Soil-plant interactions and the uptake of Pb at abandoned mining sites in the Rookhope catchment of the N. Pennines, UK – a Pb isotope study

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Abstract

This paper examines Pb concentrations and sources in soil, grass and heather from the Rookhope catchment in the North Pennines, UK, an area of historical Pb and Zn mining and smelting. Currently, the area has extensive livestock and sports shooting industries. Risk assessment, using the source-pathway-receptor paradigm, requires the quantification of source terms and an understanding of the many factors determining the concentration of Pb in plants. A paired soil and vegetation (grass and heather) geochemical survey was undertaken. Results showed no direct correlation between soil (total or EDTA extractable Pb) and vegetation Pb concentration. However, regression modelling based on the Free-Ion Activity Model (FIAM) suggested that the underlying mechanism determining grass Pb concentration across the catchment was largely through root uptake. Spatial patterns of $^{206/207}$Pb isotopes suggested greater aerosol deposition of Pb on high moorland and prevailing wind facing slopes. This was evident in the isotopic ratios of the heather plants. Pb isotope analysis showed that new growth heather tips typically had $^{206/207}$Pb values of ~1.14, whilst grass shoots typically had values ~1.16 and bulk soil and peat ~1.18. However, the $^{206/207}$Pb ratio in the top few cm of peat was ~1.16 suggesting that grass was accessing Pb from a historical/recent pool of Pb in soil/peat profiles and consisting of both Pennine ore Pb and long-range Pb deposition. Isotope Dilution assays on the peat showed a lability of between 40 and 60%. A simple source apportionment model applied to samples where the isotope ratios was not within the range of the local Pennine Pb, suggested that grass samples contained up to 31 % of non-Pennine Pb. This suggests that the historical/recent reservoir of non-Pennine Pb accessed by roots continues to be a persistent contaminant source despite the principal petrol Pb source being phased out over a decade ago.

Keywords: lead; mining; isotopic dilution, plants; Pb isotopes; UK

1 Introduction

Heavy metal contamination of agricultural land is a widespread problem in mineralised and formerly mined regions. Drainage of mine waters from adits, the weathering of spoil tips and particulate dispersion are potential sources of contamination of soil (Abrahams & Thornton, 1994; Thornton & Webb, 1975). Incidences of mineral related toxicity in new-born lambs and calves have been reported in historical lead mining districts and have been attributed to ingestion of Pb-contaminated forage or soil and severely polluted water supplies (Aslibekian & Moles, 2003; Smith *et al*. 2010; Thornton & Abrahams, 1983). In addition, many Pb mining areas in the UK are sited in upland moorland regions, where birds such as the Red Grouse (*Lagopus lagopus scotica*) live and feed primarily on the shoots, seeds and flowers of heather (*Calluna sp.*). Lead bioaccumulation in grouse can occur in the bones, cause mortality, neurological dysfunction, immunity suppression and a decrease in reproduction in birds (Kendall *et al*. 1996; Thomas *et al*. 2009). This paper presents a survey of paired vegetation and soil samples in the Rookhope catchment; a small area in rural, upland northern Britain subject to historical Pb mining and smelting. We use the results to assess the (i) spatial distribution, (ii) magnitude and (iii) source of lead within the catchment. In addition, we discuss the possible uptake mechanisms of Pb into grass and heather growing in this catchment, the major food sources for livestock and grouse.

The principal pathways for the enrichment of plants with Pb include (i) systemic uptake via the roots from the soil solution, (ii) dermal sorption from direct aerial deposition on vegetation and (iii) a combination of the above where aerial deposition becomes part of the soil Pb pool either directly or via the recycling of plant organic matter. Recent work on the uptake of trace metal cations by plants has shown that models based on the Free Ion Activity Model (FIAM) are far more effective at predicting uptake than total or ‘extractable’ concentrations (Hough *et al*. 2004; Hough *et al*. 2005). The significance of aerial deposition on the Pb content of plants was reviewed by Cannon (1976), citing studies as far back as Rains (1971) on the unresolved issue of the relative importance of Pb-rich material deposited on the plant versus direct Pb uptake. Jones and Johnston (1991) used the extensive archive of herbage collected at the Rothamstead Experimental Station, UK, to investigate the influence of changing atmospheric inputs since 1860.

The natural variation in Pb isotopes allows their use as tracers for contamination and source apportionment within environmental systems (e.g. soil, plants). Such isotope studies, coupled with the large calculated estimates of emissions to the atmosphere from both domestic and industrial sources have enabled a tool capable of separating diffuse source from local point sources (Murozumi *et al.*, 1969; Bollöfer and Rosman, 2001; MacKenzie and Pulford, 2002). The source apportionment of Pb isotopes in different environmental reservoirs has recently been reviewed by Komarek *et al.* (2008) and included the use of selective soil extractions. For example, Bacon *et al*. (2006) used sequential extractions to examine Pb mobilisation in organic rich soils from an upland catchment in Scotland. More recently, Shepherd *et al*. (2009) described a large scale regional study of Pb isotopes in stream sediments in the Wear catchment, NE England, encompassing the current study area, demonstrating a dominance of local ore Pb signatures in the North Pennine Orefield, but with a significant contribution of deposited industrial or petrol Pb downstream.

In this work we use a combination of Pb isotope analysis to assess the sources of Pb in soil-plant couples and Pb isotopic dilution methods to assess the labile pools of Pb in two peat cores. The results give insights into the relationships between the impact of past local Pb smelting and mining activity and diffuse aerial pollution in relation to plant Pb content and uptake mechanisms. This is key information required for conceptual models of risk assessment for animals grazing in mining contaminated sites.

2 Materials and methods

2.1 Study Area and Historical Context

Rookhope Burn, is a tributary of the River Wear, and is one of several small catchments in an area of abandoned mining associated with the North Pennine Pb-Zn ore-field, U.K. The Rookhope Burn rises to the east of Allenheads and flows through an alluvial channel in an easterly direction towards Rookhope village, before turning south to join the River Wear at Eastgate. A defining feature of the northern catchment boundary is the heath and bog clad ridge of Black Hags and Redburn Common, formed in Grindstone Sill sandstones of the Stainmore Formation (Yoredale Group). This moorland is used for seasonal grouse shooting. The southern boundary of the catchment is defined by a ridge of the same sandstone, covered by shrub heath and used for rough grazing. The steeper sides to the valley have better drainage and are a mixture of rough and improved grassland. These are mainly used for sheep grazing and occur on an inter-bedded sequence of thin sandstones and mudrocks of the Stainmore Formation. The upper valley bottom offers rough grazing. As the stream gradient decreases below Rookhope village into the underlying Alston Formation (a mixed sequence of limestones, sandstones and shales), a combination of improved grassland, with intermittent broad leaved and mixed woodland, is found lining the river banks down to Eastgate. This area also coincides with the development of superficial Devensian till deposits. Despite the clear evidence of Roman occupation in the Northern Pennines (Dunham, 1990) there is little evidence to suggest that there was Roman Pb mining and smelting in the study area. By the Middle Ages, mining and smelting of Pb was certainly in progress (Drury, 1987; King, 1982; Fairburn, 1996). Perhaps the peak of activity in the Rookhope Burn catchment occurred in the mid to late 19th century. Figure 1 illustrates the location of mineral veins and gives an indication of the scale of workings in the Rookhope catchment. Several examples of the mining legacy remain (spoil heaps, processing plants, mine shafts). One of the most prominent is the line of the Rookhope smelter chimney that runs up the fell side to Redburn Common, a distance of almost 2.5 km. Smith and Blackburn (2001) state that this smelt mill was built in 1737 and replaced an earlier smelt mill a little way up the valley at Scar Sike. The later smelt mill operated until 1919 (Houston, 1964), a period of Pb production and processing of at least 180 years. A paper by Louis (1917) indicates that three mines were operational in Rookhope; these were Wolfcleugh, Grove Rake, and Boltsburn. Mining continued at Boltsburn until 1940. In addition, fluorite mining continued at Grove Rake at the head of the Rookhope Burn up to 1999.

There are three major soil associations within the Rookhope catchment as designated by the Soil Survey of England and Wales 1:250000 maps. These are very acidic blanket peat (1011b; Winter Hill), soils formed from superficial deposits of Palaeozoic sandstone, mudstone and shale which have an organic rich / peaty surface horizon and are very acidic when not limed (721c, Wilcocks 1), and soils found in the lowland pastures being formed from superficial deposits of Palaeozoic sandstone and shale (713g, Brickfield 1). The Wilcocks 1 and Brickfield 1 soils are slowly permeable and are prone to waterlogging.

2.2 Soil Sampling procedures, sample preparation and analytical procedures

2.2.1 Soil Survey

Soil samples (0-15 cm) were collected on a series of transects mostly within the catchment at a nominal spacing of 500 m. There were three sample points just outside the catchment (shown in Fig 8a & b). Each sample consisted of a bulked sample of five sub-samples collected on the corners and at the centre of a 5m square grid. This catchment wide sampling strategy was undertaken to be compatible with the Geochemical Baseline Survey (G-BASE) of the UK (Johnson et al. 2005). The soils were returned to the laboratory in kraft bags, air dried and sieved to < 2 mm. Approximately 30 g of the < 2 mm fraction was sub-sampled, ground in an agate ball-mill to produce a fine homogeneous powder used for total metal and Pb isotope analysis.

2.2.2 Collection of peat cores

To complement the original soil and plant survey, the characteristics of Pb lability and solubility were examined in peat cores from two areas of the Rookburn catchment. Peat cores provide an undisturbed historical record of Pb deposition in the area and enable us to use analytical Pb isotope techniques to derive the source and historical mobility of lead. In addition, we used isotopic dilution methods to assess the mechanistic processes involved with the lability and solubility of Pb. Peat cores (0-50 cm) (n=3) were extracted from two locations using a Russian auger. Core 1 was from a lowland peat site (Grid Ref: BNG 387761 544196) whilst Core 2 was taken on the high ridge (Grid Ref: BNG 390157 544786), close to the smelter chimney site. The first core from each site was cut in two lengthwise and then into 12.5 cm sections. Half of each section had pore water extracted using the centrifugation method of Kinniburgh *et al*. (1983). The corresponding half of each core was used to determine characteristics including moisture content, pH, LOI, Pb isotopic composition and isotopically exchangeable pools of Pb. The second core was cut into sections to determine high-resolution information (1 cm) on Pb concentrations and isotope ratios. The 1 cm sections were freeze-dried to facilitate size reduction, pulverised using a hand agate mortar and pestle to > 95 % passing a 100 μm mesh and stored in plastic tubes until required for further analysis.

2.2.1.1 Total metal concentrations in soil and peat samples

Sample digestion for total metal concentrations in soils and peats were undertaken by accurately weighing 0.25 g of soil into a Savillex™ vial to which 4 ml of concentrated HNO_3 acid was added before heating at 80°C overnight until dryness, the purpose being the digestion of reactive organic phases. Digests were cooled prior to the addition of 2.5 ml HF, 2 ml HNO_3 and 1 ml $HClO_4$ concentrated and analytical grade acids, with a subsequent stepped heating program to 160°C overnight, the purpose being the digestion of silicate and oxide phases. The dry residue was re-constituted after warming with 1.25 ml MQ water, 1.25 ml HNO_3 and 2.5 ml H_2O_2, to 25 ml of 5% v/v HNO_3 and stored in HDPE bottles. Reference materials (NIST SRM2710, SRM2711, GSS-6, BGS102 and BCR-2), duplicate samples and blanks were all prepared in a similar manner to check accuracy of the analytical and digestion method. The concentrations of Pb, was determined on the total digest of the soil samples using an ARL3580 ICP-AES instrument. Calibration was undertaken, using synthetic chemical multi-element standards produced in-house from a variety of commercial sources. Similarly, multi-element synthetic quality control standards for calibration verification were produced in-house, but, where possible, from different sources to the calibration standards.

For the peat cores, Pb were determined using an Agilent 7500 quadrupole ICP-MS instrument. The instrument was calibrated using a series of synthetic chemical solutions diluted from multi-element stock solutions (SPEX Certprep™), the calibration being validated using synthetic chemical standards from a separate source. Similarly, multi-element synthetic quality control standards for calibration verification were produced in-house, but, where possible, from different sources to the calibration standards. The calibration and quality control standards were inserted every 20 samples to check possible drift over the run. Data were corrected for blank contributions and possible interferences by running a number of blanks and synthetic chemical solutions of Ba, Ce, Gd, Nd, and Sm. The digest solutions were diluted to within the caibration range prior to analysis.

2.2.1.2 Soil Extractions

A sub-set of 87 of the total of 165 soil samples were extracted using 0.05 M NH_4-EDTA, the BCR-EU standard method (Horckmans *et al*. (2007) to provide an assessment of bio-available Pb. These samples matched those sites from which vegetation samples were collected and analysed. The EDTA extraction was undertaken by shaking 1 g of milled sample with 10 ml 0.05M EDTA in a plastic centrifuge tube for 17 hours. After centrifugation, the supernatant was acidified to 1% v/v HNO_3 and stored in HDPE bottles. NH_4-EDTA was used as it is the most amenable form for direct Pb isotope analysis by ICP-MS. The concentration of Pb was determined using a Thermo Elemental PQ ExCell™ quadrupole ICP-MS instrument. The instrument was calibrated using a series of synthetic chemical solutions diluted from multi-element stock solutions (SPEX Certprep™), the calibration being validated using synthetic chemical standards from a separate source.

2.2.2 Vegetation

All vegetation was sampled using a clean pair of stainless steel shears from an area within 10 m of the associated soil sample and registered grid reference. Each sample was transferred to a plastic bag. Grass was cut down to within 2 cm of the soil surface; no specific species were sampled as different species were prevalent at different sites. Heather was sampled by removing 2-4 cm of fresh tip material. On return to the laboratory all vegetation samples were air dried at 40°C for at least 24 hours before milling to a fine powder using a large volume, low alloy steel, Mixermill and subsequently stored in plastic containers. A 0.5 g aliquot of the powdered vegetation was weighed into a Savillex™ vial and 10 ml of concentrated HNO_3 acid added before heating at 90°C for 14 hours. After cooling a further 1 ml of H_2O_2 was added and the solution evaporated to dryness. The dried digest being reconstituted in 25ml of 10% v/v HNO_3 before storage in HDPE bottles. For the purposes of quality control duplicate samples, reference materials (GBW07602 – *bush branches and leaves*; GBW07605 – *tea*, from IGGE, China; and LSG-1 – *grass*, an in-house material) and blanks were prepared with each batch of samples for analysis. The elemental concentrations of the digested vegetation samples and quality control materials were determined using a Thermo Elemental PQ ExCell™ quadrupole ICP-MS instrument for 16 elements. The instrument was calibrated using a series of synthetic chemical solutions diluted from multi-element stock solutions (SPEX Certprep™), the calibration being validated using synthetic chemical standards from a separate source. The digest solutions were diluted by a further factor of 20 prior to analysis, for some samples a further dilution being necessary for all elements to fall within the defined calibration range.

2.2.3 Lead isotope ratio determinations in soil, peat and vegetation

The Pb isotope ratios of vegetation digests, total soil and peat digests and EDTA soil partial extractions were determined using an Agilent 7500cx quadrupole ICP-MS. The instrument was prepared for isotope ratio determinations before each analytical session, by plateauing of the detector voltage, cross-calibration of the pulse counting-analogue modes and updating of the dead-time correction factors. Isotope ratio determinations were recorded on the basis of 10 replicate integrations of 30s; each integration being 1000 peak jumps (1 point per peak) across the isotopes ^{203,205}Tl and ^{206,207,208}Pb. With reference to the total Pb concentrations in the solutions, prior to analysis, all test portions were diluted using 1% HNO_3/0.5% HCl to give a count rate as close to, but below, 1Mcps on the major lead isotope ^{208}Pb to produce best counting statistics within the linear range of the pulse counting detector. In addition, the test solutions were doped with Tl sufficient to measure close to 1Mcps on ^{205}Tl. The issue of mass bias mass in the isotope ratios was addressed by determining the measured isotope ratio for NIST SRM918 regularly throughout the analytical session and producing interpolated correction factors of sample isotope ratios with reference to the accepted isotope ratios for SRM981 (Thirwell, 2002). Stability of the instrument was such that the use of the $^{205/203}$Tl ratio to determine and correct for mass bias was found to detract from the quality of analysis in terms of both accuracy and precision and therefore not used. Quality control for Pb isotope ratios was performed using an in-house solution produced from a naturally occurring UK galena –“Glendenning”. This has been run repeatedly over several years. Long term (n=37 over 18 months) precision being 0.07% for both $^{206/207}$Pb and $^{208/207}$Pb ratios. Individual sample errors in Pb isotope ratios were calculated by propagating the precision of individual sample measurements and the uncertainty in the measurements of the SRM981 sample used to correct for mass bias. Typical sample uncertainty is shown on the relevant graphs.

2.2.4 LOI and soil pH

Both Loss on ignition (LoI) and pH analysis were undertaken on < 2 mm fraction of the samples. LoI analysis was performed as a proxy for total organic content. The samples were initially dried to 105°C for four hours to remove absorbed water, before weighing into glass beakers. The beakers containing the samples were “ignited” at 450°C for a minimum of 4 hours, before cooling in a desiccator and reweighing. Soil pH was measured by suspending soil in 0.01M $CaCl_2$ solution in the ratio 1:2.5.

2.2.5 Lead Isotopic Dilution assays for Peat samples

Isotopic dilution assays were carried out on peat core samples using ^{204}Pb as the stable metal isotope. The method was similar to that used by Marzouk et al. (2011) using 0.01M $Ca(NO_3)_2$ as the equilibrating electrolyte instead of 0.0005m EDTA. For each sample, 1g of peat was weighed into six 30 ml centrifuge tubes sample and equilibrated with 0.01M $Ca(NO_3)_2$ for 3 days. Three tubes of each sample were used to measure natural Pb isotopic abundances and three were spiked with 0.4ml ^{204}Pb (99.7% ^{204}Pb, Oak Ridge National Laboratories) at a sufficient strength to double the natural ^{204}Pb pool. Suspensions were re-equilibrated for 3 days before filtering the supernatant (0.2μm cellulose acetate filters). To discriminate between true labilie Pb species and non-labile colloidal-Pb in solution, a resin stage was undertaken whereby 10ml of solution was shaken with 0.1g Chelex 100 grade resin (Bio-Rad Laboratories, UK) for an hour. The chelex-100 resin was converted from Na to Ca form to reduce the pH of the resin from 10.05 to 7.90. The resin was then eluted using 5% HNO_3. Solutions were analysed by ICP-MS (Thermo-Fisher XSeries^{II}) to determine isotopic abundances of ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb.

The labile pool or ‘E-Value’ for Pb was determined using eqn 1.

$$LabilePb = \left(\frac{M_{Pbsoil}}{W}\right)\left(\frac{C_{spike}V_{spike}}{M_{Pbspike}}\right)\left(\frac{{}^{204}IA_{spike} - {}^{208}IA_{spike}RSS}{{}^{208}IA_{soil}Rss - {}^{204}IA_{soil}}\right) \qquad \text{Eqn 1.}$$

where M_{PbSoil} is the average atomic mass of Pb, C is gravimetric Pb concentration (mg L^{-1}), V is the volume of added spike (L), W is the weight of soil (kg), IA denotes isotopic abundance of a particular isotope in the spike or soil and RSS is the ratio of isotopic abundances for ^{204}Pb to ^{208}Pb calculated for the spiked soil supernatant.

Atkinson *et al*. (2011) examined the source of non-labile and labile Pb. To characterise the Pb in the whole soil and the labile pool, ratios of Pb were measured in the acid digest and the electrolyte used to determine the labile pool, respectively. Isotope ratios in the non-labile pool were calculated from consideration of mass balance and the measured proportion of isotopically exchangeable Pb (Equation 5). Thus for $^{206/207}$Pb

$${}^{206/207}Pb_{NL} = \frac{{}^{206/207}Pb_{soil} - \left({}^{206/207}Pb_{L} x P_{L}\right)}{\left(1 - P_{L}\right)} \qquad \text{Eqn. 2}$$

where $^{206/207}$Pb refers to the isotopic ratio ($^{206/207}$Pb) in the Total (Soil), labile (L) and non-labile (NL) pools of the soil and P_L is the molar proportion of labile Pb in the soil.

2.2.5 Grass Pb uptake modelling

The model used to predict plant uptake was based on the Free Ion Activity Model, after Hough *et al*. (2004). It is based on a pH-dependent Freundlich relation that can be used to describe metal solubility in soils (e.g. Tye *et al.* 2004). The equation predicts free metal ion activity for Pb in the soil pore water (M^{2+}) from total soil metal content which is assumed to be adsorbed on humus, [M_C] (mg of a specific metal per kg of soil organic carbon), and soil pH:

$$p\left(M^{2+}\right) = \frac{p\left[M_c\right] + k_1 + k_2 pH}{n_F} \qquad \text{Eqn. 3}$$

where k_1 and k_2 are empiric, metal-specific constants and n_F is the power term from the Freundlich equation. Metal uptake by plants can be characterized by a soil-to-plant transfer factor (TF) (Eqn. 4.). This concept can be used to describe the quotient of metal concentration in the plant [M_{plant}] (Mol kg^{-1}) to metal ion activity in soil pore water (M^{2+}) (mol L^{-1}) derived from Equation 3:

$$TF = \log\frac{\left\lfloor M_{plant}\right\rfloor}{\left(M^{2+}\right)} \qquad \text{Eqn. 4}$$

Equations 3 and 4 can be combined into a single expression relating [M_{plant}] to pH and [M_C] (Equation 5) where C, β1, and β2 are empiric metal- and plant-specific coefficients.

$$\log\left[M_{plant}\right] = C_1 + \beta_1\left[pH\right] + \beta_2 \log\left[M_c\right] \qquad \text{Eqn. 5}$$

3 Results

3.1 Soil geochemistry

Key soil geochemical parameters for each sample are summarised in Table 1 for the grass dataset and Table 2 for the heather dataset. The majority of soils have high organic matter content and low soil pH indicative of either peat soils (Winter Hill) or those with organic rich surface horizons (Wilcocks 1 & Brickfield 1 associations). Land-use is predominantly rough grazing or moorland peat and heather. An important feature of relatively undisturbed soils with high concentrations of organic matter in the surface horizons is that aerially deposited contamination from mining, smelting and long range sources will be concentrated in reservoirs close to the surface as has often been demonstrated for peat deposits (Novak *et al*. 2008; Weiss *et al*. 2002).

3.2 Total and EDTA extractable Pb concentrations in soil

The total Pb content of the soils varied from background concentrations to highly contaminated (13–27600 mg/kg) and are comparable to those reported in Kabata-Pendias, (2001) for historical mining areas (Table 1 and 2). The EDTA-extractable Pb covers a wide concentration range with the maximum concentrations being approximately half of the total Pb (Table 1 & 2). Figure 2 shows the proportion of extractable Pb (%) compared to the total Pb concentration. At the lowest and highest total Pb concentrations the EDTA extractable proportion is typically lower. Solid phase Pb speciation is likely to be the underlying geochemical control: at the lowest concentrations (10's mg kg^{-1} total Pb) a higher proportion of Pb is likely to occur within the silicate lattice of the soil and is unavailable for extraction. In the soils with high concentration (1000's mg kg^{-1} total Pb), Pb is likely to be present mainly locked up within the sulphide ores, thus being insoluble to the EDTA extraction.

3.3 Concentrations of Pb in Vegetation

The range of Pb concentration in grass from the Rookhope catchment spans three orders of magnitude (0.8 – 48 mg kg^{-1}) (Table 1) with an inter-quartile range of 2.7 – 16.7 mg kg^{-1}. The highest concentrations of Pb in grass were often found close to spoil heaps or within the vicinity of smelter operations. For heather, Pb concentrations ranged from 1.17 to 7.64

mg kg^{-1} with an inter-quartile range of 1.6-2.9 mg kg^{-1}. When compared to the literature, Notten *et al*. (2008) found a Pb concentration range of 0.41-1.27 mg kg^{-1} in mixed leaf material from contaminated floodplain soil in Biesbosch, Germany, whilst Smith *et al*. (2009) gave median values of between 3 and 60 mg kg^{-1} for washed herbage from floodplain soils in Wales.

3.4 Lead uptake into grass

The relationship between grass and heather with total lead and EDTA extractable lead concentrations were investigated. Weak positive correlations between vegetation and soil Pb for grass were found but these only had probability values of 0.007 and 0.110 for EDTA extraction and the total Pb respectively. Similarly, low probability values for heather 0.100 (EDTA) and 0.069 (total) signify no or very weak correlations. The poor correlations found between total and EDTA soil Pb and the concentration in grass and heather is unsurprising. It is increasingly recognized that improved predictions of trace metal uptake into plants can be found using models such as the Free Ion Activity Model (FIAM) (Hough *et al.* 2005). These models assume the uptake of metals into plants is associated with the intensity factor of free metal ion activity (M^{2+}). It has been observed that even washing with EDTA can still leave traces of aerosol Pb (Rains, 1971; Notten *et al*. 2008) on vegetation, thus making Pb uptake modelling more difficult than other metals. However, Smith et al. (2009) found that during the summer months there was very little difference in Pb concentrations between unwashed and washed samples as there is a considerable reduction in soil contamination and rapid grass growth. Therefore, whilst appreciating the potential that some aerosol Pb may be present on the grass surface, we undertook a modelling exercise based on equation 5 to predict Pb concentrations in grass.

The grass uptake model covers a range of total soil Pb concentration of between 48-27586 mg kg^{-1}, soil pH values between 2.89 - 7.43 and organic matter concentrations of 6.1 - 95.8%. Values of C_1=3.229, β_2=0.123 and β_3=0.544 were obtained and the model had a Residual Standard Deviation of 0.33. Reasonable predictions of grass metal concentrations are produced (Figure 4) for both peat and soils within the Rookhope Catchment. This analysis demonstrates the complex relationships between soil pH, total soil metal concentration and the intensity factor (Pb^{2+}) that control the uptake of Pb^{2+} in grass at Rookhope. Competition from other cations such as Ca^{2+}, Zn^{2+} and Cd^{2+} is likely. However, in low pH soils such as peat, it is also likely that H^+ will act as the major competing ion, as demonstrated by Hough et al. (2005) for Zn and Cd uptake into grass (*Lolium perenne)*.

The results suggest that systemic uptake of (Pb^{2+}) could account for much of the grass Pb concentration across the catchment. Sources of soil Pb that the grass roots may access include (i) natural geogenic Pb, (ii) recently deposited Pb, particularly from rain that enters the soil or a (iii) pool of recent and historically deposited Pb consisting of local and long range aerially transported Pb (e.g. Pb smelting and petrol combustion). These different sources of historical/recent Pb may be continually recycled from the soil to plants through senescence and management activities such as heather burning. The significance of these different Pb sources is investigated using Pb isotopes as tracers.

3.5 Lead Isotope Ratio Geochemistry in soils and plants

To elucidate the uptake of lead in the grass and heather further we analysed Pb isotope ratios in the soil and plants. Within the UK the dominant sources of Pb released into the environment, and commonly used as end members in mixing models are the Pb used in petrol lead ($^{206/207}Pb$ = 1.06 - 1.09) which was a combination of older Australian Pb

($^{206/207}$Pb =1.04) and British Columbian Pb ($^{206/207}$Pb = 1.16) (Vinogradoff et al. 2005) and native Pennine Pb coal/ore (typical $^{206/207}$Pb values range from 1.160-1.207). The Pb used in petrol was primarily derived from the “Broken Hill Mine” in Australia (Sugden *et al*. 1993). However, other sources of aerosol Pb have been recorded in the UK with a range of 1.06 – 1.13 (Charlesworth *et al*, 2006; Noble *et al*, 2008). As ‘Broken Hill Type’ Pb was the major source of non-Pennine Pb in the UK, we therefore refer to all sources of non-Pennine Pb as ‘Broken Hill Type’ or ‘BHT’ Pb in the following discussion for simplicity. In addition, because deposition of non-Pennine Pb has occurred over a long period of time, the $^{206/207}$Pb isotope ratio found in soils and peats is likely to be an integrated ratio of recent and historical deposition and as a result of ploughing, grazing and recycling through managed heather burning.

Lead isotope ratios were determined in some of the total and EDTA extractions from soils and the vegetation (Tables 1 and 2). These were plotted together with potential end-member compositions from previously published data. A bi-variate plot (Figure 5) of the $^{206/207}$Pb versus $^{208/207}$Pb isotope ratios demonstrates that all samples fall along a simple mixing line. The soil samples, both total and partial extractions, cluster at one end of the data array (Pennine ore Pb) whilst the grass and heather samples extend down the mixing line, towards the isotopic composition of ‘BHT’ Pb. When the total and EDTA soil extractions (min. – median - max $^{206/207}$Pb = 1.174-1.179-1.182; $^{208/207}$Pb =2.456-2.461-2.466; n=40), are compared to previously reported values for Weardale-Rookhope galena samples (Rohl (1996): median $^{206/207}$Pb = 1.179; $^{208/207}$Pb = 2.461; n=14 and Shepherd *et al*. (2009): median $^{206/207}$Pb = 1.193; $^{208/207}$Pb = 2.472; n=4) or Rookhope stream sediments (Shepherd *et al*. (2009): median $^{206/207}$Pb = 1.182; $^{208/207}$Pb = 2.462; n=4) the results are in good agreement.

The vegetation array from the current study fall along a mixing line between the Weardale galena samples of Rohl (1996) and values obtained for end member aerosols from Liverpool and the Isle of Man sampled in 1997 (Charlesworth *et al*. 2006) and central London sampled in 2001 (Noble *et al*. 2008); the galena having been extensively worked and smelted within the catchment and 'BHT' aerosol Pb being a major generic contributor to diffuse Pb pollution in the recent past (Bollöfer and Rosman, 2001; Komarek *et al*., 2008). The difference in sampling dates for the London (2001) and Liverpool/IoM (1997) sets of aerosol Pb data is significant as they cross the time line for the cessation of the use of tetra-ethyl lead additives in petrol in the UK. Therefore, it is expected that both Pb concentrations and the isotopic signature of aerosol deposition will have changed in the period 1997–2001 and potentially, have further changed by 2007 when the current sample set was collected.

In Pb source apportionment it has been common to derive contributions of different sources of Pb (e.g. Pennine or 'BHT') using mixing models (e.g. Farmer et al. 2005) for soil and plant samples. The model is based on defined end members such as the mean Weardale galena value (Rohl, 1996; Shepherd et al. 2009) and the mean petrol Pb value (Sugden et al. 1993; Vinogradoff et al. (2005). However, for our soil samples the isotope ratios are all within or very close to the range of values for Weardale galena (1.178 – 1.206). Thus, it would be very difficult to obtain meaningful values for the contribution of 'BHT' Pb because of the potential variability of the Weardale end members. However, for those plant samples where the isotope ratios vary considerably from the Pennine ore we estimated the amount of non-Pennine Pb with respect to the values for galena and 'BHT' used in the model. Thus for plant samples:

$$\mathrm{Pb_{BHT}}\ (\%) = \frac{\left[\left[\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right]_{Ore} - \left[\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right]_{Sample}\right]}{\left[\left[\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right]_{Ore} - \left[\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right]_{BHT}\right]} \times 100 \qquad \text{Eqn. 6}$$

Where:

$^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{ore}}$ = 1.182 as the mean of galenas (n=14; +/- 0.014 2sd) from Weardale recorded by Rohl (1996)

$^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{BHT}}$ = 1.076 as taken from Sugden *et al*. (1993) after Delves (1988)

$^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{sample}}$ = sample values in the current study

The proportions of 'BHT' Pb found in plant samples where there is a reasonably large difference in $^{206/207}$Pb isotope ratios between the plant and the soil are shown in Tables 1 & 2. The heather shows a 'BHT' Pb contribution of between 10 and 35%, whilst the grass has a wide range of contributions between 7 and 31%.

Lead isotopic homogeneity of the different sample matrices at each site was investigated by comparing the $^{206/207}$Pb ratio of each grass, heather and soil EDTA partial extraction with the $^{206/207}$Pb ratio of the soil total Pb from the same site (Figure 6). The soil EDTA extractable Pb was essentially isotopically similar to the total soil Pb. This is perhaps not surprising as EDTA is a powerful extractant and will dissolve a high proportion of the total Pb (Figure 2). Some grass samples (n=8) give a similar isotopic ratio as their paired soil sample whilst a second group of grass samples (n=6) have lower isotopic values than their paired soil sample. The heather samples were all isotopically different from their parent soil.

To investigate the effect of different sources and element concentrations on isotope ratios, especially for samples influenced by more than one isotopic source, it is conventional to plot isotope ratio against the reciprocal of concentration. This ensures that when two isotopic end-members of fixed composition are mixed in different proportions, the samples plot along a linear array (Faure, 1977). The samples for all matrices are shown in this way in Figure 7. For clarity the vegetation and soils concentrations are plotted on different scales. Both total and EDTA extractable Pb, at concentrations lower than 200 mg kg^{-1}, form a single linear array with a uniform $^{206/207}$Pb ratio of 1.178; whilst at higher concentrations the spread of isotope ratios increases to encompass 1.174-1.182, diagnostic of the addition of two or more isotopically distinct Pb sources of both lower and higher ratios. All but one of the soil Pb isotopic ratios are similar to local ore Pb in the range 1.177-1.198 as determined by Rohl (1996). The heathers form a weak array but with a greater slope than the grass. The lower "background" $^{206/207}$Pb ratio is approximately 1.146, with higher concentration samples at 1.165 and the array projecting to an end-member close to the background soils. The grasses also form a weak diffuse array with lower concentrations tending to a $^{206/207}$Pb ratio of 1.150 and the highest grass concentrations similar to the highest soil concentrations at approximately 1.18. These results are consistent with a mixing of different concentrations and proportions of 'BHT' Pb from aerosol and local Pennine Pb from the soil.

3.5 The spatial distribution of Pb isotopes in vegetation

The spatial distribution of Pb isotope ratios in the vegetation within the Rookhope catchment was examined. Isotope ratios were split into 4 categories (Figure 8a). A majority of the grass samples with local ore Pb isotopic signatures (1.181-1.217) are found in the valley bottom. These values are consistent with the original primary ore and smelting activity and show little influence of 'BHT' Pb. Grass samples on slopes facing the prevailing wind generally have $^{206/207}$Pb values of 1.157 -1.169. Only one grass sample, found at the highest point, just out of the catchment has a value in the lowest $^{206/207}$Pb isotope ratio category of 1.146-1.156, this being similar to most of the heather samples. Grass growing on the leaward slopes generally has $^{206/207}$Pb ratios between 1.170 – 1.180. The lowest category of $^{206/207}$Pb ratios (1.146 – 1.156) contains all the heather samples, with one exception. Heather occupies most of the highest altitudes or is on slopes facing the prevailing wind. The spatial distribution of $^{206/207}$Pb ratios found is evidence for the historical and recent long range transport of 'BHT' aerosol Pb impacting sites with higher altitudes and the prevailing wind direction.

Comparisons of $^{206/207}$Pb ratios in paired grass and heather samples were undertaken at 6 sample locations. At two of the locations (sample nos: 5 & 1014), grass samples had similar $^{206/207}$Pb isotope ratios to the heather samples. The $^{206/207}$Pb ratios for grass and heather for sample 5 (leeward slope) were ~1.16. However, for sample 1014, one of the the highest sampling points in the catchment (altitude = 1840m) the $^{206/207}$Pb ratio for both grass and heather was 1.149. This is a value similar to the majority of heather samples (Table 2) facing the prevailing wind or on the high moors. However, it is the only grass sample with such a low $^{206/207}$Pb value. Thus, considering the different growth periods of the sampled grass and heather shoots, there is a strong indication that if current aerosol $^{206/207}$Pb deposition straight onto plant surfaces was a dominant contributor to plant Pb concentrations, a value of ~1.14 would be obtained. Therefore this would indicate that grass samples with $^{206/207}$Pb values of ~1.16 are obtaining their Pb from a largely different source (e.g. soil where Pennine and 'BHT' aerosol Pb are mixed). This is demonstrated at the other 4 sites where paired heather and grass samples were obtained (sample nos: 516, 1002, 1006, 1023). Heather had $^{206/207}$Pb ratios that were considerably lower (~1.14) than the grass plants (~1.16). It is likely that heather with it's taller architecture, and longer growth period is a better scavenger of current aerosol Pb, depending on spatial position.

3.7 Pb solubility and source apportionment using historical archives of Pb in peat cores

Many of the grass and heather plant samples were growing in peat or uncultivated (rough pasture) soils where high organic matter surface horizons have developed. These horizons typically provide historical/recent archives of pollution where atmospherically deposited metals accumulate. We used peat cores samples with Pb isotope geochemistry and isotopic dilution techniques to undertake a more detailed analysis of Pb source and bioavailability.

3.7.1 Total Pb concentration and source apportionment in peat cores

In the two peat cores, Pb concentration varies over two orders of magnitude (Figure 9). Lead is present at higher concentrations at the surface, substantially increases between 3-10 cm depth, peaking at 7 cm depth, and decreases with depth thereafter. Whilst the distribution profile is similar for both cores, the absolute concentrations of lead at 3-10 cm depth differ and reflect the proximity of Core 2 to the smelter chimney, where 2500 mg kg^{-1} Pb was measured at 7 cm depth. Although the enrichment of Pb at 3-10cm is lower in Core 1 (lowland core), the peak is comparatively broader, suggesting that Pb is more evenly distributed at those levels. Careful inspection of log Pb concentrations (Fig. 9, Inset) shows that Pb concentrations in Core 1 steadily decline and reach background concentrations at about 40cm, whilst in core 2, the Pb concentrations declines more rapidly and reaches background concentration at 30cm. However, the results, suggest that the vast majority of 'BHT' Pb that has accumulated has been relatively immobile and has accumulated in the top 10 cm, with possible slight enrichment of Pb down the core.

The isotope analyses of the two peat cores (Figure 9) suggests that the Pb is dominated by the Weardale galena (^{206}Pb/^{207}Pb `= 1.178 – 1.206) isotope signature (Shepherd et al., 2009; Rohl, 1996). The distribution of isotope ratios with depth is also similar for both cores. The lowest ^{206}Pb/^{207}Pb ratios (1.161-1.165) were measured at the surface and sharply increased within the first 3 cm. The lower Pb ratios can be attributed to 'BHT' Pb inputs essentially concentrated in the upper 3 cm (Figure 9). As described previously, the location of Core 2 increases its exposure and favours the capture of atmospheric 'BHT' lead, leading to lower ^{206}Pb/^{207}Pb ratios at (sub)surface levels in comparison with Core 1. These observations suggest that Pb from sources other than the Pennine Ore remain mostly concentrated in the upper peat profile (0-3 cm). At greater depths (4-50 cm), ^{206}Pb/^{207}Pb ratios showed minor temporal variations within a narrow range (1.175-1.182) in good agreement with the Pennine ore signature (Rohl, 1996). Core 2 showed slightly higher ^{206}Pb/^{207}Pb ratios compared to Core 1 throughout the profile. Interestingly, the $^{206/207}$Pb signiture does not decrease at the surface as has been found in recent studies of Pb in ombrotrophic peat bogs, where a increase in $^{206/207}$Pb ratios has been found at the surface, reflecting the withdrawal of Pb used in petrol (Farmer et al. 2006). Possible reasons for this are (i) that the surface of the peat has been bioturbed by grazing and (ii) that managed heather burning is a way in which to recycle plant Pb back to the surface of the peat (Odigie & Flegal, 2011).

If isotope and total Pb data are combined, it is apparent that the aforementioned enrichment in Pb at 3-10 cm depth in both cores probably traces the peak of Pb mining activities in the area. As mining activities ceased a few years ago, Pb releases into the environment decreased and other sources of Pb were less well masked, with the result of clear isotopic shifts. The fact that the peat array falls along a mixing line between the North Pennine ore signatures (Rohl, 1996) and the 'BHT' Pb supports them as possible end-members of sources (Figure 10). The North Pennine ore component is dominant as most samples tend to cluster towards this end, but the 'BHT' Pb contribution appears to be relevant in samples from the top of the core where the $^{206/207}$Pb isotopic ratios are lower than the range for the Weardale galena (1.178 – 1.206). Based on equation (6), the contribution of 'BHT' Pb was estimated at 16% of the total Pb at the surface of Core 1 whereas in Core 2 'BHT' Pb accounted for 19% due to its landscape position and higher exposure to atmospheric deposition.

3.7.2 Lability of lead and source apportionment in labile pools in peat cores

Isotopic dilution (ID) assays allow an improved assessment of the reactive pool of Pb in soils compared to the 0.05M EDTA extractant. The reactive pool of Pb is in equilibrium with the soil pore water and is therefore available for uptake by the grass via the FIAM. Lability of Pb in the peat cores using ID was between 40-60 % (Table 3), irrespective of depth implying degrees of organic degradation have not influenced Pb mobility. Atkinson *et al*. (2011) examined Pb lability in a peat soil (pH 5.3) amended with industrial and sewage waste and found a lability of ~65%. The Pb isotope ratios in the ID assays values are similar to those found after the EDTA extraction (Table 1). Using Eqn. 2, the isotopic ratio of $^{206/207}$Pb in the labile and non-labile pools do not show distinctive isotopic signatures attributable to a single Pb source, (e.g. Pennine Pb ore or 'BHT' Pb) and are similar (Figure 12). This suggests that the Pb from diverse sources is almost completely mixed throughout the labile and non-labile pools in the cores despite probable differing times of deposition. Figure 12 shows that for Core 1 (lowland) there are not large differences in the $^{206/207}$Pb isotope ratio between the total and labile pools. However in

Core 2, close to the smelter chimney, there appeared to be a shift in isotope values in the top 25cm, and only small differences between 25-50cm, suggesting that the labile pool contains a greater proportion of 'BHT' Pb close to the surface.

3.7.3 Pb concentrations, isotope ratios and source apportionment in peat pore waters

The pore water concentrations of Pb were ~ 400 µg L^{-1} in the top 12.5 cm and decreased with depth (6-95 µg L^{-1}) (Table 3). Values of K_d using the labile pool (M_{Lab}) and determined as in equation 7 are in the range 500-2000 L kg^{-1}.

$$K_d = \frac{[M_{Lab}]}{[M_{sol}]} \qquad \text{Eqn. 7}$$

Fig 12 shows the difference between isotope values in the labile and pore water pools. In both cores, there is a distinct shift to lower $^{206/207}$Pb values compared to the isotopic signiture of the total pool. Similar shifts are found in core 2, suggesting a more recently deposited Pb isotope signiture away from the Pennine Pb. In theory, the labile and pore water pools should have similar $^{206/207}$Pb signitures, as in the top 25cm of Core 2. However, this was found not to be the case generally, suggesting that there may be recently deposited Pb in the pore waters that has not yet reached isotopic equilibrium with the labile pool. One such source may be Pb deposited in rainwater. Recent studies by Bacon *et al*. (2006) and Dawson *et al.* (2010) have suggested that soil pore waters and spatially associated stream waters can show different Pb isotope signatures compared to the soil; indicative of a greater mobility for recently deposited anthropogenic lead of aerosol origin. However, whilst our results may suggest that the solubility of 'BHT' Pb is slightly greater, a more detailed investigation is required to demonstrate this more conclusively.

4. Discussion

The aims of this paper were to assess the spatial distribution, source and extent of Pb contamination in the soil and vegetation of the Rookhope catchment. This will aid understanding of potential Pb bio-accumulation in cattle, sheep and grouse. A number of potential pathways exist through which Pb can be ingested with plant material by grazing animals. These include (i) aerosol lead (local or 'BHT') that falls onto the soil, dissolves, mixes with lead already present and is taken up systemically through the plant roots (e.g. the FIAM model), (ii) aerosol Pb directly falling on the vegetation surface and ingested directly and (iii) soil particles containing Pb landing on vegetation through rain-drop splatter of soil. It is highly likely that for grazing animals the sources of Pb in vegetation will have contributions from each of these pathways. This study has identified that soil and plant Pb comes from a range of sources. The major Pb source is the local Pennine lead ore, but a not insignificant component of 'BHT' Pb was found in the top few cm of peat cores and vegetation (up to 34 %) depending on spatial position. The soil survey has provided important information regarding the extent of Pb soil contamination throughout the catchment. Smith *et al*. (2010) showed that ingestion of Pb from soil, either directly through grazing or through soil splash onto vegetation could account for 34-97% of Pb ingestion into sheep depending on the degree of soil contamination and season. Whilst soil ingestion may be the principal pathway, the same authors report that total daily intake of Pb via herbage ingestion could vary between 3-471 mg day^{-1}, again depending on contaminated site and season. Thus, ingestion of Pb via herbage, is an important bioaccumulation pathway for cattle, sheep and grouse.

Spatial position within the catchment was found to influence the size of the total soil Pb pool and isotopic composition (e.g. proximity to mining operations or the position in landscape with respect to altitude and prevailing wind). However, our results suggest that across the different contaminated soils of the catchment, the underlying mechanism determining grass Pb concentration was through plant uptake. This hypothesis is strongly supported by the reasonable parameterisation of the FIAM model. This result differs slightly from the interpretation of results presented by other authors where it is suggested that plant concentrations of Pb are dominated by deposition. For example Bacon et al. (2005) suggested that only ~20% of Pb came from the soil in a study where they spiked the soil with ^{207}Pb. Watmough & Hutchinson (2004) also found a high proportion of pollution Pb in woodland vegetation. However, in both these studies the results did not differentiate between direct deposition on leaves or the deposition of Pb to soil and the subsequent uptake through the root system. It has been considered that Pb is rapidly fixed in soils but the recent use of isotope dilution techniques have shown that the reactive pools of Pb in soils are surprisingly large. In this study the labile pools of Pb in peat were found to be between 40-60 % whilst in another recent survey of soils from the Rookhope catchment the lability of Pb was found to be between 20 - 80 % of total metal concentration (Marzouk, 2012). In another study, Degryse et al. (2007) suggested that the lability of Pb in soil was greater than what was intuitively expected, as it has always been assumed that Pb sorbed strongly to poorly crystalline FeO and organic matter. In addition, they suggested that ageing, sorption and precipitation reactions may also be limited. A further indication of the extent of Pb uptake through plant roots in contaminated soils, such as the ones in our study, can be found in experiments assessing remediation strategies. Both lime or phosphate applications have been found to decrease dramatically the uptake of Pb by grass in contmainated soils (Gray et al. 2006; Friesl-Hanl et al. 2009) confirming that uptake of Pb by roots takes place in contaminated soils.

However, it is important to assess the results of the FIAM in conjunction with the soil and plant $^{206/207}$Pb isotope results. If the FIAM model is the underlying mechanism that accounts for much of the plant Pb uptake across the soils of the catchment, it would be expected that the plant $^{206/207}$Pb ratio would not differ considerably from the soil $^{206/207}$Pb ratio. Ideally this comparison would be made with the labile Pb pool as it is this that supplies the solution phase (Tye et al. 2003). Results in Table 1 where paired soil and grass isotopes are presented show that the dataset breaks down into two groups. One group (Sample nos: 25, 28, 509, 518, 534, 539, 1002, 1041, 0018) where the isotope ratios are similar for soil and plants and a second group (Sample nos: 0005, 0524, 1014, 1023, 1046, 0014) where the plant $^{206/207}$Pb data is lower ($^{206/207}$Pb = 1.15-1.16) than the soil ($^{206/207}$Pb = 1.17-1.18). The first group of samples are generally those samples found at the bottom of the valley and include soil samples that have been mixed when the pasture was improved. The second group of soils are those identified in Section 3.5 and represent sample sites facing the prevailing wind and on the high moors. These spatial locations are expected to have had greater deposition of aerosol Pb over many years and are predominatly peat soils. We believe that the discrepancy between soil and plant isotopes found in the second group of soils is largely a result of the low resolution (0-15 cm) sampling used in this study. However, we stated previously (Section 3.7.1) that the Pb enrichment in the peat cores represents the integrated non-Pennine 'BHT' Pb deposition. Therefore, assuming only small amounts of Pb mobility after deposition, the top of the peat core should be most representative of recent Pb deposition. When compared to the $^{206/207}$Pb ratios in the majority of grass samples, these values are found to be reasonably close to the plant isotope values, (Top 1cm peat values for $^{206/207}$Pb in cores 1 & 2 = 1.1615 & 1.1655; Plant values 1.149-1.165; median=1.1600). Thus, recently deposited Pb is likely to be assimulated by the plants as it becomes part of the labile pool and before progressive sorption and fixation processes occur over time to some degree. The suggestion that plant uptake is the underlying mechanism for grass Pb concentration across the catchment is further demonstrated by the difference in paired heather and grass $^{206/207}$Pb ratios as described in Section 3.5. It appears likely, that that the grass is obtaining Pb from a combination of Pennine and 'BHT' sources, but predominantly from the soil.

The high resolution analysis (1cm increments) of peat cores has demonstrated that much of the deposited 'BHT' Pb is relatively immobile and remains in the top few cm in peat or undisturbed organic rich soil profiles. The use of isotope dilution and pore water analysis on the peat cores has developed our understanding of the behaviour of Pb in organic rich soils/peat. We found relatively high Pb lability as well as mixing of the different Pb sources throughout the labile and non-labile pools. Thus, it can be postulated that grass roots are also likely to extract Pb from environments of high 'BHT' Pb bioavailability in the top few cm. For example, in Core 2, these environments (1cm sections) could have up to 2500 mg kg^{-1} Pb with 40-60% lability. This is particularly relevant when in waterlogged conditions, such as peat, much of the root growth is likely to be shallow so as to stay in more oxygenated environments. These factors may contribute to the high levels of 'BHT' Pb levels found in the grass. Whilst, this discussion has focused on the uptake of Pb to grass, it is likely that some of the uptake of Pb to heather may be through the root system, although isotope ratios ($^{206/207}$Pb = 1.14 - 1.15) suggest a greater direct deposition on the plant surfaces. However, the soil pH data range was too narrow to model effectively in this study to assess whether it would follow the FIAM.

We estimated the proportion of non-Pennine ore lead in some grass and heather samples. It was estimated from the simple mixing model (eqn. 6) that up to 31% in grass and 37% in heather was present. Sources of 'BHT' Pb will include both historical and current deposition. A further recycling pathway will include the redistribution of Pb from the peridical burning as the heather is managed. It is likely that the contribution from aerosol deposited Pb is not as great as it was in recent decades. This can be seen in data from the UK National Air Quality Archive, (2009). Selected data are shown in Table 4. The sites cover two major conurbations from the UK: Glasgow, historically associated with heavy industry and London having lighter industry, but a high degree of car congestion; Styrrup is a rural location but very close to the A1(M) and therefore subject to high speed traffic deposition and Windermere, a rural location, with a low traffic density. The major change in Pb load, by up to an order of magnitude in the urban sites, occurred with the reduction in petrol lead between 1980 and 1997; During the period 2001-2007 a further decrease by a factor of two in air lead concentration was observed. Perhaps most importantly though, is the decrease in the national contribution of vehicular traffic to atmospheric lead from total domination in 1980 to significant contribution in 1997 to insignificant contribution since 2000. However, along with the decline in Pb aerosol concentration is knowledge of how Pb isotope ratios have changed with time. Bacon *et al*. (1996) analysed Pb isotope ratios for grass collected annually since 1860, at Rothamsted in the south of England. They observed a constant $^{206/207}$Pb isotope ratio (1.170) resulting from coal burning and industrial use of UK ore lead, but only until ~1880, before declining to values of 1.098 between 1980-1985. Importantly, they noted that the initial rise in ratio was well in advance of the introduction of tetra-ethyl lead in petrol and an additional anomalous high ratio between the years 1945-1950, indicating short as well as long term changes in the use of overseas lead in industry. Farmer *et al*. (2002) found similar trends when analysing a sphagnum moss archive from Scotland. This is a reminder that it is incorrect to assume measured isotope ratios anomalous to UK lead ore signatures result only from the addition of lead via petrol. This may have been substantially true in 1980 with a 90% contribution to aerosols from traffic, but is certainly not the case since the 1990’s. Current (2007) estimates of Pb deposition in Weardale are <1g km^{-1} a^{-1} according to the DEFRA metal deposition inventory for the UK. (http://pollutantdeposition.defra.gov.uk/node/409).

One consequence of plant Pb uptake being via the uptake of (Pb^{2+}) is that in old mining areas, a simple soil geochemical survey based on total or EDTA extractable metal concentrations will not easily identify areas of vegetation with high Pb concentrations. For example in many of the peat soils (e.g. WD0005, WD0006, WD0014; Table 1), where very low pH values occur with high soil Pb concentrations, the grass Pb concentrations are actually lower than in many of the other samples, probably because H^+ competition reduces metal uptake (Hough *et al*. 2005).

5 Conclusions

A combined vegetation and soil survey was undertaken within the Rookhope Catchment to assess the extent of Pb contamination in soils, grass and heather as an aid to understanding potential bio-accumulation in grouse, sheep and cattle. We found spatial differences in Pb concentration and isotope composition related to the historical proximity to mining and smelting activity as well as landscape position, controlled largely by altitude and prevailing wind direction. The application of a FIAM for lead uptake in grass across the catchment using the data from the simple soil geochemical survey of total metal, pH and LOI concentrations produced reasonable predictions of lead concentrations, whilst there always being potential for some aerosol Pb to be retained on the vegetation. Despite recent steep declines in 'BHT' aerosol Pb, the grass and heather Pb isotope data from elevated and prevailing wind locations showed that it can still contain considerable quantities of 'BHT' Pb. If grass conforms largely to the FIAM for plant Pb uptake as suggested, it is apparent that the grass is accessing a historical/recent soil pool of lead that has built up over many decades, where ‘BHT’ Pb still resides in the top few cm. In the acidic peats, the use of isotopic analysis has demonstrated that there is almost complete mixing of Pb between the labile and non-labile pools of Pb and generally high lability, allowing the grass access to the reservoirs of ‘Broken Hill type’ Pb and increasing its content in the vegetation. These results demonstrate that although petrol Pb was phased out in 2000, it resides in soil reservoirs and is highly persistent in the environment. The results of the current study also has important ramifications for sampling strategies where plant uptake processes need to be considered in addition to soil Pb data to understand the potential bio-accumulation of Pb in cattle, sheep and grouse. Results demonstrate that sampling strategies need to be developed for particular soil types and scenarios. For undisturbed, organic rich soils there is a need for high resolution sampling strategies in the top few cm of peats and organic rich horizons to develop improved understanding of Pb lability, source and the subsequent interactions with pore waters and plant uptake.

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Table 1: Soil and vegetation characteristics for the grass-soil dataset collected from the Rookhope Catchment. Land-use categories are Moorland / Peat (M/P), Heather Moorland (HM), Rough pasture (RP), Improved Pasture (IP), Roadside (R), Mining Spoil (MS), Alluvial (A), woodland (W), Disused railway (RW).

Sample	Easting	Northing	Landuse	Soil pH	Soil OM (%)	Total soil Pb mg kg	Total Soil 206/207 Pb	0.05M EDTA mg kg	0.05M EDTA 206/207 Pb	Plant Pb mg kg	Plant 206/207 Pb	Plant %BHT Pb
5	390545	544712	M/P	2.99	88.6	4237	1.179	2211	1.180	3.2	1.159	22
6	391047	544716	M/P	2.87	85.7	2189		1458		5.5		
7	391045	544211	RP	3.23	31.4	870		614		32.0		
12	390539	543221	RP / R	4.93	8.2	5526		2796		12.7		
13	391045	543214	RP	3.79	13.0	187		121		2.8		
14	391045	543714	M/P	3.19	86.3	828	1.182	442	1.178	1.3	1.161	20
18	390048	543176	MS	4.13	7.1	1639	1.179	469	1.180	28.8	1.181	1
19	389991	542768	RP	4.33	62.2	346		242		1.2		
24	393908	542233	MS	7.43	2.4	27586		11335		25.6		
25	391578	542699	RP	4.26	10.7	439	1.179	259	1.180	19.5	1.181	1
26	391206	542177	RP	3.83	6.9	193		62		5.3		
27	391203	542252	RP	5.84	6.1	48		9		3.3		
28	390183	542145	M/P	3.82	81.1	465	1.176	320	1.176	3.0	1.173	8
33	391825	541896	RP	3.48	11.5	224		136		9.6		
35	392650	542667	RP	4.16	14.8	721		418	1.181	19.2	1.181	0
39	393952	542617	RP	4.88	19.6	2590		1402		10.0		
501	392545	543212	RP	3.98	11.7	2076		1042		9.0		
509	394904	546295	RP	3.83	16.1	191	1.176	75	1.177	1.8	1.17	11
514	394057	542332	A/W	6.67	12.2	3580		1831		44.5		
516	388028	545654	M/P	2.97	95.7	835		521	1.177	0.9	1.16	
517	388051	545329	M/P	2.94	94.9	581		230		1.2		
518	388145	544740	M/P	3.86	10.1	534	1.179	280	1.180	4.0	1.173	8
520	388468	544718	RP	5.35	10.8	148		57		2.1		
521	388940	544694	M/P	3.73	90.1	628		386		2.1		
522	394997	541646	RP	4.79	12.1	79		30		0.8		
524	395537	542200	RP	3.05	21.3	220	1.179	129	1.178	1.8	1.165	16
525	394632	541576	RP/R	6.35	9.9	8513		3173		20.2		
526	395559	540194	RP	3.99	9.6	99		38	1.178	3.3	1.172	10
527	395559	540194	RP	3.81	10.6	122		43		3.0		
528	394930	541076	IP	5.06	11.0	354		149		7.6		
532	394657	540324	IP	5.27	6.4	3958		2218		2.8	1.18	
533	394657	540324	IP	4.74	8.8	1384		753	1.182	3.9	1.17	1
534	393383	539367	R/RW	4.46	16.1	158	1.180	64	1.178	3.4	1.182	0
536	393305	540180	RP/RW	4.04	13.4	123		41		2.7		
539	392801	541417	RP	3.48	8.4	141	1.178	57	1.179	6.9	1.175	7
1001	392433	543043	RP/MS	3.93	6.1	2876		1784		48.0		
1002	392153	543277	RP	3.22	18.3	668	1.181	383	1.180	27.0	1.178	3
1003	391548	543693	HM	3.1	26.2	709		428		20.5		
1005	391530	544749	M/P	2.89	89.4	1233		801		4.1		
1006	392138	544804	HM	3.22	51.2	466		312	1.174	6.1	1.161	19
1007	392196	544243	HM	3.02	18.7	327		230		4.8		
1010	394607	544703	HM	3.05	24.1	340		219		6.3		
1014	393096	545194	M/P	2.98	94.8	737	1.174	451	1.176	3.3	1.149	31
1018	394106	543279	HM	3.8	7.3	489		320		16.7		
1019	394153	543852	RP	4.05	8.3	201		66		2.2		
1020	394124	544310	HM	3.25	31.6	443		227		6.3		
1023	387055	543237	HM	3.00	95.8	1121	1.177	701	1.178	2.3	1.157	24
1025	387585	544296	RP	3.97	26.2	336		129		1.0		
1026	388080	544206	M/P	3.36	81.2	576		414		2.1		
1028	393077	543266	IP	5.08	10.6	296		92		1.9		
1039	394611	544220	RP	3.04	11.3	175		145		11.4		
1040	395117	544200	HM	2.92	65.6	525		364		3.7		
1041	395137	544853	HM	3.39	27.5	640	1.181	349	1.182	13.3	1.18	1
1046	394473	542740	RP	4.05	9.6	120	1.181	40	1.179	3.0	1.164	17
1050	388050	543261	HM	2.89	18.2	151		66		5.4		

Table 2: Soil and vegetation characteristics for the soil-heather dataset. Land-use categories are as for Table 1.

Sample	Easting	Northing	Landuse	Soil pH	Soil OM (%)	Total soil Pb (mg kg)	Total Soil $^{206/207}$Pb	0.05M EDTA Pb mg kg	0.05M EDTA $^{206/207}$Pb	Plant Pb mgkg	Plant $^{206/207}$Pb	Plant % BHT Pb
5	390545	544712	M/P	2.99	88.6	4237	1.179	2211	1.180	5.72	1.167	14.12
21	389539	542214	HM	3.27	18.7	193	1.179	97	1.178	2.91	1.149	31.22
23	389079	543253	HM	2.91	56.9	349		204		1.36		
504	393542	543713	HM	3.17	22.8	312		262		1.56		
507	395027	545350	HM	3.06	15.8	178		62		2.80		
511	394089	545353	M/P	2.89	91.7	727		469		1.84		
512	393620	545320	H/M	2.94	65.1	1499		993		0.97		
515	387501	545203	M/P	3.23	94.2	810		459		2.31		
516	388028	545654	M/P	2.97	95.7	835		521	1.177	2.22	1.146	33.91
1001	392433	543043	RP/MS	3.93	6.13	2876		1784		6.17		
1002	392153	543277	RP	3.22	18.3	668	1.181	383	1.180	1.55	1.152	27.74
1006	392138	544804	HM	3.22	51.2	466		312	1.174	2.32	1.149	31.05
1010	394607	544703	HM	3.05	24.1	340		219		1.68		
1013	393094	544716	M/P	2.89	92.2	514		286		1.87		
1014	393096	545194	M/P	2.98	94.8	737	1.174	451	1.176	3.07	1.148	31.77
1015	392599	544682	M/P	2.88	94.4	368		224		1.41		
1020	394124	544310	H/M	3.25	31.6	443		227		1.97		
1021	387070	544223	M/P	2.97	96.1	631		434		2.17		
1022	386505	543735	M/P	3.08	95.1	663		429		1.17		
1023	387055	543237	M/P	3.00	95.8	1121	1.177	701	1.178	2.85	1.146	33.54
1024	387553	543780	HM	3.14	81.4	483		233		1.49		
1040	395117	544200	HM	2.92	65.6	525		364		3.20		
1041	395679	544801	HM	3.22	19.5	115	1.181	50	1.182	5.64		
1043	395091	543204	HM	2.90	83.6	522		305		1.84		
1044	395056	542679	HM	3.77	4.70	55		13		4.20		
1045	394473	542740	HM	4.05	9.58	120		40		7.64	1.164	17
1050	388050	543261	HM	2.89	18.2	151		66		2.55		
1051	388581	543233	HM	2.92	85.2	332		226		2.69		

Table 3: Characteristics of peat cores taken from 2 sites within the Rookhope Catchment

Easting	Northing	Sample	Depth	pH	OM (%)	Total Pb (mg kg^{-1})	Labile Pb (mg kg^{-1})	% Lability	Pore water Pb (µg L^{-1})
387761	544196	CORE 1	0-12.5 cm	3.03	50.94	803	503	58	369
		Lowland peat	12.5-25 cm	3.11	52.58	269	157	54	91
			25-37.5 cm	3.07	53.66	38.2	20	54	21
			37.5-50 cm	3.01	54.33	11.7	7	56	12
390157	544786	CORE 2	0-12.5 cm	3.54	52.92	1392	898	61	466
		Upland peat	12.5-25 cm	3.31	53.65	96.7	41	42	96
			25-37.5 cm	3.58	54.29	15.9	8	51	15
			37.5-50 cm	3.36	54.44	13.4	6	47	6

Table 4. Changes with time in air particulate Pb concentration and the proportion of lead derived from vehicular emissions across UK environments.

	1980	**1997**	**2001**	**2006**
Glasgow (µg m^{-3})	0.46	0.044	0.025	0.008
Brent, London (µg m^{-3})	0.77	0.089	0.030	0.015
Styrrup, S.Yorkshire (µg m^{-3})	0.18	0.036	0.020	0.006
Windermere (µg m^{-3})	0.047	0.009	0.005	0.004
National contribution of vehicular traffic to atmospheric lead (%)	90	68	1	2

Figure Captions

Figure 1: Location map of Rookhope Area in NE England showing mineral veins, adits and geographical features.

Figure 2: The proportion (%) of 0.05M EDTA extractable Pb compared with total soil lead.

Figure 3: Concentration relationship between plant and (a) EDTA extractable soil Pb and (b) total soil.

Figure 4: Results of using the predictive model based on the FIAM to describe grass Pb uptake using Eqn 3. The solid line represents the 1:1 relationship and the dashed lines represent the 95% confidence intervals.

Figure 5: $^{206/207}$Pb versus $^{208/207}$Pb isotope ratio plot for all sample matrices compared to potential end-member sources.

Figure 6: Comparison of lead isotope ratios for (a) grass, (b) heather and (c) 0.05M EDTA exatraction compared to the $^{206/207}$Pb ratio found in the total soil Pb pool at each sampling site.

Figure 7: Influence of Pb concentration on Pb isotope ratios in (a) Total soil, (b) 0.05M EDTA extracts, (c) grass and (d) heather.

Figure 8: Spatial distribution of lead isotope ratios in (a) grass and (b) heather showing the influence of geomorphology and wind direction. Three sample points laying just outside the catchment are shown.

Figure 9: Total Pb Concentrations (log concentrations, Inset) and $^{206/207}$Pb isotope signature in two peat cores taken in Weardale.

Figure 10: Comparison of $^{208/207}$Pb and $^{206/207}$Pb ratios in peat samples taken from two cores in Weardale. Core 1 was sampled at a lowland peat site whilst Core 2 was taken on high ground close to a smelter chimney.

Figure 11: Comparison of $^{206/207}$Pb ratios in the labile and non-labile pools of 2 peat cores using isotopic dilution assays and calculated using Eqn. 5.

Figure 12: Comparison of $^{206/207}$Pb found in the total, labile and pore water pools of 2 peat cores taken from Weardale.

Fig 1:

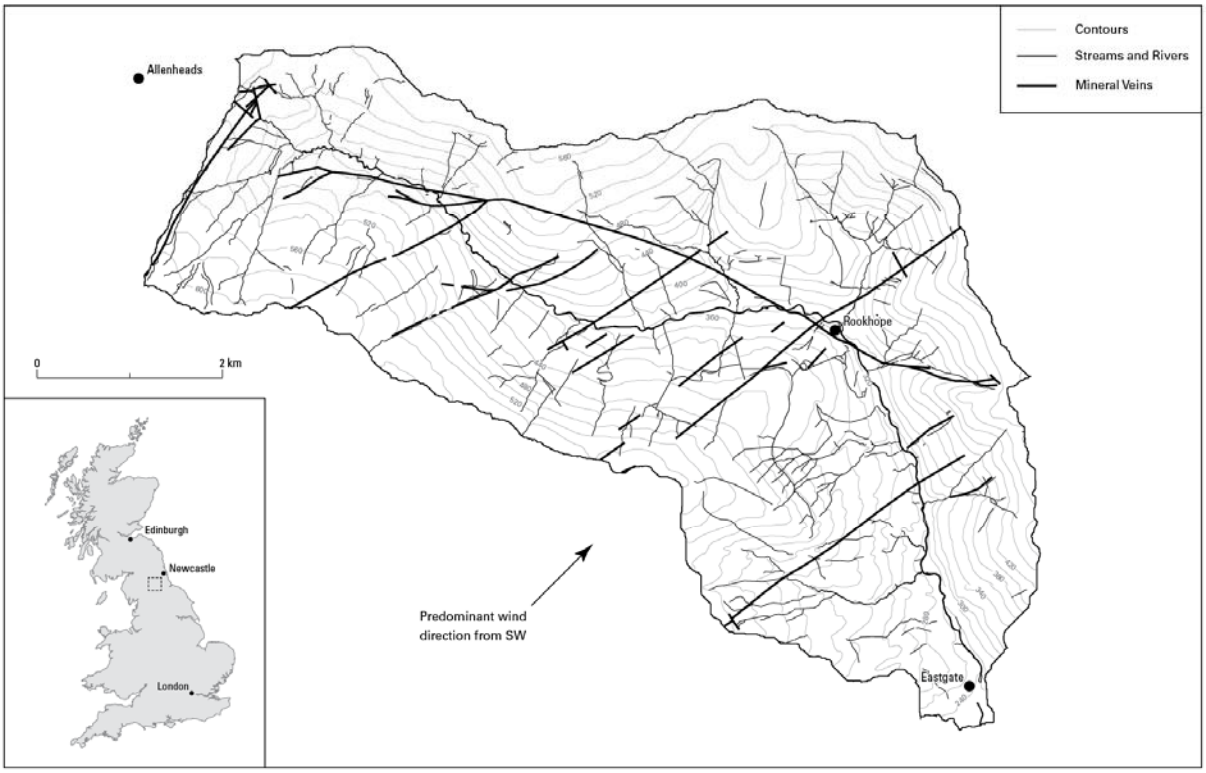

Contours
Streams and Rivers
Mineral Veins
Allenheads
Rookhope
Eastgate
0
2 km
Predominant wind direction from SW
Edinburgh
Newcastle
London

Fig 2:

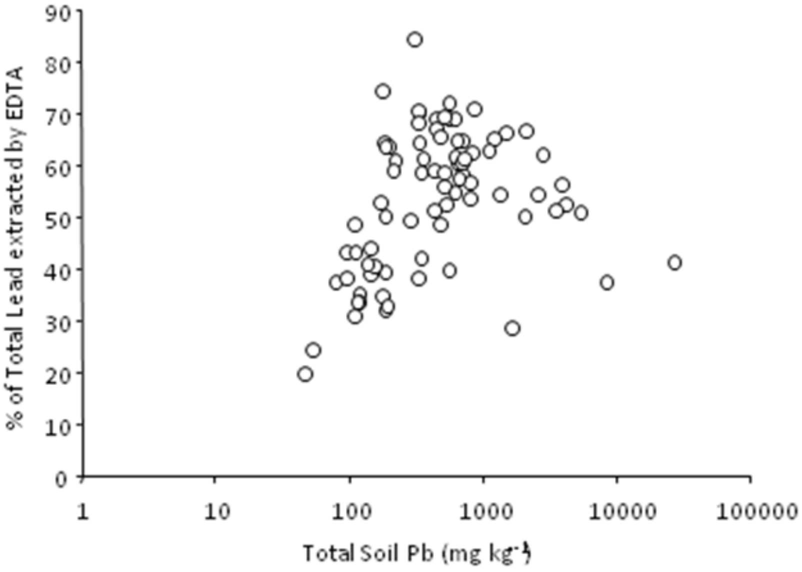

% of Total Lead extracted by EDTA
0
10
20
30
40
50
60
70
80
90
1
10
100
1000
10000
100000
Total Soil Pb (mg kg^{-1})

Fig 3:

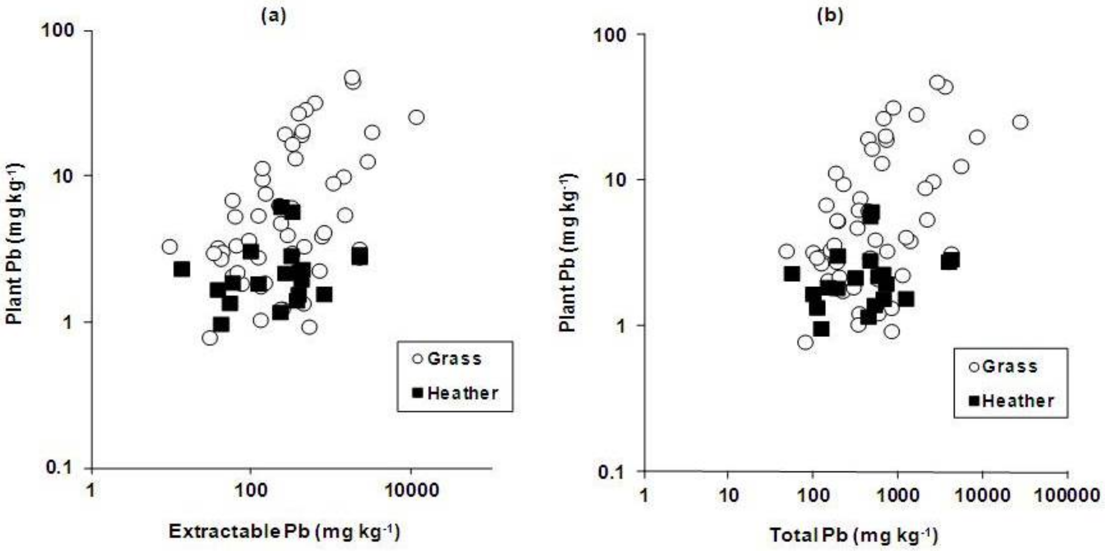

(a)
100
10
1
0.1
Plant Pb (mg kg-1)
1
100
10000
Extractable Pb (mg kg-1)
○ Grass
■ Heather
(b)
100
10
1
0.1
Plant Pb (mg kg-1)
1
10
100
1000
10000
100000
Total Pb (mg kg-1)
○ Grass
■ Heather

Fig 4:

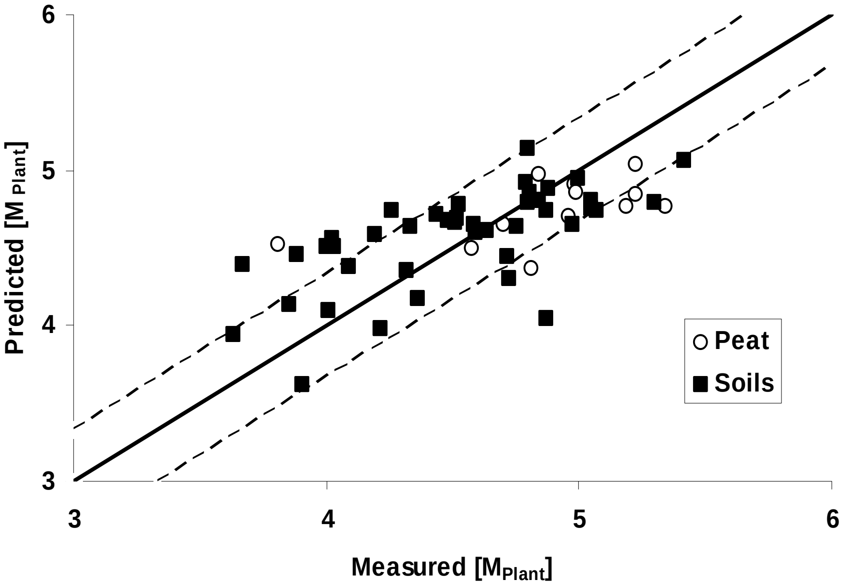


Fig 5:

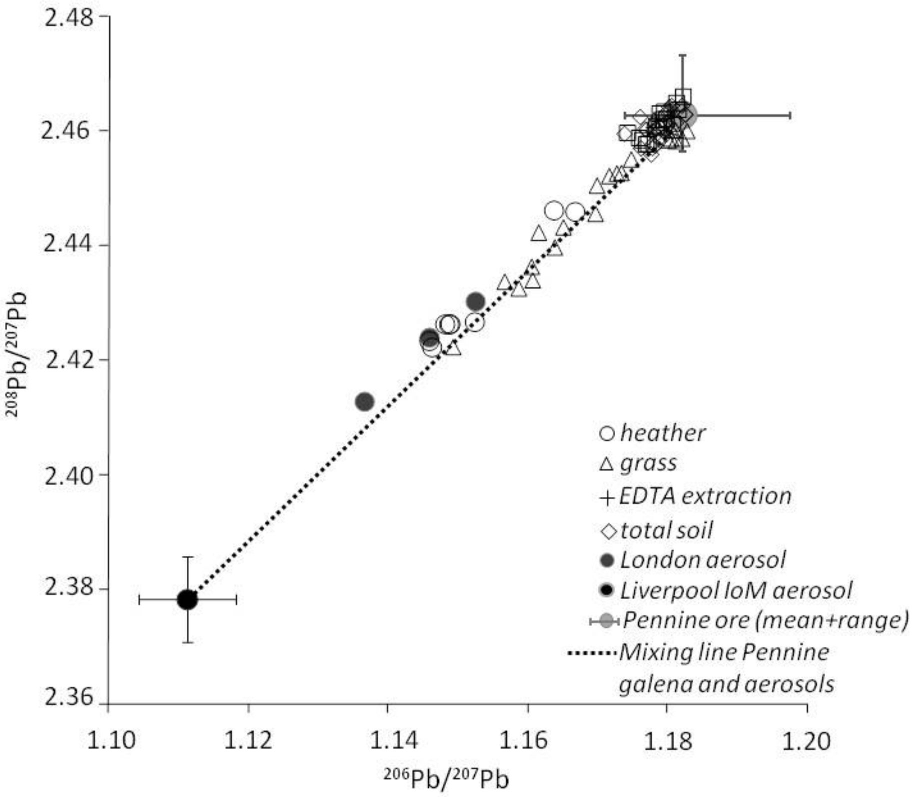

2.48
2.46
2.44
2.42
2.40
2.38
2.36
$^{208}Pb/^{207}Pb$
1.10
1.12
1.14
1.16
1.18
1.20
$^{206}Pb/^{207}Pb$
heather
grass
EDTA extraction
total soil
London aerosol
Liverpool IoM aerosol
Pennine ore (mean+range)
Mixing line Pennine galena and aerosols

Fig 6:

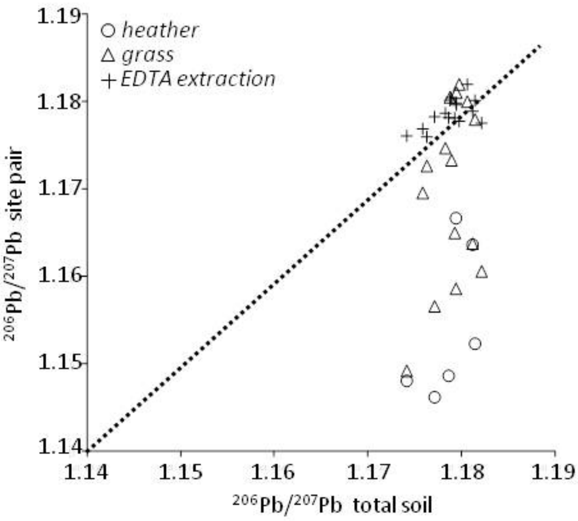

○ heather
△ grass
+ EDTA extraction
^{206}Pb/^{207}Pb site pair
1.19
1.18
1.17
1.16
1.15
1.14
1.14
1.15
1.16
1.17
1.18
1.19
^{206}Pb/^{207}Pb total soil

Fig 7:

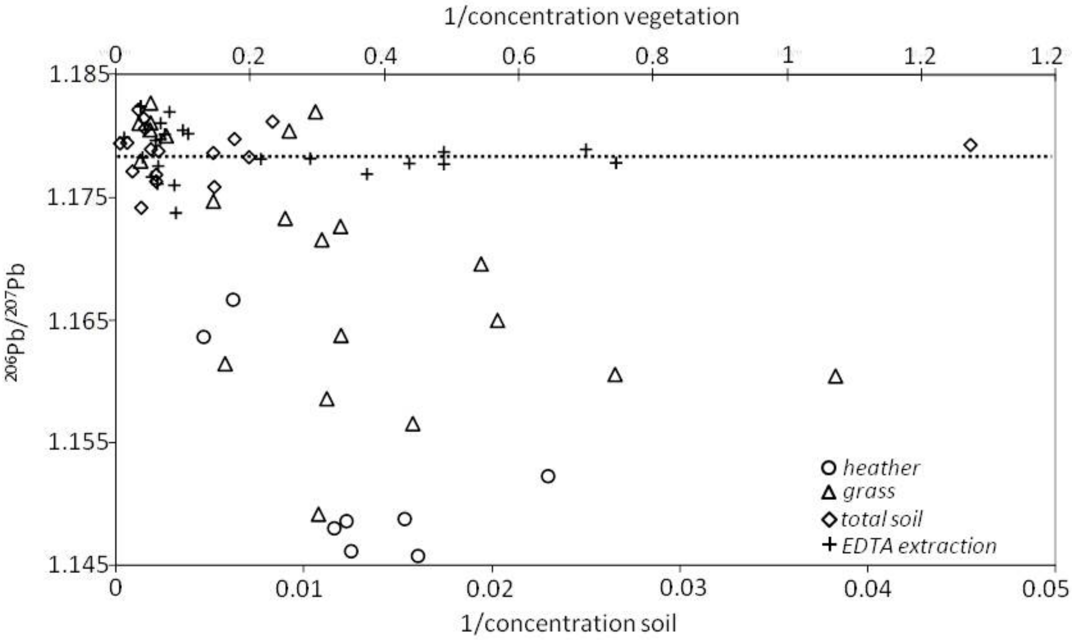

1/concentration vegetation
0
0.2
0.4
0.6
0.8
1
1.2
1.2
1.185
1.175
1.165
1.155
1.145
$^{206}Pb/^{207}Pb$
heather
grass
total soil
EDTA extraction
0
0.01
0.02
0.03
0.04
0.05
1/concentration soil

Fig 8a & b:

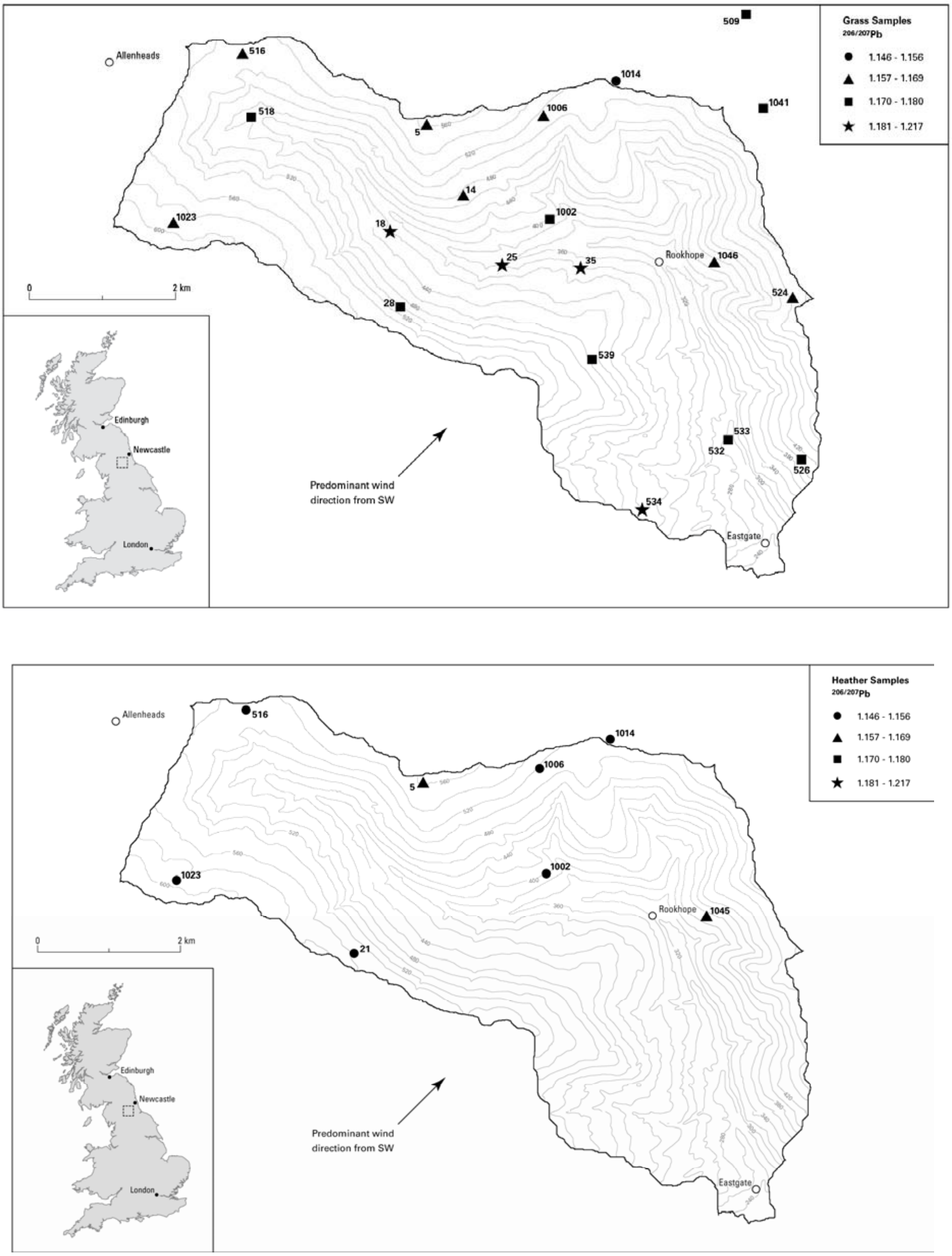

Grass Samples
206/207Pb
1.146 - 1.156
1.157 - 1.169
1.170 - 1.180
1.181 - 1.217
Allenheads
Rookhope
Eastgate
509
516
1014
1041
1006
5
518
14
1002
1023
18
25
35
1046
524
28
539
533
532
526
534
0
2 km
Edinburgh
Newcastle
London
Predominant wind direction from SW
Heather Samples
206/207Pb
1.146 - 1.156
1.157 - 1.169
1.170 - 1.180
1.181 - 1.217
Allenheads
516
1014
1006
5
1002
1023
Rookhope
1045
21
0
2 km
Edinburgh
Newcastle
London
Predominant wind direction from SW
Eastgate

Fig 9:

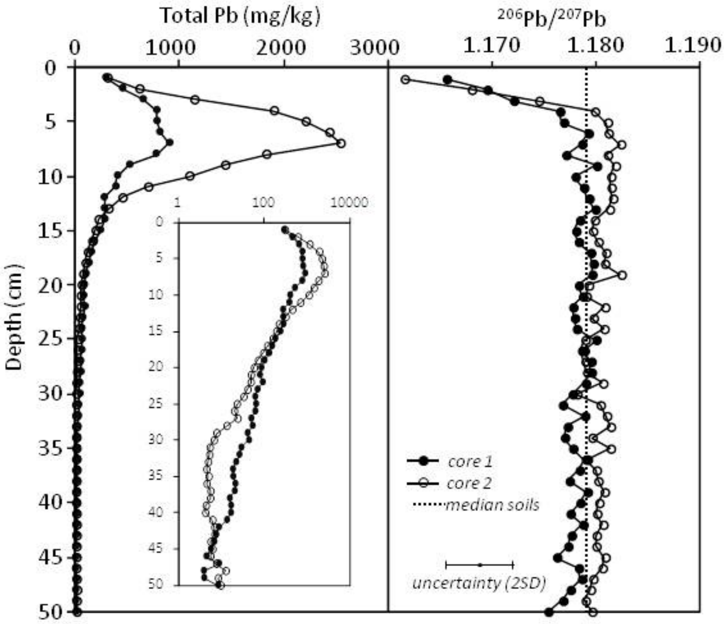
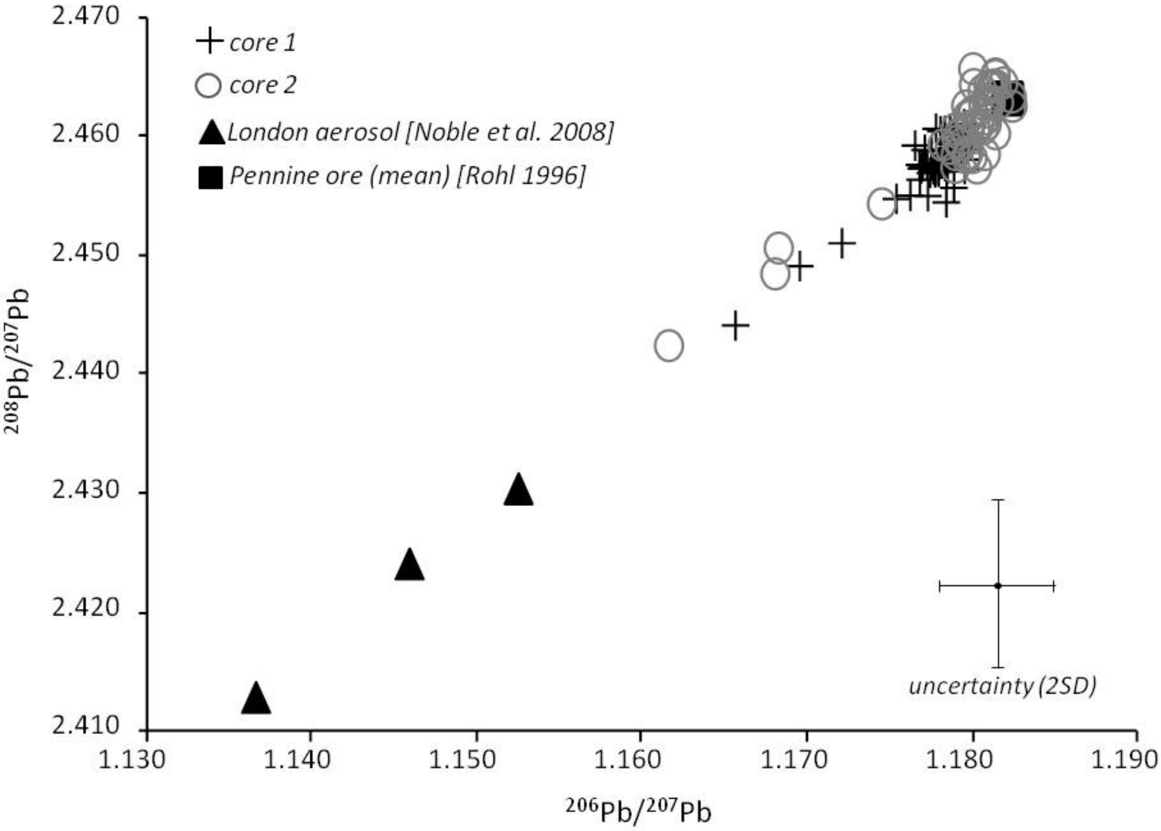

Total Pb (mg/kg)
0
1000
2000
3000
Depth (cm)
0
5
10
15
20
25
30
35
40
45
50
1
100
10000
^{206}Pb/^{207}Pb
1.170
1.180
1.190
core 1
core 2
median soils
uncertainty (2SD)

Fig 10:



2.470
2.460
2.450
2.440
2.430
2.420
2.410
^{208}Pb/^{207}Pb
1.130
1.140
1.150
1.160
1.170
1.180
1.190
^{206}Pb/^{207}Pb
core 1
core 2
London aerosol [Noble et al. 2008]
Pennine ore (mean) [Rohl 1996]
uncertainty (2SD)

Fig 11:

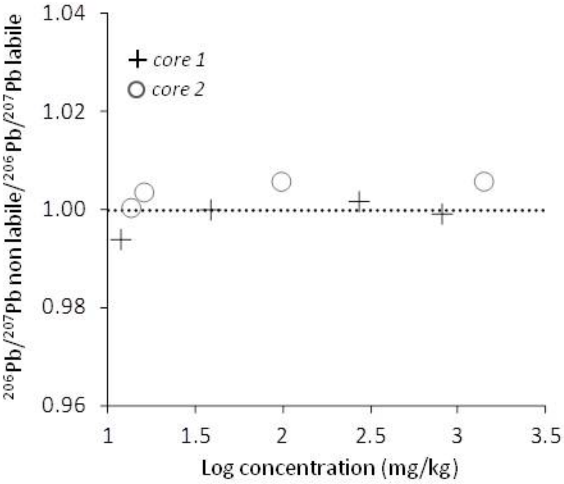
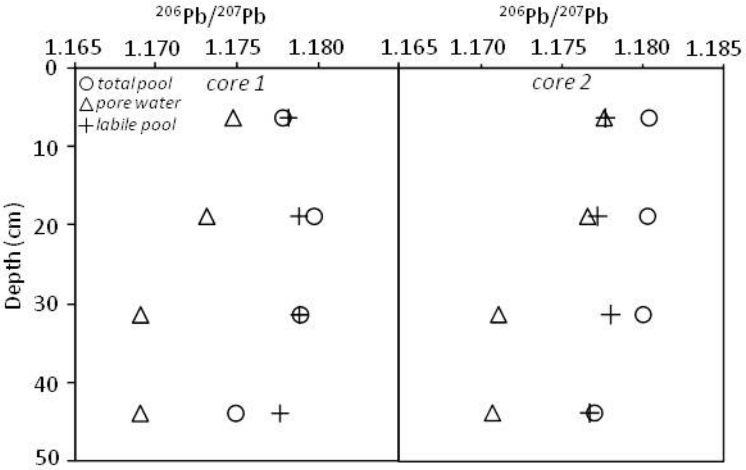

$^{206}Pb/^{207}Pb$ non labile/$^{206}Pb/^{207}Pb$ labile
1.04
1.02
1.00
0.98
0.96
1
1.5
2
2.5
3
3.5
Log concentration (mg/kg)
+ core 1
○ core 2

Fig 12:


$^{206}Pb/^{207}Pb$
$^{206}Pb/^{207}Pb$
1.165
1.170
1.175
1.180
1.165
1.170
1.175
1.180
1.185
0
10
20
30
40
50
Depth (cm)
○ total pool
△ pore water
+ labile pool
core 1
core 2