility of heavy metals in peat. The debate cannot be resolved until the behaviour of these elements in peat is better understood.

Peat cores were collected from hollows and hummocks on Ringinglow Bog in the southern Pennines. The cores were sliced into contiguous 1-cm slices. Samples were analysed for total concentrations of major elements (Al, Ca, K, Mg, Na) and trace metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) using atomic absorption spectrophotometry. Multivariate statistical analysis was conducted on the data.

Preliminary results indicate relatively high concentrations of Cd, Cu, Fe, Pb and Zn reflecting the influence of industrial activities in Sheffield and Manchester. As aluminium, cadmium, copper, lead and zinc exhibit similar profiles they may be suitable surrogates for monitoring historical pollution. However, other elements (*e.g.* Fe, K, Mn, Na) are clearly influenced by bog hydrology or plant translocation and would be inappropriate monitors.

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## Introduction

Knowledge and understanding of historical trends in pollutant deposition can provide a useful analogue for the prediction of impacts of contemporary pollution. Ombrotrophic peat profiles have been analysed for this purpose for some time (Lee and Tallis, 1973; Livett *et al.*, 1979; Coleman, 1985; Jones, 1985). Ombrotrophic peat is the most appropriate medium as the receptor surface is discrete from any groundwater influences. Hence, the only input of water and elements is via wet and dry deposition processes from the atmosphere. Large areas of raised and blanket mires are found in the British Isles and present a continuous stratigraphic record of atmospheric deposition. Consequently, such peats provide the potential to study the record of deposition of heavy metals since Roman times (Livett, 1988).

Several assumptions underpin the use of ombrotrophic peat as a monitor of atmospheric deposition of heavy metals (Livett, 1988). Firstly, that the heavy metals enter the peat system from atmospheric sources only; the use of deep, ombrotrophic peat cores supports this assumption. Secondly, that the peat sampled has chronological integrity; this cannot always be guaranteed as peat digging or other activities may have caused a hiatus

in the peat record. Thirdly, that the elements are not redistributed or remobilised following deposition; this is by far the most contentious of the assumptions. In early attempts to exploit the historical monitoring approach, the apparent 'fixation' of metal elements by peat was accepted on rather tenuous evidence. A further consideration of the approach is the requirement (ideally) to date the core: this would permit the determination of metal deposition fluxes. However, this is only of value if remobilisation of elements is shown not to occur.

Heavy metal behaviour in ombrotrophic peat has been studied at a variety of scales from fine resolution (Livett *et al.*, 1979; Jones, 1985; Norton and Kahl, 1987) to the composite Canadian *Sphagnum* profile reported by Shotyk *et al.* (1992). Despite this, many uncertainties remain with respect to heavy metal behaviour in peat. Livett (1988) contends that there are fewer problems of interpretation for peat cores as geochemical monitors than aquatic sediments.

The authors of this study believe that many issues concerning the response of heavy metals to the varying conditions in a bog remain unresolved. Although circumstantial evidence indicates that copper, lead and zinc may retain their deposition records in peat, until such heavy metal records have been evaluated critically, their use as monitors of atmospheric deposition must be questioned.

The aim of this paper is to assess the reliability of heavy metal records in ombrotrophic peat as a

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precursor to the reconstruction of historical trends in heavy metal pollution. There is extensive blanket peat cover in the Pennines. Such peats will have acted as receptors for the deposition of pollutants generated by major industrial areas including Manchester and Sheffield plus metalliferous mining areas within the Peak District. Therefore, such sites are ideal for the investigation of the heavy metal content of peats.

### Site Details

Ringinglow Bog (53° 21'N, 1° 36'W; grid ref. SK 270834) is an area of ombrotrophic blanket peat in the southern Pennines at an altitude of 400 m, 10 km south-west of Sheffield. Peat cover is thick (4–6 m) over large areas of the bog. Most of the peat body comprises *Sphagnum* peat. However, in parts of the bog there is a sharp transition between upper layers of *Eriophorum* (cotton grass) peat and lower, unhumified *Sphagnum* remains. This vegetation change may reflect the impact of an increase in atmospheric pollutants as *Sphagnum* has been shown to be susceptible to increased levels of SO<sub>2</sub> (Ferguson *et al.*, 1978).

Sheffield and the surrounding district has a long history of industrial development. The activities for which the area is most noted are lead mining and smelting, coal mining, iron smelting and steel manufacture. In addition, the expansion of both Sheffield and Manchester is linked intimately with phases of industrial development (Jones, 1985).

### Methodology

Two peat cores (50 cm in length) from a hummock and adjacent hollow, were collected from Ringinglow Bog. This was to allow comparison of the heavy metal content of peat from two contrasting micro-environments. Plastic drainpipe core tubes were used to prevent the contamination that metal corers might cause. Clymo (1988) found that friction between the corer wall and peat tends to cause compression or expansion. The area/perimeter quotient of a corer ( $= \text{diameter}/4$ ) should be large enough to prevent strong compression. His experiment showed that quotient values of 3 cm (diameter = 12 cm) or more are satisfactory. Consequently, peat cores with an internal diameter of 16 cm were chosen for this investigation. This gave the additional advantage of providing samples large enough for multi-purpose analysis.

On return to the laboratory, cores were extruded and their stratigraphy noted. Both cores were predominantly *Eriophorum-Sphagnum* peat with the upper 4 cm of the hollow core comprising fresh *Sphagnum moss*. The cores were then sliced into contiguous 1-cm slices and dried to constant weight in an oven at 100°C. In view of the risk of contamination when removing the cores from the bog, basal samples were discarded. Thus, 48 samples were obtained from the hollow core and 46

samples from the hummock core. Dry peat was then homogenised in a mortar-and-pestle. For each sample, 5 g of peat was placed in a porcelain crucible and ashed in a muffle furnace at 600°C overnight. 10 ml hydrofluoric acid was added to 0.2 g ash in a centrifuge tube and evaporated to dryness at 96°C. 4 ml 4M hydrochloric acid and 2 ml 69% nitric acid were added, and the tube was then heated for half an hour to dissolve the residual material. The residual solution was transferred to 10-ml volumetric flasks for each of the 94 samples for analysis of major elements (Al, Ca, K, Mg, Na) and trace elements (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) using a Pye-Unicam SP90 atomic absorption spectrophotometer.

### Statistical Analysis

Several processes may influence element behaviour after deposition. Most important of these include metal complexation by organic matter; adsorption; diffusion; capillarity; evaporation; plant uptake; co-precipitation; and dissolution. Therefore, the concentration of an element in peat will reflect its sources; original speciation; chemical behaviour; relationship with other elements; and response to physical, chemical and biological processes operating within the bog. Consequently, given such complexity, it is dangerous to make inferences on the basis of elements studied in isolation. Possible options to evaluate metal behaviour in peat systems are either to perform sequential extraction procedures (Jones, 1987) and/or to apply appropriate multivariate statistical techniques which will discriminate dominant sources of variation (Hamalainen and Albano, 1992).

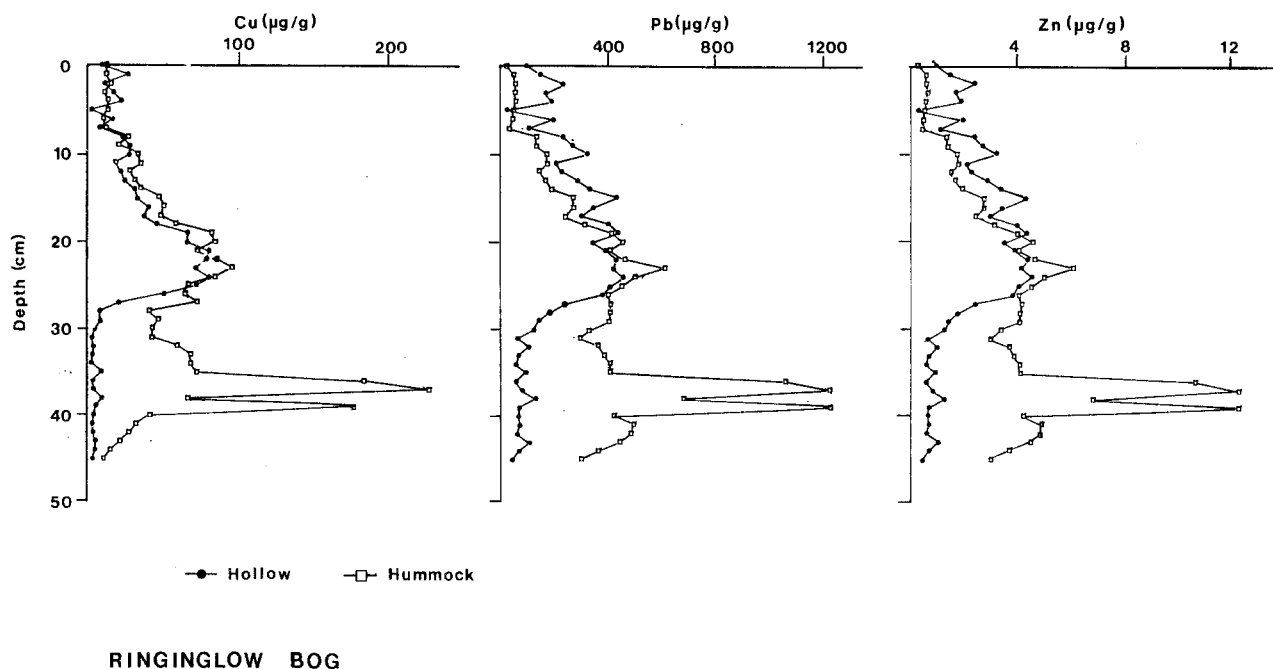
The data obtained in this study comprise approximately 3,500 individual results, *i.e.* triplicate analyses of each centimetre slice for each element studied. In order to elucidate metal behaviour data should not be considered in isolation; potential inter-relationships must be accounted for. The application of simple univariate statistics to complex material with numerous variables is inevitably limited and there is a danger that false correlations may arise (Bohlin *et al.*, 1989). Hence, it is more appropriate to apply multivariate statistical techniques in such studies (Joreskog *et al.*, 1976).

A matrix of multivariate data may comprise tens to hundreds of 'objects', each characterised by a moderate to large number of 'variables'. In the present case, the 'objects' are the samples from the peat cores while the 'variables' are the element analyses.

The multivariate methods used in this study are ordination methods where samples are represented as points in a two- or few-dimensional space. Similar samples will be located together in that space while dissimilar samples will be located apart. The extraction method chosen was principal components analysis (PCA). PCA is an efficient way to display dominant sources of variation in

**Table 1** Summary of total metal concentration data ( $\mu\text{g g}^{-1}$ ) in hollow and hummock peat cores, Ringinglow Bog, southern Pennines.

	Hollow		Min	Max	Hummock		Min	Max
	Mean	SD			Mean	SD		
Ash (%)	4.06	2.03	1.40	9.40	6.36	3.10	1.70	17.9
Cu	24.2	24.7	2.30	82.2	54.8	45.4	12.7	228
Pb	204	139	27.6	457	358	274	33.7	1,230
Zn	118	124	0.0	480	56.2	28.5	0.0	175
Cd	3.20	3.79	0.0	12.8	2.09	1.82	0.20	8.20
Ni	7.89	5.28	1.00	18.6	10.9	5.10	4.30	23.4
Cr	10.6	9.06	0.30	33.5	15.9	10.8	4.10	38.7
Fe	4,230	6,530	900	30,200	3,560	3,760	697	16,000
Mn	12.9	4.44	2.70	23.4	25.4	14.7	9.00	63.0
Na	287	109	81.5	623	377	170	41.2	1,140
K	394	455	8.80	2,070	918	379	281	2,150
Al	1,890	1,510	163	7,150	4,040	2,610	0.0	14,600
Ca	300	211	23.5	730	80.8	61.8	0.0	270
Mg	482	307	70.0	113	246	110	126	644

**Figure 1** Distribution of total copper, lead and zinc concentrations in hummock and hollow peat, Ringinglow Bog, southern Pennines.

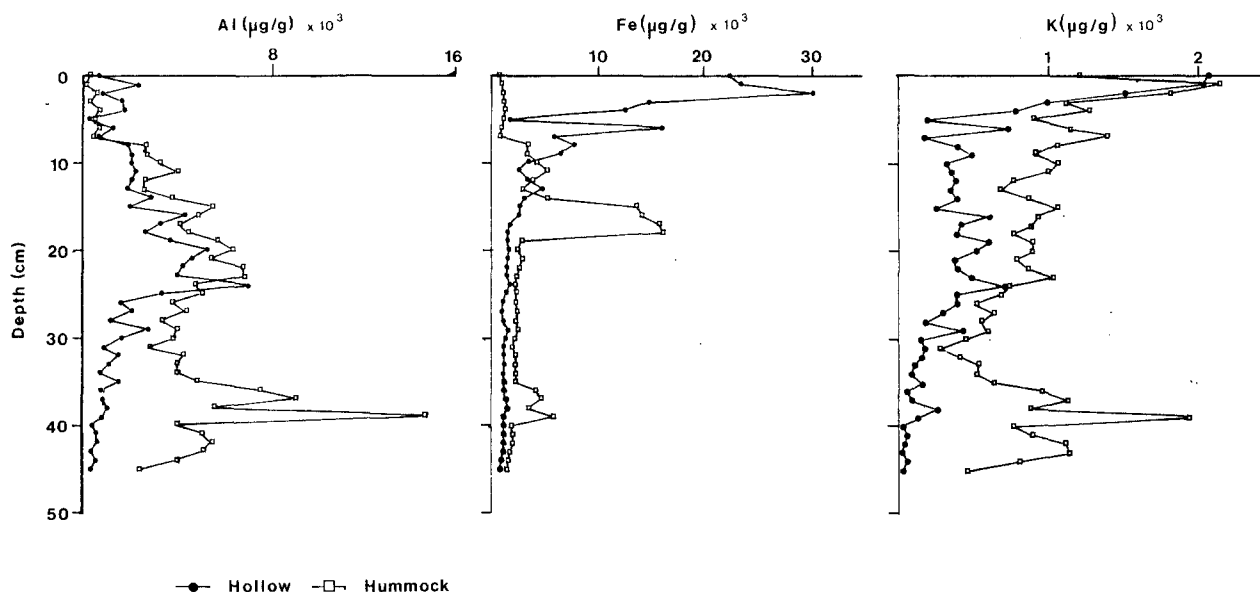
multivariate data. In principal components analysis, the key step is to delineate the number of principal components (or eigen vectors) which account for the greatest variance in the data. The varimax method was chosen as the rotation algorithm which attempts to minimise the number of variables that have high loadings on a factor. This should enhance the interpretability of the factors. Oblique rotation was then conducted.

Pearson's product moment correlation coefficients were also determined for both hollow and hummock data.

## Results

In this paper, summary results are presented for 13 elements but detailed discussion will be confined to aluminium, copper, iron, lead, potassium and zinc.

The concentrations of heavy metals in peat from Ringinglow Bog are high, reflecting long-term exposure to industrial pollution (Table 1). In both hummock and hollow peats, mean core concentrations follow the sequence  $\text{Fe} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Mn} > \text{Cr} > \text{Ni} > \text{Cd}$ . However, micro-environmental differences are apparent. For example, 9 of the 13 metals analysed record higher



## RINGINGLOW BOG

**Figure 2** Distribution of total aluminium, iron and potassium concentrations in hummock and hollow peat, Ringinglow Bog, southern Pennines.

concentration maxima in hummock peat.

Profiles of total metal concentration with depth through hummock and hollow peat cores are shown for Cu, Pb and Zn in Figure 1 and for Al, Fe and K in Figure 2. Aluminium, copper, lead and zinc exhibit considerable consistency. These four elements present virtually identical distributions through the peat. In the hollow, highest concentrations are recorded at 16–24 cm depth and, in most cases, subsidiary maxima are also attained at 21–24 cm depth. In every case, peat below 30 cm records low concentrations of these metals. In the hummock, profiles are distinguishable by the presence of two zones of high concentrations: a minor peak at 19–24 cm and a 'spike' of much higher concentration at 35–40 cm. At the time of sampling, the water level in the hummock was at approximately 22 cm. Therefore, the upper zone of high concentration may reflect the interface between saturated and unsaturated peat.

Iron accumulates at the surface of the hollow peat. In the hummock, iron distribution parallels that of the other four elements with two zones of accumulation. However, in this instance, the upper zone (at 15–18 cm) features the larger concentration 'spike'. The peak at 35–40 cm is clearly distinguishable but the values attained are only 30% of those of the upper zone.

Potassium presents a markedly different distribution. The element accumulates at the surface in both micro-environments. However, the lower 'spike' that is a feature of the other metal profiles in the hummock is also present in the potassium profile. In this case, it is spread over a greater depth, *i.e.* 35–44 cm.

Pearson's correlation coefficients for elements in the hollow and hummock peat are presented in

Tables 2 and 3, respectively. The following trends are evident: metals which show similarities between both hummock and hollow peat; and metals which demonstrate different relationships between the two micro-environments.

Metals showing simple statistical similarities in both hummock and hollow peat include:

- (1) strong correlation of copper with Cd, Pb and Zn;
- (2) strong correlation of Cu, Ni, Pb and Zn with Al;
- (3) good correlation of Ni with Zn;
- (4) strong correlation of Cr with Ni.

In contrast, some metals show statistical differences between the two micro-topographies:

- (1) sodium shows a high correlation with K in the hollow peat only;
- (2) calcium is correlated with Mg in the hollow peat only;
- (3) iron is correlated with K and Na in the hollow peat only;
- (4) manganese is correlated with K and Mg in the hummock peat only.

From the factor analysis, the eigen values, percentage contribution by each eigen value and accumulated percentages of total contributed by each eigen value of hollow and hummock peats are presented in Table 4. Three factors have been extracted for both hummock and hollow peats. Together these factors account for 86% of the variation in both micro-environments. Plots of factor loadings for the hummock and hollow peats are presented in Figure 3. From these results the elements can be divided into three groups:

- (1) aluminium group (factor 1) which contains Al, Cd, Cu, Ni, Pb and Zn in the hollow peat; and Al, Cd, Cu, Na, Pb, Zn and ash content in the hummock peat;
- (2) iron group (factor 2) which contains Fe, K, Mn

**Table 2** Pearson's correlation coefficients for total metal concentration in hollow peat, Ringinglow Bog, southern Pennines.

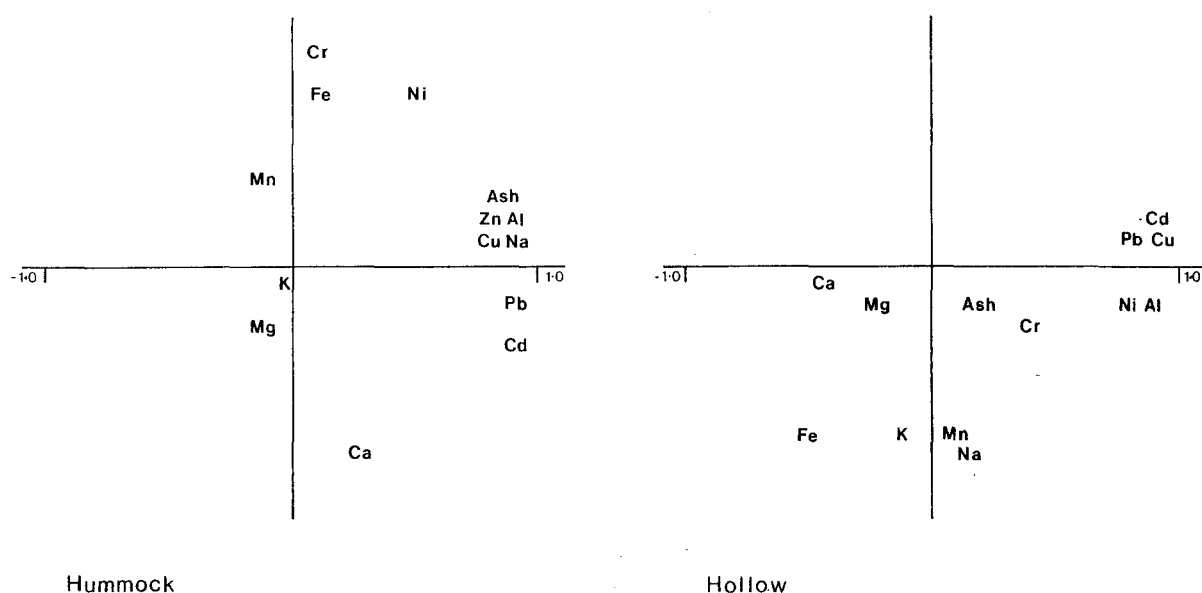
	Ash													
	Depth	Content	Cu	Pb	Zn	Cd	Ni	Cr	Fe	Mn	Na	K	Al	Ca
Depth	1.00													
Ash	-0.76	1.00												
Cu	-0.30	0.58	1.00											
Pb	-0.43	0.69	0.91	1.00										
Zn	-0.29	0.44	0.90	0.76	1.00									
Cd	-0.25	0.50	0.86	0.88	0.76	1.00								
Ni	-0.55	0.68	0.87	0.89	0.79	0.86	1.00							
Cr	-0.74	0.78	0.64	0.77	0.53	0.70	0.86	1.00						
Fe	-0.66	0.43	-0.09	-0.02	0.01	-0.21	0.09	0.32	1.00					
Mn	-0.50	0.25	0.11	0.22	0.20	0.07	0.43	0.50	0.45	1.00				
Na	-0.52	0.58	0.41	0.39	0.48	0.27	0.54	0.51	0.68	0.54	1.00			
K	-0.70	0.64	0.23	0.23	0.31	0.10	0.39	0.51	0.88	0.49	0.88	1.00		
Al	-0.31	0.51	0.89	0.82	0.82	0.84	0.91	0.67	-0.10	0.26	0.49	0.24	1.00	
Ca	0.74	-0.79	-0.72	-0.72	-0.65	-0.64	-0.78	-0.76	-0.31	-0.21	-0.46	-0.53	-0.69	1.00
Mg	0.77	-0.77	-0.55	-0.65	-0.45	-0.48	-0.65	-0.64	-0.30	-0.22	-0.34	-0.44	-0.52	0.87

**Table 3** Pearson's correlation coefficients for total metal concentration in hummock peat, Ringinglow Bog, southern Pennines.

	Ash													
	Depth	Content	Cu	Pb	Zn	Cd	Ni	Cr	Fe	Mn	Na	K	Al	Ca
Depth	1.00													
Ash	0.60	1.00												
Cu	0.41	0.73	1.00											
Pb	0.70	0.84	0.91	1.00										
Zn	0.43	0.80	0.71	0.74	1.00									
Cd	0.69	0.70	0.81	0.92	0.71	1.00								
Ni	-0.05	0.69	0.58	0.45	0.70	0.28	1.00							
Cr	-0.26	0.46	0.29	0.11	0.34	-0.08	0.86	1.00						
Fe	-0.08	0.47	0.16	0.08	0.37	-0.04	0.65	0.72	1.00					
Mn	-0.58	0.01	0.01	-0.16	0.15	-0.24	0.46	0.39	0.39	1.00				
Na	0.56	0.90	0.81	0.90	0.88	0.78	0.63	0.29	0.21	-0.02	1.00			
K	-0.41	0.04	0.01	-0.01	-0.01	0.79	0.17	0.08	-0.01	0.37	0.11	1.00		
Al	0.59	0.93	0.82	0.90	0.82	0.51	0.66	0.41	0.30	-0.05	0.94	0.01	1.00	
Ca	0.30	0.03	0.26	0.37	0.20	-0.09	-0.33	-0.62	-0.35	-0.07	0.18	0.11	0.06	1.00
Mg	-0.46	-0.17	-0.05	-0.13	0.01	-0.48	-0.01	-0.12	-0.12	0.74	-0.05	0.75	-0.15	0.34

**Table 4** The eigen values, percentages of total contributed by each eigen value and accumulated percentages of total contributed by each eigen value of hollow and hummock peats.

	Eigen value	Percent variation	Accumulated percentage
<i>Hollow peat:</i>			
Factor 1	8.727	58.2	58.2
Factor 2	3.065	20.4	78.6
Factor 3	1.159	7.7	86.3
<i>Hummock peat:</i>			
Factor 1	7.042	46.9	46.9
Factor 2	3.501	23.3	70.3
Factor 3	2.458	16.4	86.7



**Figure 3** Plot of loading factors for heavy metals in hummock and hollow cores, Ringinglow Bog, southern Pennines.

and Na in the hollow peat; and Ca, Cr, Fe and Ni in the hummock peat;

(3) magnesium group (factor 3) which contains Ca, Cr, Mg and ash content in the hollow peat; and K, Mg and Mn in the hummock peat.

### Discussion

The elements analysed in this study were derived from various sources. Lithospheric material mobilised by deflationary processes will provide one component of the input to the bog surface. However, the relatively high concentrations of metals in Ringinglow Bog indicate additional anthropogenic sources. Such sources at Ringinglow Bog will include early metalliferous mining and smelting activity in Derbyshire, domestic and industrial fossil fuel combustion processes, *e.g.* automobiles, iron smelters, steel blast furnaces and electricity generation in Manchester and Sheffield. Numerous studies have identified these activities as sources of Cd, Cr, Cu, Ni, Pb and Zn (Davison *et al.*, 1974; Beavington, 1977; Van Craen *et al.*, 1983). Metals from a common source may present similar deposition profiles in ombrotrophic peat cores. However, such internal consistency could also imply similar responses by the elements to the processes operating in the bog environment.

In this investigation aluminium, copper, lead and zinc have similar concentration profiles and also correlate significantly. In addition, factor analysis places them in the same group. These results are consistent with data from other peatlands in the English Midlands and Scotland (Jones, 1985). Similar results have been reported by investigators in the USA (Schell *et al.*, 1989; Cole *et al.*, 1990; Norton, 1990) and Canada (Shotyk *et al.*, 1990). Most of these authors attribute the relative enrichment of surface peats in these metals to inputs from anthropogenic sources. However, recent

studies have cast doubt on such conclusions and have evaluated element diagenesis in peat. Thus, Urban *et al.* (1990) suggest that hummock-hollow differences result from post-depositional mobility. They propose a mechanism whereby elevated concentrations of dissolved organic carbon facilitate the leaching of lead from peat hollows. However, in their study, lead concentration reached subsurface maxima at the level of the water table. Evidence from Ringinglow Bog is less conclusive. The water level in the hollows at time of sampling was close to the surface but the subsurface maximum in the hollow is attained at 18–25 cm depth. In the hummock, subsurface maxima do occur at the water level.

It follows that if a hypothesis of post-depositional diagenesis is invoked for lead, then such mechanisms must also apply to the aluminium, copper and zinc records. Corroborative evidence is scant, but Shotyk *et al.* (1992) state that aqueous species of Zn and Pb are likely to predominate over solid phases in the acid bog environment under both strongly oxidising and strongly reducing conditions. In this context, preliminary data from sequential extraction of Ringinglow Bog peat (Jones, 1987) are interesting. Approximately 50% of the total lead and zinc is associated with the more labile fractions: the proportions are even higher in hollow peat. In contrast, copper shows a strong affinity for the 'organic' and 'residual' fractions in both micro-environments; this is particularly marked in the hollow.

Aluminium behaviour in peat is more problematic. Aluminium profiles from this and other studies frequently show similar trends to those for Cd, Cu, Pb and Zn. However, evidence from Scottish peat cores (Jones, 1985) is less conclusive. Aluminium in the atmospheric aerosol will derive from both natural and anthropogenic sources. Where

natural sources dominate (e.g. in the less polluted atmosphere of Scotland), the peat record for aluminium differs from those of other metals. Conversely, in polluted areas, the deposition record is similar to these metals. Thus, the more heterogeneous the aerosol, the more complicated the deposition record for aluminium. Norton (1990) claims that, in acidic peats, aluminium will have an affinity for complexation with dissolved humic substances. Similar evidence for British peats is lacking.

Potassium and manganese profiles in Ringinglow peat are virtually identical with maximum concentration at the peat surface and rapid, progressive depletion with depth. Although manganese (like iron) is likely to be responsive to changes in redox, it is also a plant micro-nutrient. Thus, the surface enrichment of both manganese and potassium may result from plant uptake. Other subsurface features of the profile may reflect changing pH and redox.

The subsidiary peaks in concentration recorded for all metals at 35–40 cm depth in the hummock core are most interesting. Similar peaks have been recorded for both copper and lead in other hummock cores from Ringinglow Bog (Jones, 1985) but, in those cases, zinc and iron did not display such enrichment. A chronology based on pollen analysis and  $^{210}\text{Pb}$  measurement placed the sub-surface enrichment at pre-1900 and, therefore, could indicate early Pennine industrial activity. If that applied to the present study, it could be assumed that potassium too had an anthropogenic origin. However, there is little in the industrial history of the area to support such a contention. The similarity of aluminium and potassium data in the hummock may indicate a common lithospheric origin. As the hummocks and hollows are adjacent, strictly speaking they should not be thought of as discrete environments. Consequently, the possibility of lateral influences should be considered. For example, little is known of the processes operating at the interface of the hummock base with the surface of the hollow. Clearly, this enrichment is worth further investigation and the authors are currently studying the evidence for similar peaks in other elements for other cores from Ringinglow Bog.

### Conclusions

The analyses from Ringinglow Bog confirm that comparatively high concentrations of heavy metals are found in peats from areas with a long history of exposure to industrial activities. There is a high degree of internal consistency in some of the element–depth profiles. Factor analysis of this large data set has confirmed the apparent consistency implied by these profiles. In the past such consistency has been interpreted as being indicative of little or no post-depositional diagenesis. This study suggests that cadmium, copper, lead and zinc may retain their deposition records in peat.

However, other elements display more variable behaviour.

There is strong evidence for small scale variation in metal concentration across the surface of peat bogs. This reflects a response to the influences of hydrological, micro-topographical and vegetational change across the bog. Such observations have considerable implications for appropriate sampling strategies.

This investigation shows that peat-based reconstruction of historical heavy metal deposition remains fallible. There is still insufficient evidence to support the assumption that all metal deposition records retain their chronological integrity. Clearly, many aspects of heavy metal response to the varying conditions in a bog remain unresolved.

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