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Eprints ID : 11485

To link to this article : DOI:[10.1016/j.jas.2014.01.011](https://doi.org/10.1016/j.jas.2014.01.011)
URL : <http://dx.doi.org/10.1016/j.jas.2014.01.011>

To cite this version : Küttner, Ankie and Mighall, Timothy and De Vleeschouwer, François and Mauquoy, Dmitri and Martínez Cortizas, Antonio Manuel and Foster, Ian D.L. and Krupp, Eva *A 3300-year atmospheric metal contamination record from Raeburn Flow raised bog, south west Scotland*. (2014) *Journal of Archaeological Science*, vol. 44 . pp. 1-11. ISSN [0305-4403](https://doi.org/10.1016/j.jas.2014.01.011)

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A 3300-year atmospheric metal contamination record from Raeburn Flow raised bog, south west Scotland

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A B S T R A C T

There is now a plethora of records of atmospheric metal deposition across Europe based on total concentrations and calculated enrichment factors. However, to place such records into an archaeological context and to identify anthropogenic contamination signals more accurately, it is important to separate the signals derived from anthropogenic activities from those of a natural origin. This study presents a new 3300-year record from a bog in the vicinity of Hadrian's Wall and the Northern Pennine orefield in order to generate a new atmospheric metal deposition record for this archaeologically important part of the British Isles. For this purpose multi element geochemistry was undertaken to apportion the contribution of trace metals (lead, zinc, copper, arsenic and mercury) and sulphur as a result of mining/metallurgy and/or geogenic processes. To extract the different contributions through time we used total concentrations and enrichment factors (EF), and applied principal component analysis (PCA) to the dataset. The PCA extracted 7 components: at least two components are necessary to elucidate the trace metal distribution. Zinc, arsenic and lead are mostly related to atmospheric pollution, while mercury and copper appear to be more closely associated with organic matter. Based on these results four phases of lead contamination have been identified that date to: I, c. 2350–1500 cal BP; II, c. 1050–700 cal BP; III, c. 500–350 cal BP and IV, 250 cal BP–present. Copper enrichment also occurs during the Bronze Age (c. 3150–2800 cal BP). Peaks in other metals do not always correspond with lead and they may have been caused by other land use changes or processes that operate internally within the bog. Although the lead can be attributed to both anthropogenic and geogenic sources, its down profile pattern is in accordance with contamination records elsewhere in Britain and Europe, and the lead enrichment recorded at Raeburn Flow suggests that the Northern Pennine orefield was exploited for metals during the late Iron Age and Roman period.

Keywords:

Trace metals
Raised bog
Roman
Scotland
PCA
Metallurgy
Mining

1. Introduction

Hadrian's Wall is one of the most iconic Roman archaeological features in Britain. The wall and its associated frontier has attracted a wealth of archaeological studies that have reconstructed all aspects of the social and economic livelihoods of people living along this frontier (e.g. Breeze and Dobson, 1987; Jones and Mattingly, 1993), as

well as environmental changes caused by activities such as agriculture (e.g. Dumayne and Barber, 1994; Manning et al., 1997). Lead mining is known to have taken place across Europe and in the British Isles throughout the Roman period, but hitherto archaeological evidence from the Northern Pennine orefield, which is closest to Hadrian's Wall and its hinterlands has been less forthcoming (e.g. Jones and Mattingly, 1993). In a previous study Mighall et al. (2004) found no evidence of lead enrichment during the Roman period in three peat records in Weardale and Teesdale and they suggested that any pre-medieval activity may only have been on a scale that was insufficient to generate a detectable contamination signal. This is

surprising, given the relatively close proximity of the Northern Pennine orefield to Hadrian's Wall, which seems to be an obvious source of metals for the Romans to exploit along with other lead rich deposits found, for example, in SW Britain at Charterhouse in the Mendips, Alderley Edge in Cheshire and central-north Wales (Timberlake et al., in press). Such issues have wider significance in understanding the Roman's role in commanding and controlling the native economy (cf Manning et al., 1997) and therefore are worthy of further investigation.

The Romans are renowned for their exploitation of metals; especially lead which was used for a variety of purposes including aqueduct piping, plumbing, pewter, coffins and gutters for buildings, and for its association with silver, e.g. in coinage. Such was the demand for lead, Nriagu (1998) estimated that the peak in annual production during the Roman Empire was about 32,000 metric tons. This demand is also reflected in signals preserved in terrestrial archives such as peatlands and lake sediments. These archives have shown that the start of atmospheric metal contamination can be traced back to the Bronze Age, to as early as c. 2530 BC in Spain and c. 2400 BC in Britain (Martínez Cortizas et al., 2013). However, the most widespread early contamination phase appears to have commenced in the late Iron Age and peaked during the Roman period (Martínez Cortizas et al., 2013). Martínez Cortizas et al. (2013) describe this common narrative of historical contamination in more detail with higher concentrations of lead commencing around 1000–500 BC, peaking by the 1st–2nd centuries AD and collapsing by c. AD 400; a pattern that has been reconstructed by numerous researchers from peat bogs in Sweden, Britain, Germany, France and Switzerland (De Vleeschouwer et al., 2010). Indeed, Renberg et al. (2001) suggest that the chronology of this pattern is so consistent it can be used as a chronological marker.

The mineralized deposits of the Northern Pennine orefield are located primarily in the Weardale and Teesdale regions of County Durham, extending westward into the Alston Moor and Escarpment regions of Cumbria, northward into Northumberland and southward into North Yorkshire (<http://www.ukminingventures.com>). Despite the wealth of Roman archaeology to the north of this mineralised region, the first documented evidence of mining in the Northern Pennines dates to the 12th century AD, but there is some circumstantial evidence for earlier activity. A Roman date is preferred by Wooler (1924), Raistrick and Jennings (1965) and Lord and Morgan (2003) and it is suggested by others albeit tentatively (Jones and Mattingly, 1993), whilst Coggins (1986) speculates that pre-Roman activity may have taken place. Firm archaeological evidence for Roman exploitation is, however, still lacking.

The aim of this study is to reconstruct the atmospheric metal deposition history using a peat core from Raeburn Flow (SW Scotland), which lies 12 km from Hadrian's Wall and approximately 55 km from the Northern Pennine orefield in order to generate a new and more accurate record of atmospheric contamination history for this region. To achieve this aim we have analysed the geochemistry of the Raeburn Flow peat for the last c. 3300 years, with supporting radiocarbon dates. We applied multivariate statistical techniques (PCA) in order to separate potential signals derived from human activities, which could include both enhanced soil dust deposition and metal pollution, from those derived from natural processes, which could include naturally enhanced soil dust deposition and internal processes within the peat related potentially to diagenesis.

2. Materials and methods

2.1. Location, sampling and sub-sampling strategy

Raeburn Flow is a raised bog located in a special area of conservation (SAC) and a dedicated 'Site of Special Scientific Interest'

(SSSI) north of the Solway Firth in the Scottish Borders, Scotland, UK (Fig. 1). The site was previously studied with respect to ecological and climatic reconstructions using plant macrofossil and testate amoebae analyses (Mauquoy and Barber, 2002). Past peat cutting along the southern and eastern edges has lowered the water table and *Pinus sylvestris* and *Betula pubescens* have recently begun to establish across the bog surface. The raised bog phase spans at least the last 5000 years across parts of the bog (Mauquoy and Barber, 2002). A 360-cm long core (55° 02' 03.83" N and 03° 06' 27.41" W), consisting of *Sphagnum* peat, was retrieved in February 2011 using a Russian corer with a length and diameter of 50 × 7.5 cm respectively. Cores were wrapped in plastic cling film and protected in PVC tubing for transport. Additionally, rainwater was collected during the coring to determine the calcium/magnesium ratio at the site (cf Shoty, 1996). The cores were cut into 1 cm-thick slices in the laboratory and stored at 4 °C prior to analyses. All analyses were undertaken on single slices. Subsamples for total geochemical analysis were then freeze-dried and subsequently ground and homogenised.

2.2. Geochemical analyses

Fifty samples at 8-cm intervals were digested at Ecolab, Toulouse (France), following the protocol for total HF–HNO₃ digestion detailed in Le Roux and De Vleeschouwer (2011). Due to high organic content in a number of samples, an additional cleaning step using *aqua regia* was employed. Aliquots were measured by quadrupole ICP-MS at the *Géosciences Environnement Toulouse* laboratory (GET Observatoire Midi-Pyrénées, Toulouse) for a suite of 35 elements including lead, zinc, arsenic, copper, titanium, zirconium and sulphur. Five different certified reference materials (NJV 94-1 *Carex* energy peat, NJV 94-2 *Sphagnum* energy peat, NIST-1515 apple leaves, NIST-1547 peach leaves and NIMT/UOE/FM/001 ombrotrophic peat) were used to monitor the analytical quality of the measurements. All measured elements were above limits of detection. Accuracy was above 90% for all the measured elements excepted for titanium (75%). The measurements of two blank samples revealed values below limits of detection.

Mercury concentrations were determined using a direct mercury analyser at GET (Milestone[®]DMA-80). All samples were measured in duplicates. Certified Reference Material NIST-2685b was repeatedly measured throughout the whole measurement session. Results showed a high recovery rate of approximately 98% with an RSD of approximately 5%. Because the mercury analyser burns the sample at high temperature (850 °C), the ash content of each sample was also measured by weighing each sample before and after the mercury analyses.

2.3. Enrichment factors

We use enrichment factors (EF), calculated using the equation proposed by Shoty (1996), to identify periods of increased trace elements believed to have derived from human activities. As no clear background values for the pre-anthropogenic period can be derived with confidence, we use upper continental crust (UCC) values (Rudnick and Gao, 2003). Titanium (Ti) was used as the reference lithogenic element (as supported by the PCA results).

2.4. Chronology

An age-depth model was generated using ¹⁴C and ²¹⁰Pb radiometric dating techniques. Radiocarbon dates were determined at Chronolab, Belfast, using Accelerator Mass Spectrometry (AMS). Three samples of fresh peat were carefully cleaned to minimise the risk of contamination and *Sphagnum* macrofossils were handpicked

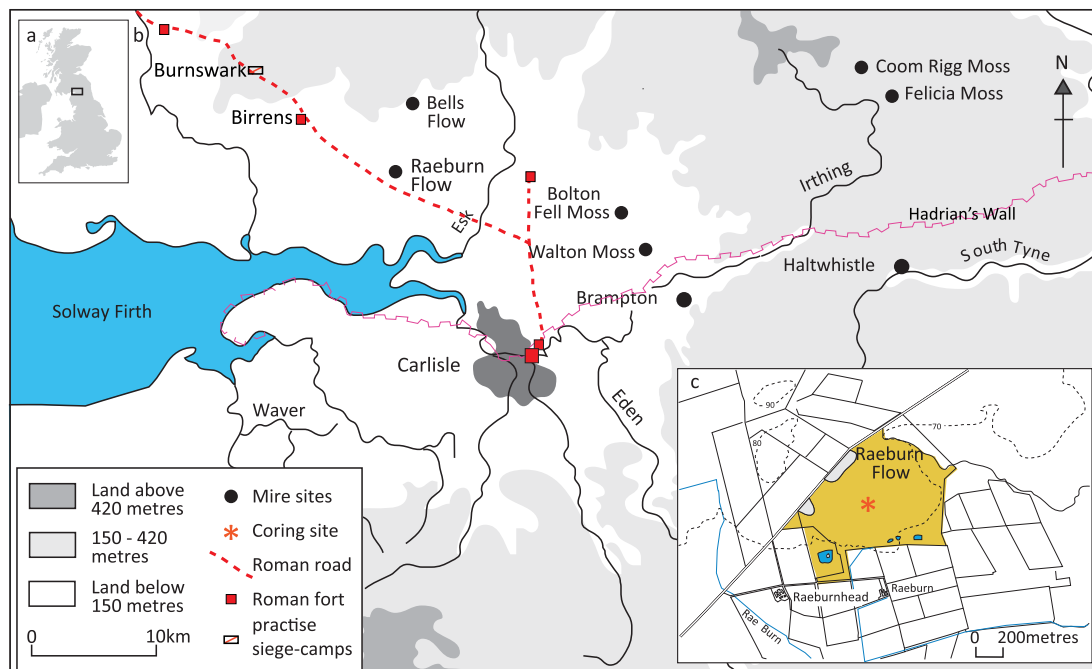


Fig. 1. a: Location in the UK; b: Location in the SW of Scotland; c: Raeburn Flow showing the sampling site. The red star points out the coring location. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and sent for dating (Nilsson et al., 2001; Piotrowska et al., 2011). The radiocarbon dates were calibrated using the IntCal09 Northern Hemisphere terrestrial calibration curve (Reimer et al., 2009) (Table 1).

To provide a chronology for the last 100–150 years, the unsupported ^{210}Pb activity was ascertained (Appleby and Oldfield, 1978; Appleby, 2001). ^{210}Pb and ^{214}Pb activities were measured using EG&G ORTEC hyper-pure Germanium detectors in a well configuration (11 mm diameter, 40 mm depth) housed at Coventry University. The CRS model was used to calculate ages as accumulation rates varied along the core (Appleby et al., 1988). The Bacon software package (Blaauw and Christen, 2011) was used to create age-depth models to infer approximate ages for all levels. We used the proxy.ghost function provided in Bacon to display our age-depth model as a greyscale plot. This function allows the reader to visualise the chronological probability distributions inherent in the proxy data sets with the inferred ages based on the radiocarbon and ^{210}Pb dates.

2.5. Statistics

Following the procedure described by Martínez Cortizas et al. (2013) and Hermanns and Biester (2013), we used factor analysis

Table 1
Stratigraphical description of the Raeburn Flow core based on plant macrofossil composition with maximum a posteriori age estimates.

Depth (cm)	Age (cal BP)	Descriptors
0–38	~–60 to 200	The base is dominated by monocots shifting to <i>S. magellanicum</i>
38–98	~200 to 830	Dominated by fluctuating concentrations of <i>S. austinii</i> , <i>S. magellanicum</i> and <i>S. Sec. Acutifolia</i>
98–142	~830 to 1360	Dominated by <i>S. Sec. Acutifolia</i>
142–302	~1360 to 2740	Dominated by consistently high values of <i>S. austinii</i> , with an intermittent spike in <i>E. vaginatum</i> at 228 cm
302–364	~2740 to 3390	Characterised by fluctuating dominance between <i>S. austinii</i> and monocots

by principal components (PCA) to identify sources and processes related to the distribution of 35 measured elements using the SPSS 20 software package. The values were first transformed to z-scores to enable comparison of the complete data set by reducing the actual range of variation and to avoid any scaling effects (Eriksson et al., 1999). Z-scores were calculated separately for the samples above and below 35 cm (calculated as: $[X_i - X_{avg}]/\text{STD}$, where X_i is the concentration of a given element in a given sample, X_{avg} is the average of the population and STD is the standard deviation). The samples above 35 cm (250 cal BP until present) were excluded from the analytical phase of the PCA, but the scores for these are based on the extracted components as well. This procedure was followed as the very high concentrations for several of the major and minor elements and trace metals would bias the PCA results. Non-linear multidimensional scaling (NMDS, run in R package vegan) revealed their distinctive dissimilarity as the samples of relatively high contamination plotted separately from the remaining levels. Varimax rotation was chosen to maximize the PCA loadings of the variables on the components (Hermanns and Biester, 2013). Similarly distributed elements will load into the same principal component and are most likely controlled by the same environmental factor(s). Hence, interpretation of the signals with regard to the underlying cause or causes of the variation of a group of elements should be more evident.

3. Results

3.1. Stratigraphy and age-depth modelling

A brief stratigraphy of the 364 cm-deep core is provided in Table 1. The core is dominated by *Sphagnum* species with fluctuating concentrations of undifferentiated monocots and a peak in *Eriophorum* at 228 cm.

The radiocarbon dates are presented in Table 2. A combination of ^{210}Pb , which constrains approximately the last 150 years, and the ^{14}C dates yielded a near linear age-depth model (Fig. 2). The

Table 2
Radiocarbon dates for Raeburn Flow.

¹⁴ C lab code	Depth in cm	¹⁴ C age ± error	cal BP	cal BP (confidence interval)
UBA-19914	100.5	958 ± 23	796–974	796–974 (63.3%)
UBA-19913	224.5	1926 ± 27	1820–1932	1820–1932 (100%)
UBA-19912	364.5	3122 ± 27	3318–3400	3318–3400 (79.5%)

observed profile spans approximately 3300 years with a mean 95% confidence interval of 278 yr. The age–depth model derived using Bacon, suggests a reasonably stable accumulation rate of roughly 1.1 mm yr⁻¹. All dates are cited in calibrated years BP unless otherwise stated. Cited age ranges are of the minimum and maximum estimates based upon the 95% confidence ranges of all the selected iterations of the age–depth model (Blaauw, 2010) and they are rounded to the nearest decade.

3.2. Geochemistry

Only elements that are considered key to addressing the objectives of this study are presented and discussed here. Fig. 3 depicts concentrations for lead, zinc, arsenic, copper, mercury, sulphur, titanium and zirconium, as well as enrichment factors for the trace metals, ash content, zirconium/titanium and calcium/magnesium ratios against age. Table 3 presents the mean, maximum and minimum values for the key elements used in this study. The calcium/magnesium ratio (Fig. 3) confirms the ombrotrophic nature of the Raeburn Flow core down to 360 cm. Apart from the surface sample, the ratio is consistently below the measured value for rainwater at RBF (approximately 1.9). Ash content is also well within the range of values cited by Shotykh (1996) to infer ombrotrophic conditions. The highest ash contents were measured in the upper 35 cm of the core (approximately 2.2%) and at 256 cm (3.4%), although the average content below 35 cm is 1.1%. These percentages are well below the accepted value of 3% for ombrotrophy, which is only exceeded in the presence of secondary sources of mineral matter such as lateral mineral inputs and industrial processes (Naucke, 1980).

Four periods of increased inorganic content, characterised by high ash content, titanium and zirconium concentrations, which we consider to be indicative of increased dust deposition, are identified in the Raeburn Flow peat record (Fig. 3a) from: c. 3050 to 2600 cal BP (1), c. 2400 to 1950 cal BP (2), c. 900 to 550 cal BP (3) and c. 350 cal BP to present day (4). The second phase is characterised by an initial peak in ash content followed by an increase in titanium and zirconium c. 100 years later. A possible fifth period is recorded between c. 1400 and 1150 cal BP characterised by a peak in titanium and zirconium, although ash content does not increase at this time. The uppermost period shows a proportional shift towards higher values for zirconium compared to titanium concentrations. Titanium and zirconium are strongly correlated ($r > 0.9$, $p < 0.01$) below the top 35 cm down to 360 cm.

The highest concentrations of lead (331 µg g⁻¹), zinc (105 µg g⁻¹), copper (16 µg g⁻¹), mercury (0.19 µg g⁻¹) and sulphur (6713 µg g⁻¹) were recorded during the first half of the 20th century, whilst arsenic peaks approximately a century earlier with a maximum concentration of 10.9 µg g⁻¹ (Fig. 3b). A number of element-specific sub-surface peaks are also recorded in the concentration and enrichment factor profiles: lead between 224 and 240 cm (c. 2200–1780 cal BP) and from 96 to 84 cm; zinc peaks at 168 cm (c. 1570–1260 cal BP); arsenic at 240 cm (c. 1930–2200 cal BP); copper at 200 cm (c. 1970–1750 cal BP) and 336 cm for copper and mercury (c. 3250–2900 cal BP).

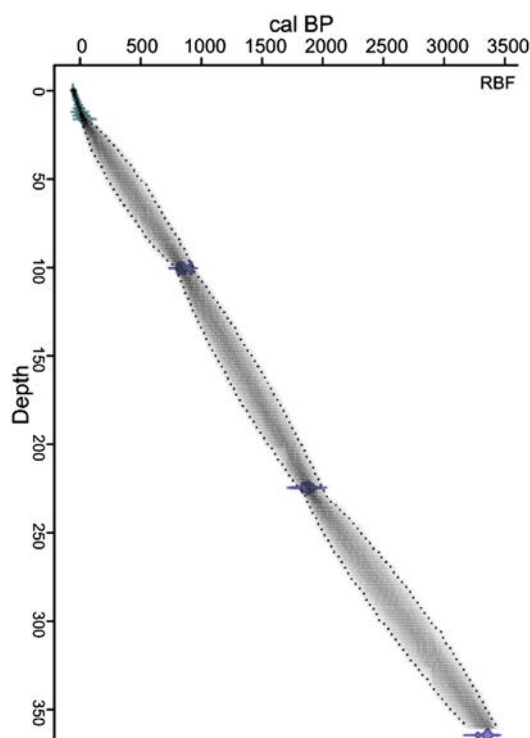


Fig. 2. Age–depth (in cm) model generated using Bacon using ²¹⁰Pb and ¹⁴C dates.

3.3. Principal component analysis

Seven principal components (PC) were extracted, explaining 88% of the total variance, with the first two components accounting for 47%. Table 4 and Fig. 5 provide details of the factor loadings of selected elements on PCs which are of most relevance for the objectives of this study. For the majority of elements at least 80% or more of their variance is explained by the extracted components. One exception is copper with just 56% extraction and therefore 44% of the variance is unaccounted for. The records of factor scores for each component are presented in Fig. 4. Factor scores are ‘non-dimensional, average centred values that measure the intensity of each factor’ (Martínez Cortizas et al., 2013, p78).

To discuss the factors that explain the distribution of the trace metals, only PC1, 2, 4, 5 and 6 are considered here. PC3 and PC7 only show minimal down profile variations and they are not discussed further. PC1 shows consistently high, positive factor loadings for lithogenic elements such as aluminium (0.81), zirconium (0.88), rubidium (0.83), vanadium (0.74) and titanium (0.85) and this component most likely represents the geogenic contribution (cf Martínez Cortizas et al., 2013). Part of the variance of lead (17%, Table 4) and arsenic (20%) is also explained by PC1. PC2 has large to moderate positive loadings of many metals (zinc 0.84, arsenic 0.79, lead 0.73, iron 0.64, nickel 0.60) including elements present in metal sulphides, associated with metallurgical activity, whilst copper (0.46) and sulphur (0.43) have moderate positive loadings. Thus, positive factor loadings in PC2 may represent atmospheric metal (anthropogenic) contamination. In contrast, mercury (0.62) and copper (0.52) show moderate, positive factor loadings in PC4 with a high, positive loading for sulphur (0.72). This may indicate that most sulphur is in organic form and thus mercury and copper are largely organically bound. The part of the sulphur variance in the second component may correspond to inorganic sulphur (in sulphides). But part of the variation in mercury (20%) and copper (21%) concentrations is further explained by PC2, thus by

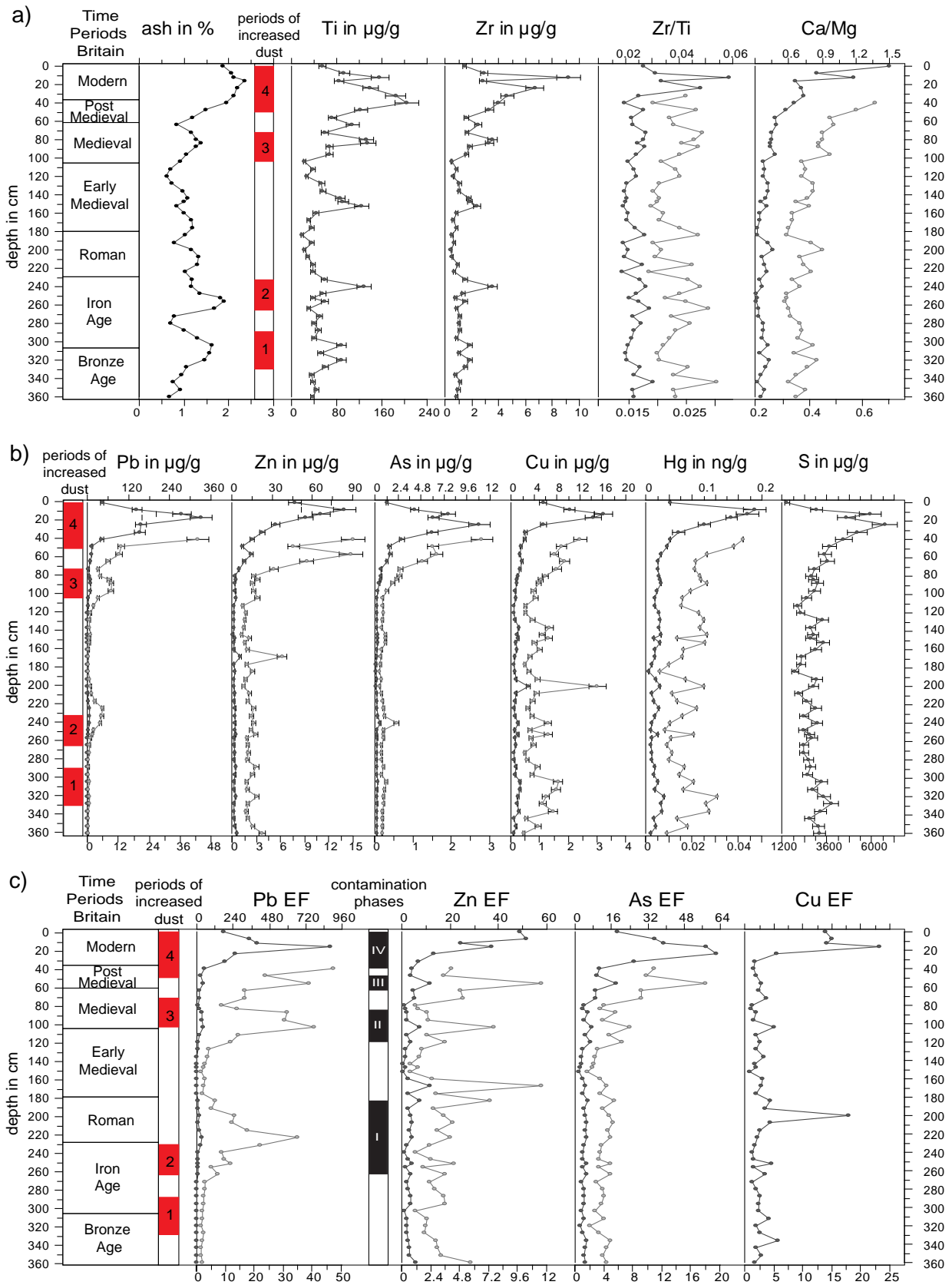


Fig. 3. a: Profiles of ash content, Ti, Zr, Zr/Ti and Ca/Mg ratio from Raeburn Flow. Ash content values presented in the figure are averaged to make general trends in shifts clearer in the plot. The measured rainwater ratio baseline is not shown as it lies outside the plotted area; b: Profile concentrations ($\mu\text{g g}^{-1}$) of the heavy metals (Pb, Zn, Hg, Cu); c: Enrichment factors calculated with Ti for the trace metals presented in 2b. Periods of increased dust as identified using ash content and the lithogenics and contamination phases based on Pb EFs are also plotted.

Table 3
Summary geochemical data (in $\mu\text{g g}^{-1}$) from Raeburn Flow.

	Pb	Zn	As	Hg	Cu	Ti	Zr
Mean	25.3	11.05	1.08	0.03	2.02	69.3	1.83
Median	1.44	2.53	0.24	0.02	0.99	55	1.24
Min	0.28	1.19	0.13	0.01	0.46	19.6	0.48
Max	331.6	105.2	10.8	0.19	16.2	204.5	9.2
Estimated background site (~2500–3500 cal BP)	0.52	2.38	0.23	0.02	1.02	51.9	1.17
Rudnick and Gao (2003)	17	67	4.8	0.05	28	3837	193

atmospheric metal deposition. PC5 has large positive loadings of strontium (0.98), calcium (0.91) and magnesium (0.67), which point to a source rich in carbonates (with probably both calcite and dolomite), possibly the sedimentary limestones that are among the host rock formations of the ore-bearing deposits in the Northern Pennine orefield. PC6 has large loading of sodium (0.86) and moderate loading of potassium (0.65). Both are largely mobile elements, which are quickly released from the minerals upon weathering. The record shows a continuous variation from positive scores from the base of the core until 2 m and negative scores to the top of the core (except for the uppermost sample) (Fig. 4). This distribution may reflect their mobility.

Zirconium and titanium are the best proxies for the deposition of soil dust (i.e. they show the largest loadings in PC1; Table 4; Fig. 5) in the Raeburn Flow record and thus the most appropriate elements to account for the content of mineral matter in the peat and for the calculation of metal enrichment factors (i.e. account for the geogenic source).

Table 4
Main principal components of interest in this study, factor loadings (first five columns from the left; the colours identify the principal components) and percentage of the variance of each element explained by each component (second five columns; contributions to 10% or more of the variance are coded with the colour of the respective principal component) for selected elements from Raeburn Flow. "Com" is the commonalities of the elements (i.e. the percentage of variance of each element accounted for all the extracted principal components).

	PC1	PC2	PC4	PC5	PC6	PC1	PC2	PC4	PC5	PC6	Com
Zr	0.88	0.21	0.18	-0.20	0.05	77	5	3	4	0	97
Ti	0.85	0.26	0.25	-0.15	0.01	72	7	6	2	0	98
Rb	0.83	0.31	0.07	-0.22	0.09	69	9	1	5	1	96
Cr	0.81	0.41	0.15	-0.16	0.07	66	17	2	3	1	92
Al	0.80	0.40	0.33	-0.04	-0.04	64	16	11	0	0	98
V	0.74	0.36	0.43	0.00	-0.07	54	13	18	0	0	93
Zn	0.22	0.84	0.07	-0.23	-0.02	5	70	1	5	0	83
As	0.44	0.79	0.15	-0.18	-0.01	20	63	2	3	0	95
Pb	0.41	0.73	0.08	-0.16	-0.03	17	53	1	2	0	84
Fe	0.45	0.64	0.10	0.43	-0.33	20	41	1	19	11	93
Ni	0.59	0.60	0.24	0.06	-0.15	35	36	6	0	2	80
S	0.34	0.43	0.72	-0.09	0.01	12	19	52	1	0	86
Hg	0.30	0.44	0.62	0.01	-0.36	9	20	38	0	13	84
Cu	0.15	0.46	0.52	0.00	0.03	2	21	27	0	0	56
Sr	-0.04	0.00	0.08	0.98	-0.02	0	0	1	95	0	97
Ca	-0.26	-0.22	-0.13	0.91	0.00	7	5	2	83	0	97
Mg	-0.37	-0.40	-0.35	0.67	0.21	14	16	12	45	4	93
Na	-0.15	-0.21	-0.14	0.11	0.86	2	4	2	1	74	89
K	0.58	0.10	0.20	-0.13	0.65	33	1	4	2	42	93

3.4. Enrichment factors

Calculated enrichment factors are shown in Fig. 3c for lead, zinc, arsenic and copper. The earliest phase of metal enrichment occurs between c. 3150 and 2800 cal BP (336 cm) with small peaks in copper EF. Lead EF first increases at 254 cm and peaks at 224 cm (c. 1790–1990 cal BP). Copper EF and concentrations then peak at 200 cm (c. 1750–1970 cal BP) but a corresponding increase in mercury concentrations is less obvious. Zinc concentrations and EF peak at 168 cm (c. 1270–1580 cal BP) and both lead and zinc EF have prominent peaks at 104 cm (810–960 cal BP). Minor EF peaks are also recorded for arsenic and copper. Arsenic also increases immediately before 104 cm. Lead, zinc and arsenic EF also peak at 56 cm (c. 280–570 cal BP).

4. Discussion

Ash content and elevated concentrations of lithogenic elements are often used as proxies for dust input from natural/geogenic sources and they have been interpreted as reflecting land use changes such as deforestation and soil erosion (e.g. Hölzer and Hölzer, 1998; Kempster and Frenzel, 1999; Martínez Cortizas et al., 2005). Four periods characterised by peaks in ash content and elevated concentrations of conservative lithogenic elements (e.g. titanium, zirconium) and a further peak in just titanium and zirconium have been identified in the Raeburn Flow peat core (Fig. 3a). These are: period 1 between 3050 and 2600 cal BP, period 2 from 2400 to 1900 cal BP, period 3 from 900 to 550 cal BP and period 4 from 350 cal BP to just below the bog surface (c. AD 1950).

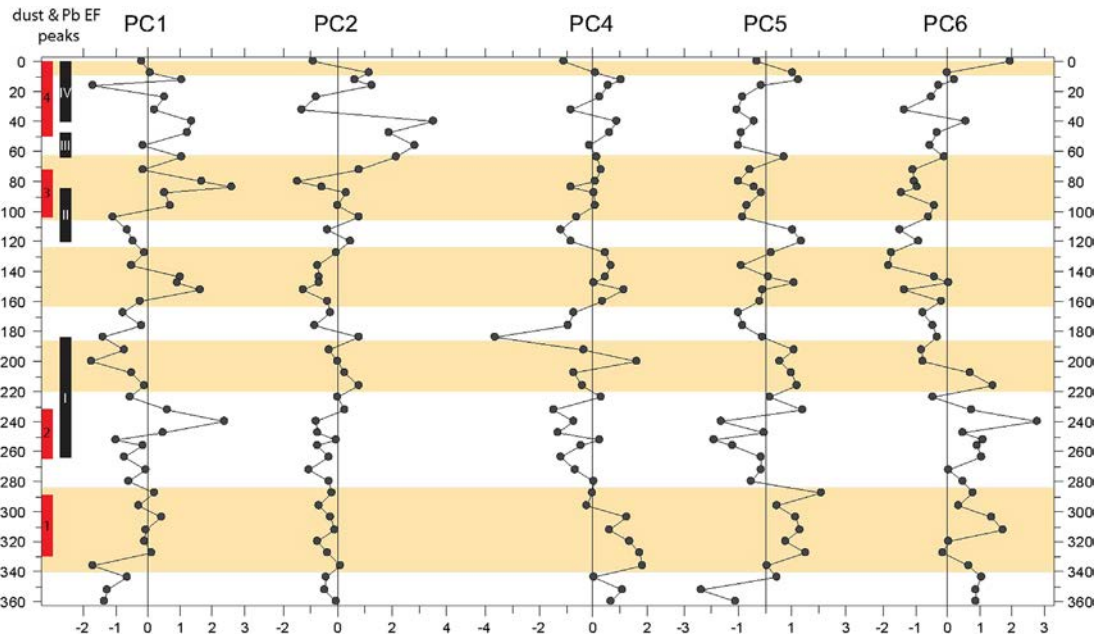


Fig. 4. Principal component scores against depth. Pb EF indicated by the black bars on the left side and red bars for the periods of increased dust deposition for comparison. Also shown are the drier phases (shaded in yellow based on changes in the water table reconstructed from testate amoebae). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Dust atmospherically deposited on to the bog surface during period 1 is interpreted as being a result of land use changes (i.e. deforestation and agriculture), especially as there is no simultaneous trace metal enrichment indicative of metallurgic-derived contamination. Whilst there is no local record of land use changes for Raeburn Flow, other pollen diagrams in the region do record evidence of human activity during the Late Neolithic and Bronze Age (e.g. [Yeloff et al., 2007](#)). At Rookhope in the Northern Pennine orefield, the first significant phase of woodland clearance occurred during the Late Bronze Age/Early Iron Age transition (c. 780 cal BC/2730 cal BP) ([Mighall et al., 2004](#)). Dust periods 2–4 generally overlap with the

trace metal enrichments and will be discussed in chronological order below.

When we combine the results from the concentration data, EF and PC2 there is strong support for evidence of mining and/or metallurgical activity. The earliest phase of metal enrichment occurs between c. 3150 and 2800 cal BP (336 cm) with a small peak in Cu and EFs and higher mercury concentrations ([Fig. 3c](#)). Four phases of lead enrichment with increased concentrations/EFs of one or a combination of zinc, arsenic, copper and mercury were identified at Raeburn Flow. These phases correspond with the late Iron Age/Roman occupation (I, c. 2350–1500 cal BP), early medieval–medieval period (II, c. 1050–700 cal BP), post-medieval period (III, c. 500–350 cal BP) and Industrial/modern period (IV, c. 350 cal BP–present). The overall pattern of PC2 ([Fig. 4](#)) fits the distribution of the contamination phases identified based upon the concentration and EF of lead, zinc and arsenic ([Fig. 3b, c](#)). Seventy, 63 and 53% of the zinc, arsenic and lead variances, respectively, are associated with this component.

4.1. Bronze Age

The earliest phase of copper enrichment occurs during the mid to late Bronze Age between c. 3150 and 2800 cal BP. There are no known prehistoric copper workings in northern Britain. The closest sites are located further south, at Alderley Edge and Ecton, while the majority of known Bronze Age copper mines are in north and central Wales ([Timberlake, 2003, 2009](#); [Timberlake and Prag, 2005](#)) and south-west Ireland ([O'Brien, 2004](#)). Only the early copper workings at Derrycagoon in SW Ireland, which took place between c. 650 and 950 cal BP ([O'Brien, pers comm.](#)), overlap with the age of the copper contamination identified at Raeburn Flow. All the other known prehistoric mines pre-date this phase of contamination, although mining occurred in the Late Bronze Age at the Great Orme in north Wales ([Timberlake, 2009](#)). Therefore in the absence of firm archaeological evidence locally it is not possible to fully explain the enrichment of copper and the elevated mercury concentrations. Other possible causes are discussed below.

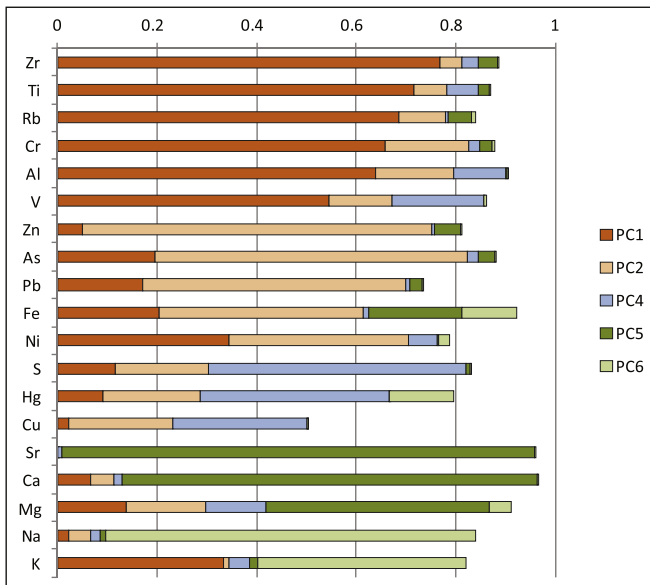


Fig. 5. Communalities accounting for each element's variance allocated to each principal component.

4.2. Late Iron Age and Roman times

The rise in lead concentrations (phase I) and EF at Raeburn Flow pre-dates the Roman invasion of northern England between AD 71 and 83 and subsequent occupation (Breeze and Dobson, 1987). This suggests the existence of a late prehistoric Pb extraction industry and that the Romans continued and expanded this industry in the region. In the absence of stable lead isotope data, it is not possible to identify specific sources for the Pb and the overlap of the signatures of British ores renders it difficult to characterise a specific British source (Le Roux et al., 2004). The Northern Pennine orefield, situated to the south of Raeburn Flow, is the most likely local source although contributions from other sources including Leadhills to the west, Lake District to the SW (Grayson and Plater, 2009) and/or to long range transport from Spanish sources cannot be discounted (e.g. Pontevedra-Pombal et al., 2013). In contrast Mighall et al. (2004), who studied peat records within the Northern Pennine orefield (c. 55 km southeast of this study site, Fig. 1), did not record any significant increase in metals during pre-Roman and Roman times, although evidence for woodland clearance and agriculture was recorded in pollen diagrams from the same sites. Mighall et al. (2004) suggested the lack of a substantial Roman contamination peak implied that local lead ores remained unexploited or that any activity was on such a small scale, it did not generate a contamination signal. This hypothesis seemed to be supported by a lack of definitive archaeological evidence for late prehistoric and Roman mining and metallurgy in the Northern Pennines, which is limited to lead objects found at Iron Age sites and the discovery of some lead pigs and a possible smelting site on Wolsingham moor in Weardale (Wooler, 1924; Raistrick and Jennings, 1965). The atmospheric lead record from Raeburn Flow means that this hypothesis now has to be re-evaluated. A Roman road also runs on a north-south axis within 2 km of Raeburn Flow (Fig. 1) and a number of forts and practice siege camps are situated by the road, including Burnswark (Fig. 1), where 67 lead sling bolts were found during excavations (Wilson, 2002). Some local lead working could also have taken place.

Increased lead concentrations and EF from the Late Iron and Roman times (phase I) are consistent with studies elsewhere in the British Isles e.g. Le Roux et al. (2004) at Lindow Bog in Cheshire and Borth Bog in central Wales (Mighall et al., 2009). Similarly, Roman peaks have been detected in Flanders Moss in central Scotland (Cloy et al., 2005, 2008) and the Faroe Islands (Shotyk et al., 2005). Phases of enrichment also match numerous records for lead contamination published across Europe (De Vleeschouwer et al., 2010, and references therein) and the worldwide Pb production (Settle and Patterson, 1980).

The increase in lead contamination during Roman times is also consistent with wider landscape changes in the region, particularly associated with the construction and occupancy of Hadrian's Wall. Notwithstanding poor dating precision at some sites, local and regional reconstructions of vegetation change have been conducted close to the Wall and its hinterland and provide evidence of woodland clearance and agriculture during the Late Iron Age and Roman period (e.g. Dumayne and Barber, 1994; Manning et al., 1997; Yeloff et al., 2007). Similar changes have also been recorded in the Northern Pennine orefield (Mighall et al., 2004). The second phase of increased dust deposition (increases in ash, titanium and zirconium) at Raeburn Flow from c. 2400 to 1900 cal BP also coincides with the first half of the lead enrichment phase I and this is consistent with the evidence of wider changes in land use across the region (Fig. 3). However, the reason why ash content peaks before titanium and zirconium by approximately 100 years is unknown. Evidence of woodland regeneration is also a common feature in most pollen diagrams in the region following the

withdrawal of the Roman forces. This also is in accordance with the decline in lead concentrations and EF at Raeburn Flow implying that large scale lead extraction also ceased at this time.

Towards the end of the Roman lead enrichment phase, there is a noticeable peak in both copper concentrations and EF (c. 1740–1970 cal BP) as the lead EF and concentrations decline (Fig. 3c). The Alston block of the Northern Pennine orefield does contain minor amounts of copper, which are known to have been exploited in the late 19th and early 20th centuries AD, and trace amounts of mercury are associated with sphalerite (Ixer and Vaughan, 1993). As noted above, people have exploited copper deposits since the Bronze Age and while the Romans used mercury in cosmetics, extracted from mines in Spain with evidence dating back to around 2500 years BP (Martínez Cortizas et al., 1999), there is no archaeological evidence for any copper mining or mercury extraction in northern Britain. In the absence of such evidence these peaks cannot be fully explained by mining and metallurgical activities.

The PCA analysis suggests that copper and mercury are related to different sources and influenced by several factors as their variance is shared between more than one principal component (Table 3; Fig. 5). While approximately 20% of variance for both copper and mercury is related to PC2 (mining/metallurgical contamination), the results show that they also have moderately positive loadings in PC4 (which is the single component accounting for the largest proportion of the variance of both elements) and weak positive loadings in PC 1 and 3 (data not shown) respectively. A correlation between the PC2 scores and copper and mercury concentrations revealed that only the past 1100 (first 120 cm) and 1600 (first 176 cm) years show a correlation coefficient higher than 0.5, whereas in the older section of the profile mercury is correlated to PC4 (Fig. 4). This effect is less distinctive for copper, but becomes noticeably stronger in samples older than 2350 cal BP, implying that other factors besides anthropogenic contamination have influenced both elements. Sulphur has a very strong positive loading in PC4 (Table 4; Fig. 5). Organic sulphur can dominate the total concentration of sulphur in ombrotrophic bogs (Novak and Wieder, 1992) and this suggests that PC4 may represent organically-bound copper and mercury. Syrovetsnik et al. (2007) also note that a sizeable portion of copper is organically-bound and this fraction increases with peat depth. Moreover, only 56% of the variance in copper is explained by the PCA, with 44% related to some other unknown sources/processes. Although PC1 accounts for a minor proportion (9%) of the Hg variance, both copper and mercury also appear to be unrelated to ash content and those elements indicative of natural dust deposition or volcanic activity. Another natural source of mercury is sea spray (Zuna et al., 2012) but this is difficult to evaluate with the present data. Post-depositional mobility is also unlikely to account for these peaks as copper and mercury appear to retain their chronological integrity under ombrotrophic conditions (Fitzgerald et al., 1998; Mighall et al., 2002a; Novak et al., 2011).

Climate might also be a factor driving enrichment of trace metals in the bog. Our analysis also found that peaks in copper concentration and enrichment and mercury concentration coincide with drier conditions (as shown in Fig. 4) in the earlier part of the record around 2670 cal BP and between 1580 and 1720 cal BP (Fig. 3b, c). This also coincides with peaks in charcoal (Küttner, 2013). Furthermore, previous research has indicated that changes in climate causing increased decomposition of the peat mass can enrich trace metal concentrations in bogs (Martínez-Cortizas et al., 2007; Biester et al., 2003, 2012). However, when we used the water table depth (reconstructed using testate amoebae data, Küttner, 2013) as a passive variable, neither PC4 nor copper and mercury concentrations showed a significant relationship. Despite this,

varying carbon loss skewing the enrichment factors remains a valid concern (Biester et al., 2003; Martínez-Cortizas et al., 2007).

4.3. Early medieval–medieval period

Despite the intimate association between lead and zinc in metallic ores, no zinc enrichment was recorded in either the concentrations or EF at Raeburn Flow during the Roman period. The first noticeable peak in zinc concentrations and EF occurs at 168 cm during the early medieval period (c. 1270–1570 cal BP; Fig. 3b, c). While mostly associated with contamination as indicated by its strong positive loadings in PC2, this peak in zinc is unlikely to be a by-product of mining as both lead concentrations and EF remain low. It would be highly unusual to ascribe this phase of zinc enrichment to metallurgical activity in the absence of enrichment of other metals, especially lead and copper. Zinc was not intentionally exploited in prehistoric times but copper–zinc ores were smelted together. The Romans are also thought to have used zinc (ZnCO_3) to make brass and other copper-based alloys primarily for coinage and to produce decorative items (Craddock, 1978, 1995). There is plenty of archaeological evidence for Roman copper alloys in northern Britain (Dungworth, 1997, 2002) but copper concentrations and EF also remain low. After the fall of the Roman Empire, zinc production probably declined at least until the 10th century AD (Hong et al., 1997). Natural zinc can originate from rocks and soil dust, volcanoes and biogenic sources. However, those elements indicative of increased dust deposition, including ash content, titanium and zirconium, do not show a corresponding increase with zinc during this time and the zirconium/titanium ratio is unresponsive (Fig. 3), which may be the result of different rates of weathering as the elements are not in the same mineralogical phase. Internal bog processes may have also influenced the zinc record. Zinc is considered to be mobile in peat (Shotyk, 1988). Some sub-surface peaks have been attributed to precipitation at the water table, whilst other anomalous peaks could not be explained (Shotyk, 1988). Livett et al. (1979) and Livett (1988) suggest that zinc is susceptible to leaching in peat and therefore may be displaced from its true level in the peat profile. However, with the exception of the surface sample, zinc and arsenic EF records display similar trends ($r = 0.798$) suggesting that zinc has retained its chronological integrity over time. Studies by Novak et al. (2011) and Rothwell et al. (2009) also found negligible mobilisation of zinc and arsenic respectively. Alternatively both elements may have moved; a process that has been recorded in other studies in Britain (Jones, 1987; Mighall et al., 2002b) and elsewhere (e.g. Rausch et al., 2005).

The second increase in lead and zinc occurred between c. 1050 and 700 cal BP (phase II), concomitant with a small double peak in arsenic EF (Fig. 3c). Fairburn (1996) suggests that iron and lead emissions must have been substantial during the medieval period. Historical documents note the destruction of woodland for iron and lead forges in AD 1306. The elevated arsenic concentrations and EF are most likely the by-product of lead–zinc mining. Widespread arsenic contamination has been recorded in stream sediments from the Northern Pennine orefield (Lord and Morgan, 2003). Arsenic-bearing phases in galena concentrates and arsenic adsorbed by detrital iron–manganese oxides in ironstones are known to exist in the orefield, and although they are considered to be rare (Dunham, 1990), they are the most likely source of contamination recorded at Raeburn Flow during phases II, III and IV.

4.4. Post-medieval

Lead, zinc and arsenic concentrations and EFs all increase during Phase III (c. 500–350 cal BP). These peaks coincide with

the continued development of the lead mining industry with historical leases being granted for mining from 850 BP onwards (e.g. Drury, 1992; Pickin, 1992; Mighall et al., 2004). Moreover, German workers re-organised the English lead mines and new technological improvements such as new furnaces for smelting may have also enhanced lead contamination (Le Roux et al., 2004). Increased concentrations and EFs of zinc and arsenic are most likely to be associated with the exploitation of the lead deposits. Arsenic is an element that is often enriched in coals and commonly associated with copper, lead and gold ores (Oremland and Stolz, 2003). The increase in arsenic in the uppermost part of the core, during phases III and IV, is probably the result of mining and coal combustion (Shotyk et al., 1996; Rothwell et al., 2009), although it can also be taken up by plants (Zaccone et al., 2008). Coal combustion is also a source of mercury emissions (Zuna et al., 2012).

4.5. Industrial-modern period

All the metallic elements increase in the last few hundred years (Fig. 3). This coincides with a peak of the lead extraction industry, which occurred in the 18th and 19th centuries followed by a marked reduction of lead by AD 1940 and zinc by AD 1965 (Ixer and Vaughan, 1993). Sulphur also shows its highest concentrations at this time. Sub-surface peaks in sulphur are common in ombrotrophic mires in the Northern Hemisphere. Increased atmospheric sulphur deposition from coal combustion and the mining and processing of metal sulphide ores are the most likely sources (e.g. Novak and Wieder, 1992). The increase in lithogenic elements and ash content is simultaneous with the trace metals and is indicative of wider landscape changes including soil erosion associated with agriculture but also open-cast mining of iron ores and extensive quarrying. However, the uppermost part of the core is also affected by ongoing peat forming processes such as decomposition, plant uptake/recycling, element mobility and fluctuations at the acrotelm/catotelm transition and they may have also played a role in influencing the distribution of some of the elements (Jones, 1987; Shotyk, 1988; Espi et al., 1997; Biester et al., 2012). A decline in the concentrations, ratios and EFs occurs in the uppermost samples. This is commonly recorded in bogs across the British Isles (e.g. Farmer et al., 1997; West et al., 1997; Le Roux et al., 2004; Mighall et al., 2002b, 2004, 2009; Cloy et al., 2008) and reflects the demise of the metal extraction industry and subsequently the phasing out of leaded gasoline.

5. Conclusions

The atmospheric metal deposition record from Raeburn Flow in southern Scotland provides a history of metal contamination extending back over two millennia. This record is significant as it detected lead and zinc enrichment during the Late Iron Age and Roman times that can be attributed, for the first time, to mining and/or metallurgical activity associated with the Northern Pennine orefield. The combined use of total concentrations, enrichment factors and PCA is recommended when reconstructing atmospheric metal deposition records from bogs in order to discriminate between metallurgically-derived contamination from other geogenic sources. Moreover, the interpretation of such records needs to be placed into an archaeological context to improve our understanding of the history of metal contamination through time. Whilst the history of the lead record can be accounted for, the origins and mobility of some of the enrichments of zinc, copper and mercury are less well understood in this study.

Acknowledgements

We thank Ecolab and GET Toulouse for support and expertise. Dr. G. Le Roux & M.-J. Tavella, from EcoLab are thanked for their help in digesting samples at EcoLab's clean lab. J. Sonke and A. Lanza-nova are thanked for their help in measuring sample solution at the GET's ICP-MS and the Hg data. We thank Alison Sandison and Jenny Johnson at the University of Aberdeen for cartographical support and the University of Aberdeen for a College PhD studentship for AK. Jonathan Warren (SNH) and the landowners of Raeburn Flow kindly gave permission to core Raeburn Flow. We thank two anonymous reviewers for their valuable comments and sugges-tions, which helped to improve the paper.

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