Sources, lability and solubility of Pb in alluvial soils of the River Trent catchment, U.K.

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Abstract

Alluvial soils are reservoirs of metal contaminants such as Pb that originate from many different sources and are integrated temporally and spatially through erosional and depositional processes. In this study the source, lability and solubility of Pb was examined in a range of alluvial soils from the middle and lower River Trent and its tributary the River Dove using Pb isotope apportionment and isotopic dilution. All samples were collected within 10 m of the river bank to represent the soil that is most likely to be remobilised during bank erosion. Paired samples were taken from the topsoil (0-15 cm) and subsoil (35-50 cm) to assess differences with depth. Lead concentrations in soil ranged from 43 to 1282 mg/kg. The lability of soil Pb varied between 9-56% of total metal concentration whilst Pb concentrations in pore water varied between 0.2 and 6.5 µg/L. There was little difference in the % Pb lability between paired top and sub soils, possibly because soil characteristics such as pH, iron oxides and clay content were generally similar; a result of the recycling of eroded and deposited soils within the river system. Soil pH was found to be negatively correlated with % Pb lability. Source apportionment using $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios showed that the isotopic ratios of Pb in the total, labile and solution pools fitted along a mixing line between Broken Hill Type ('BHT') Pb, used as an additive in UK petrol, and the local coal/Sourthern Pennine ore Pb. Various anomalies were found in the Pb isotopes of the bankside alluvial soils which were explained by point source pollution. Statistically significant differences were found between (i) the isotopic composition of Pb in the total soil pool and the labile/solution pools and (ii) the isotopic composition of Pb in the labile and solution pools, suggesting an enrichment of recent non-Pennine sources of Pb entering the soils in the labile and solution pools.

Keywords: alluvial soil; Pb isotopes; leaded petrol; source apportionment; stable isotope dilution; lability; E-value

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1. INTRODUCTION

Fluvial environments are a major pathway for the dispersal of trace pollutants (Bird, 2011) with alluvial soils being a major sink. For trace metals, the dominant (>90%) dispersal mechanism is via particulate-associated transport (Carter et al., 2006; Gibbs, 1973), particularly under flood conditions (Macklin et al., 1997). This can lead to the spatially extensive dispersal of contaminants from both point and diffuse sources (Bird, 2011). Overbank sediments in floodplains act as a focus for deposition and short- to long-term storage of metals (Bird, 2011; Marron, 1992), thus alluvial sediments and soils can be viewed as historical repositories of contaminants (Hudson-Edwards et al., 1998). However, these repositories cannot be viewed as permanent sinks, as, depending on spatial position metals are likely to be remobilised and released back into the drainage network through bank erosion caused by channel movement, undermining or bank collapse (Lawler, 1993; Trimble and Mendel, 1995).

The UK has an extensive Pb mining history in areas such as the Pennines, Peak District, Wales and the south west of England. Total concentrations of Pb in alluvial soils downstream from mines have been examined because of potential Pb poisoning to livestock, terrestrial and aquatic ecosystems. For example, Smith et al. (2009) reported problems of metal contamination occurring at great distance downstream of the original mining/mineralisation source in Wales. The orefields of the North Pennines, Yorkshire and Derbyshire were amongst the most productive Pb mining areas of Britain (Macklin et al., 1997) and Pb inputs to fluvial systems in Northeast England have received considerable attention (Carter et al., 2006; Dawson and Macklin, 1998; Dennis et al., 2009; Hudson-Edwards et al., 1997; Hudson-Edwards et al., 1999; Macklin et al., 1997; Shepherd et al., 2009).

The Geochemical Baseline Survey (G-BASE) of the UK (British Geological Survey, 2006) identified the alluvial soils of the Trent valley and some of its tributaries (Dove, Derwent) as having elevated concentrations (>200 mg/kg) of Pb. Median concentration of Pb in

the soils formed from the Triassic mudstone, the dominant soil parent material within our study area, is 35 mg/kg. The primary source of extraneous Pb in the alluvial soil was considered to be a legacy of the mineralization/mining area in the Derbyshire Peak District. However, other sources of Pb contamination could include (i) industrial activity from urban areas such as Derby and Nottingham, (ii) coal combustion in a number of power stations sited throughout the Trent valley and (iii) the later legacy of 'Broken Hill Type' (referred as 'BHT') Pb used as an additive to petrol but phased out by the year 2000. The Pb from leaded petrol has been found to contribute up to 35% of the total Pb in integrated inventories of deposited Pb in the UK (Bacon, 2002; Farmer et al., 2005). Other anthropogenic-related point- or diffuse-pollution sources of Pb can come from direct discharges of municipal or industrial effluents to rivers (Dawson and Macklin, 1998).

This study investigated whether there were spatial changes in source, concentration and lability of Pb in alluvial soils of a tributary (River Dove) and the middle and lower floodplain of the River Trent, one of the UK's major rivers. As alluvial soils build up over substantial periods of time, it was decided to investigate the sources and lability of Pb in both top and subsoils to (i) determine whether greater fixation processes have occurred in the deeper subsoils as they have been in situ for longer periods and (ii) to assess the possibility of downward migration of Pb within the soil. This is because subsoils are likely to end up being re-mobilised by erosion of the river bank and re-cycled as topsoils. The age of the alluvial soils on the modern floodplain is <10000 years old. The most recent terraces of the River Trent in the study area include the Hemington Terrace and the Holme Pierrepoint Terrace and these have been dated at 10000 and 26000 yrs BP (Howard et al. 2007). To develop this understanding both Pb isotope geochemistry and isotope dilution methods to measure reactive pools of Pb were used.

Pb isotope geochemistry has proved to be a powerful tool and has been used to trace sources, reconstruct historical trends in Pb deposition and trace the impact of the introduction and subsequent withdrawal of leaded petrol for many years (e.g. Bacon et

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al., 1996; Farmer et al., 2000 and 2001; MacKinnon et al., 2011; Sugden et al., 1993). Its use has been especially successful in the UK because the indigenous UK coal and Pennine ore Pb has a very different Pb isotope ratio to the typical 'Broken Hill' type Pb used in petrol (Bird, 2011; Komárek et al., 2008). In the UK, the dominant sources of Pb used and subsequently released into the environment are petrol lead ($^{206}Pb/^{207}Pb$=1.06-1.09) which consists of a combination of Australian Pb ($^{206}Pb/^{207}Pb$=1.04) and British Columbian Pb ($^{206}Pb/^{207}Pb$=1.16) (Sugden et al., 1993), native Pennine ore Pb and UK coal-derived Pb (typical $^{206}Pb/^{207}Pb$≈1.16-1.19 (Vinogradoff et al., 2005)). 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). Whilst peat bogs and lake sediments have been extensively studied over the last decades as they provide undisturbed long-term records of Pb deposition (Chenery et al., 2012; Eades et al., 2002; Farmer et al., 1996, 1997a, 1997b, 2005; Hansmann and Köppel, 2000), it is only relatively recently that Pb isotopes have been applied as a method for provenancing the origin of Pb in riverine environments (Bird, 2011). Shepherd et al. (2009) described a regional study of Pb isotopes in stream sediments from Northern England and concluded that the Pennine ore signature was dominant although the anthropogenic Pb contribution could be significant.

Current UK regulations on metal contamination are based on the total concentration in soil, e.g the sewage sludge directive (MAFF, 1993) or the Soil Guideline value (Environmental Agency, 2002). However, this does not provide any indication of the chemically reactive or labile fraction of a given element in a soil system. Significant research effort over the last few years has been directed at developing isotope dilution methods to determine the reactive pool of an element in soils, this being the pool of metal in equilibrium with the soil pore water (Hamon et al., 2008; Smolders et al., 1999; Young et al., 2005). The use of stable isotopes to determine the lability of Pb in soils has been the subject of relatively few studies (Atkinson et al., 2011; Degryse et al., 2007;

Gäbler et al., 1999; Tongtavee et al., 2005). In addition, Atkinson et al. (2011) undertook a source apportionment study of labile and non-labile pools of four Pb-contaminated soils and observed significantly different isotopic signatures in both pools.

This study uses Pb isotope geochemistry and isotopic dilution techniques to identify the source, concentration and reactivity of Pb in a range of alluvial soils taken from the catchment of the River Trent. In addition, the source and size of the total, labile and solution pools of Pb in paired top and sub soils were examined to develop our understanding of Pb behaviour in alluvial soils deposited over thousands of years. Information regarding the reactivity of Pb in alluvial soils is currently limited in the literature.

2. MATERIALS AND METHODS

2.1. STUDY AREA

The River Trent flows north through the Midlands and has a catchment area of nearly 10 500 km^2 (Large and Petts, 1996). It has a number of tributaries, including the Rivers Dove and Derwent which drain the mineralised Carboniferous Limestone Formation (Figure 1) of the Southern Pennine Orefield. The main ore minerals are galena (PbS), sphalerite (ZnS) and pyrite (FeS$_2$), with minor amounts of cerussite (PbCO$_3$) and smithsonite (ZnCO$_3$) (Ford, 1976; Li and Thornton, 2001). Lead mining in the Southern Pennine Orefield was first documented during Roman times and peaked during the 18th-19th century (Ford and Rieuwerts, 2000; Li and Thornton, 2001). Mining and smelting activities have caused widespread pollution and extensive remains of the former mining and Pb smelting activities (e.g. spoil heaps, mine shafts, smelting mills) are still present. An estimated area of 250 km^2 of land in Derbyshire is affected by Pb contamination (Colbourn and Thornton, 1978). Lead-rich sediments still pulse into the Trent tributaries in their upper catchments (Bradley and Cox, 1990) and can be stored in floodplain soils dowstream.

A 50 km long reach of the lower River Dove and a further 180 km reach of the middle and lower River Trent (Figure 2), which flows over the Mercia Mudstone Group, were examined. The lower Trent has been regulated for flood control and navigation (Large and Petts, 1996). Quaternary sand and gravel river terraces have been reworked to form the alluvial deposits (locally up to 10 m thick) on which the Holocene alluvial soils rest (Howard et al., 2007). Evidence that the floodplain deposits along the River Trent have been reworked throughout their entire depth in historic times has been found (Large and Petts, 1996).

The close proximity of the Derbyshire-Nottinghamshire-Yorkshire coalfields (Figure 1) referred to as Midlands coal in the following discussion, means that mining, smelting and industry have been additional sources of Pb contamination to the Trent catchment since the 18th century. The River Trent has provided cooling water to a number of power stations across Nottinghamshire and Lincolnshire that fired locally mined coal (Figure 2). Local coal was also used for smelting iron ore mined close to the river Trent outlet (British Geological Survey, 2006). Agriculture in the Dove valley is dominated by pasture for grazing whilst from the confluence of the Dove and Trent, arable agriculture dominates.

2.2. SOIL SAMPLING AND SAMPLE PREPARATION

2.2.1. SOIL AND SOIL PORE WATER COLLECTION

Soil samples were collected at 27 sites, 7 of which were from the River Dove floodplain, one was at the confluence between the Dove and Trent and the remainder along the Lower Trent floodplain (Figure 2). The soil samples were taken at depths compatible with those in the national geochemistry baseline survey of the UK (G-BASE) i.e. 0-15 cm (topsoil) and 35-50 cm (subsoil) (Johnson et al., 2005). Soils were collected from a range of agricultural and woodland sites where the alluvial soils have been able to form naturally. Samples were not collected between Newark and Scunthorpe on the River

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Trent because of the construction of artificial embankments as flood defences. Five sampling sites were located in woodland, whilst the remaining sampling sites were predominantly on improved/rough pasture or arable land within 10 m of the river bank. At 19 sites, paired top and sub-soil samples were collected.

Each sample consisted of ~1.5 kg of a bulked sample of five sub-samples collected at the corners and the centre of a 5 m^2 grid. A portion of soil was used to extract pore water using the method of Kinniburgh and Miles (1983). Pore waters were filtered and kept for further analysis of non-purgeable organic carbon (NPOC), major and trace elements, major anions and pH. The remaining soil was oven dried (<30°C), sieved to <2 mm and used for determination of pH, particle size distribution, loss on ignition (LOI), extractions and isotope dilution analyses. Approximately 30 g were ground to produce a fine homogeneous powder for acid digestion.

2.2.2. GENERAL SOIL CHARACTERISATION

Soil pH was determined in 0.01M $CaCl_2$ at a liquid/solid ratio=2.5 L/kg. LOI was undertaken at 450°C as a measure of soil organic matter. Particle size analysis was determined using a laser diffraction particle size analyser after organic matter had been destroyed using H_2O_2 until no further reaction with fresh H_2O_2. Estimates of soil amorphous and poorly crystalline iron oxides were determined using 0.2M ammonium oxalate and 0.125M oxalic acid and shaken in darkness for 2h following a method adapted from Schwertmann (1973). Total free iron oxides in soils were extracted by shaking 25% (w/v) Na-citrate and of 10 % (w/v) Na-dithionite (Olsen and Roscoe, 1982). Sample digestion for total metal concentrations was performed by accurately weighing a portion of soil into a Savillex™ vial and adding concentrated HNO_3 acid before heating at 80°C until dryness. These digests were then cooled prior to the addition of HF, HNO_3 and $HClO_4$ concentrated and analytical grade acids, with a subsequent stepped heating program up to 170°C. The dry residue was re-constituted with MQ water, H_2O_2 and HNO_3 to 25 mL of 5% v/v HNO_3. Reference materials (NIST SRM2710, SRM2711,

GSS-6, BGS102 and BCR-2), duplicated samples and blanks were all prepared in a similar manner to check accuracy of the analytical and digestion method.

2.2.3. ISOTOPIC DILUTION ASSAYS TO DETERMINE LABILE PB

Isotope dilution assays were undertaken using 0.0005M EDTA as suspending electrolyte. This strength of EDTA has been proven to solubilise sufficient Pb to be analytically robust without accessing the non-labile pool (Atkinson et al., 2011). Six replicates of 2.0±0.1 g <2 mm sieved soil were placed in centrifuge tubes and shaken in 25 mL 0.0005M EDTA electrolyte for 3 days, after which equilibrium is assumed to be achieved. After this period, three replicates of each soil suspension were spiked with 0.4-0.6 mL solution containing ^{204}Pb, whilst the three remaining were kept to measure the natural isotopic abundances of these elements. The spiked suspensions were re-equilibrated for a further 3 days. All suspensions where then centrifuged and filtered through 0.20 μm cellulose acetate filter prior to determination of isotopic abundances for Pb.

The samples were divided in four batches with similar levels of contamination based on Pb concentrations in soil. The spike concentrations were chosen to double the natural ^{204}Pb pool of the most contaminated soil in each batch. Blanks were all prepared in a similar manner. The labile pool or E-value was determined using Eqn.1 (Atkinson et al., 2011):

$$E-value = \left(\frac{M_{Pb}}{W} \right) \left(\frac{C_{spike}V_{spike}}{M_{Pbspike}} \right) \left(\frac{^{204}IA_{spike} - {^{208}}IA_{spike}R_{SS}}{^{208}IA_{soil}R_{SS} - {^{204}}IA_{soil}} \right) \quad \text{Eqn 1.}$$

where M_{Pb} is the average atomic mass of Pb, C is gravimetric Pb concentration (mg/L), 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 R_{SS} is the ratio of isotopic abundances for ^{204}Pb to ^{208}Pb calculated for the spiked soil supernatant. Typical coefficients of variation for the labile pools of three replicates were in the range 1.3-4.8%, with a median value of 2.6%.

To elucidate the main sources of labile and non-labile Pb, the natural isotopic composition of the labile pool was measured. Based on the size and the isotopic ratios of labile and total pools, the isotopic composition of the non-labile pool can be determined by means of Eqn.2 (Atkinson et al., 2011):

$$^{206}Pb/^{207}Pb_{Non-labile} = \frac{^{206}Pb/^{207}Pb_{totalpool} - \left(^{206}Pb/^{207}Pb_{labile} \times \frac{labilepool}{totalpool} \right)}{1 - \frac{labilepool}{totalpool}} \qquad \text{Eqn. 2}$$

2.3. ANALYTICAL PROCEDURES

2.3.1. ELEMENTAL CONCENTRATIONS

The concentrations of major and trace elements in pore waters and soil digests were determined using an Agilent 7500 quadrupole ICP-MS. The instrument was calibrated using a series of synthetic chemical solutions diluted from multi-element stock solutions (SPEX Certprep™), the calibration was validated using synthetic chemical standards from a separate source. Major anions in pore waters were analysed by ion chromatography (Dionex ICS-5000) whilst non-purgable organic carbon (NPOC) was measured using a Shimadzo TOC-Vcph analyser. Solution pH and HCO_3^- were measured using a Radiometer Analytical TIM865 titration manager. The Fe concentration in soil extracts was analysed by ICP-AES (Optima 7300 DV). Results were expressed as % FeO on a dry bulk basis, although Fe can be present in different modes of occurrence in soils.

2.3.2. PB ISOTOPES ANALYSES

The Pb isotope ratios of pore waters, soil digests and isotope dilution extracts were determined using an Agilent 7500 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 on the basis of 10

replicate integrations of 30s; each integration being 1000 peak jumps (1 point per peak) across the isotopes ^{206}Pb,^{207}Pb and ^{208}Pb. The issue of mass bias was addressed by determining the isotope ratio for NIST SRM981 and interpolate correction factors with reference to the accepted isotope ratios (Thirlwall, 2002). All test portions were diluted to produce best counting statistics within the linear range of the pulse counting detector.

Quality control for Pb isotope ratios was performed using an in-house solution produced from a naturally occurring UK galena –"Glendenning" with precision being 0.07% for both ^{206}Pb/^{207}Pb and ^{208}Pb/^{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. Typical sample uncertainties estimated are as follows: 2SD[^{206}Pb/^{207}Pb]=0.011-total pool; 0.007-labile pool; 0.012-solution pool. 2SD[^{208}Pb/^{207}Pb] =0.023-total pool; 0.014-labile pool; 0.026-solution pool.

2.4. STATISTICAL ANALYSIS

Statistical analyses were undertaken to examine whether there was a difference in the isotope ratios between the total, labile and solution pools. The dataset consisted of a total of 138 measurements, one measurement from each of the three pools from each of 46 soil samples. In the analysis, soil sample is included and treated as a blocking factor, which accounts for dependence between observations made on the same sample, and removes between-sample variation from the residual mean square. Sources of analytical error (e.g. in the 10 replication isotope measurements for each sample) will contribute to the residual mean square. The first ANOVA was therefore undertaken according to the model (Eqn.3):

$$^{206}Pb/^{207}Pb = \mu + sample.effect + pool.effect + residual \qquad \text{Eqn. 3}$$

where μ is the mean ^{206}Pb/^{207}Pb ratio.

The overall effect of pools on the ^{206}Pb/^{207}Pb ratio (3 degrees of freedom) is of limited interest so the pool data using specific orthogonal contrasts was explored. The choice of

contrasts was: (I) the ratios of $^{206}Pb/^{207}Pb$ in the total pool against those in the labile and solution pools and (II) the difference between $^{206}Pb/^{207}Pb$ ratios in the labile pool and the solution pool. In contrast I, the labile and solution pools were combined because theoretically the pore water should derive from the labile pool. In contrast II, it was examined whether a difference existed between the labile and solution pools as the hypothesis states that they should be derived from the same pool. These two orthogonal contrasts are mutually independent and so the sum of squares for pool effects in the ANOVA can be partitioned into two components, each with 1 degree of freedom.

3.   RESULTS AND DISCUSSION

3.1. SOIL GEOCHEMISTRY

The dataset covers a range of soil composition and properties (Table 1). The pH of soil samples was between 5.3 and 8.0, with most soils being near-neutral (pH 6.7-7.4) due to the influence of limestone bedrock of the Peak District (River Dove particularly) or agricultural lime added to soil. The present dataset is in the upper range of pH values compared to other floodplain sediments in the UK (Davies and Lewin, 1974; Dawson and Macklin, 1998). The pH measured for paired topsoils and subsoils from the same profile is similar or slightly more alkaline with depth (Figure 3), which Gooddy et al. (1995) attributed to the consumption of surface-derived H^+ by reaction with soil minerals. As expected, LOI contents (4-18%, Table 1) were greater in topsoil (1.5 times on average) than in the paired subsoil (Figure 3). This is likely a result of the topsoil being a source of modern carbon inputs from plant growth or as carbon associated with clay particles being deposited in floodplains. Another influence may be that the deposition of soils at 50 cm depth was in some cases pre-Holocene, when net primary production was much lower. Thus, lower inputs of C would have been added to alluvial soils.

Iron oxides are relatively abundant in soils and are known for their capacity for adsorbing metals. Total free iron oxides in soils (expressed as FeO) did not vary widely

across the dataset, ranging from 2 to 5%. Amorphous iron oxide concentrations, for which Pb has a strong affinity (Sauve et al. 2000) were in the 0.5-3% range (expressed as FeO). No distinctive trend with depth was observed (Figure 3). The proportion of clay sized particles varied between 17 and 54%, the predominant textural class across the dataset being clay and clay loam. Figure 3 shows that topsoils tend to be enriched in clay with respect to the paired subsoil.

3.2. POOLS OF PB IN ALLUVIAL SOILS

3.2.1. TOTAL POOL

The range of total Pb concentration in soils spans almost three orders of magnitude (43-1282 mg/kg), with an interquartile range of 126-384 mg/kg (Table 1). For Pb loadings up to 200 mg/kg, the concentrations in the top soil samples tend to be equal or higher than in the corresponding subsoil (Figure 3). However, this trend is reversed in few Pb-enriched soil profiles (sites 21 and 14) which came from a section of the Trent close to Gunthorpe. These samples are further investigated in Section 3.3.2. Linear correlation coefficients were calculated between total Pb and the concentration of potential sorptive surfaces i.e. iron oxides and organic carbon (LOI), but no direct and conclusive relationships were found.

3.2.2. LABILE POOL

3.2.2.1. E-VALUES

The labile pool (E-$value$) of Pb for soils (Table 1) spans over one order of magnitude (10-315 mg/kg) and is correlated (R^2=0.70) with the total pool. The lability expressed as % E-value relative to the total Pb concentration in soil ranged from 9 to 56%, with a narrow interquartile range (22-36%). These values are in the lower range of those reported in the literature for labile Pb in contaminated soils i.e. 31-78% (Atkinson et al.,

2011; Degryse et al., 2007; Gäbler et al., 1999; Tongtavee et al., 2005) and peat i.e. 40-60 % (Chenery et al. 2012).

Atkinson et al. (2011) and Degryse et al. (2007) both suggested that the lability of Pb in soil was greater than what can be intuitively expected, as it has always been assumed that Pb sorbs strongly to poorly crystalline FeO_x and organic matter. Our results suggest that (i) ageing, sorption and precipitation reactions may be limited (Degryse et al., 2007) and (ii) Pb throughout our sampling area is hosted in phases easily transferable to the labile pool.

Before major anthropogenic activity (mining and industrialisation), the weathering and transport of mineralised Pb deposits in the Peak District would have been the major initial source of Pb enrichment to these alluvial soils. Once mining had become established it is likely that there would be increases in Pb inputs to the River Dove and then to the Trent via a number of pathways including (i) a greater exposure of Pb-bearing minerals to the atmosphere, (ii) greater particulate Pb contributions from the erosion of spoil heaps, and (iii) atmospheric deposition via smelting. Typical Pb lability in soils on Dove floodplain, which are likely dominated by mineralisation/mining-related pollution, ranged from 30 to 50%. This suggests that much of the Pb does not occur in inaccessible primary mineral matrices (such as galena) or occluded within the mineral matrix of soil. Li and Thornton (2001) undertook sequential extractions on soils from the Southern Pennine Orefield (Derbyshire) and found that Pb was strongly associated with carbonates (up to 55%) and Fe-Mn oxides (c.30%). In addition, up to 50% total Pb was found to be associated with the carbonate/specifically adsorbed phase in smelting-contaminated soils.

Along the River Trent the increased industrialisation, urbanisation and road systems will have resulted in greater traffic-related Pb emissions. A large contribution of road dust with associated weathered by-products of combusted tetra-ethyl Pb may have been added to the soil. Sequential extraction experiments on road dust yielded 40-50% Pb

with exchangeable nature and easily mobilisable under environmental conditions (Bäckström et al., 2004; Kumar et al., 2010). Biggins and Harrison (1978) identified $PbSO_4 \cdot (NH_4)_2SO_4$ as the dominant Pb-bearing species in atmospheric particulates collected next to a major road in Lancaster (UK). This is an intermediate compound formed by the reaction of car exhaust-emitted halides (PbBrCl) with atmospheric ammonia and acid sulphates (Biggins and Harrison, 1978). The exposure and water leaching of $(NH_4)_2SO_4 \cdot PbSO_4$ produces $PbSO_4$, the main Pb compound in street dust and soils (Biggins and Harrison, 1980; Cao et al., 2008) and could contribute to the labile pool as it weathers. Coal combustion may also contribute to the exchangeable pool of Pb in these alluvial soils, being most likely emitted in oxide or chloride form, although this depends on the specific type of coal fired. It is therefore expected that many mineral and sorptive phases will contribute to the solid-solution equilibria.

3.2.2.2. E-VALUE VS DEPTH

Our dataset shows a sharp decline in lability with increasing soil pH (Figure 4). The spatial distribution of % E along the sampling area mirrors that of soil pH (Figure 5). Soil pH affects adsorption strength and therefore is likely to influence E-value concentrations (Young et al., 2007). Other studies have reported that decreased lability of Cd and Zn is associated with stronger adsorption, which is essentially pH-dependent (Tye et al., 2002; Young et al., 2007). Lead solubility in moderately contaminated soils is usually controlled by sorption and complexation processes rather than precipitation (McBride et al., 1997; Welp and Brümmer, 1999). No correlations were found with any of the other sorptives phases such as organic matter (LOI), FeO or clay.

Alluvial soils would have aggraded slowly during the Holocene, with the subsoils (35-50cm) having been in-situ for considerably longer periods than the topsoils, thus theoretically allowing longer periods to enable metal fixation. However, there is no evidence of greater fixation of Pb in the subsoil of the paired samples as the concentration (E-value) and proportion (%E) of labile Pb showed no discernible trend

between top and subsoils (Figure 3). Most soil characteristics likely to be involved in the sorption of metals (e.g. clay, soil pH, FeO) do not show a distinctive enrichment but paired top and subsoil samples generally had similar soil properties. These observations reflect the processes involved with alluvial soil formation, where the continued erosion and subsequent deposition of bank deposits means that some of the freshly deposited soil may have been recycled from the lower parts of the soil profile upstream. Studies have shown that if fresh Pb^{2+} is added to soils, the majority of the fixation occurs within ~300 days (Tye et al., 2004). Much of the Pb has probably been in contact with the soil for considerable periods (possibly 1000's of years) and has reached a pseudo-equilibrium with the soil properties before being eroded and re-deposited. In addition, at the resolution of the sampling (e.g. 0-15 cm) it was likely that it would be difficult to identify any differences in Pb lability in freshly deposited material. Thus the mixing and recycling of soils appears to have been a major influence allowing lability to be predominately controlled by soil pH (Figures 4 and 5).

3.2.3. SOLUTION POOL

Pb levels in pore waters range from 0.17 to 6.47 μg/L, with an interquartile range of 0.46-1.70 μg/L (Table 1). The concentrations are systematically higher in topsoil pore waters when compared to the subsoil counterparts (Table 1). The pH of pore waters varied between 5.0 and 8.9 and showed little variation with depth. NPOC concentrations also showed little variation with depth. There was not a significant correlation between Pb concentration in pore water and pH, although it was noted that Pb concentrations sharply decreased at soil pH>7 due to the greater Pb sorption with increasing pH (Tye et al., 2004). No correlation was found between Pb concentrations in pore solution and NPOC or any sorptives phases (LOI, FeO or clay).

3.3. ISOTOPIC COMPOSITION OF PB POOLS

3.3.1. SOURCE APPORTIONMENT

The isotope ratios for the total, labile, non-labile and solution pools of Pb are depicted in Figure 6 along with the major potential past and present anthropogenic and geogenic sources of Pb in the UK, namely local Pennine Pb ore, leaded petrol and coal combustion (Shepherd et al., 2009). All the investigated samples form a linear array falling along a mixing line connecting three major Pb sources:

(i) *Petrol-derived Pb*: prior to the withdrawal of leaded petrol, petrol Pb in the UK consisted of a mixture of Australian ("Broken Hill Mine") and British Columbian ores depleted in ^{206}Pb with respect to UK ores. The ^{206}Pb/^{207}Pb ratio has been estimated at 1.076 (Sugden et al., 1993 after Delves, 1988).

(ii) *Coal:* Regions close to the study area have produced coal and there has been a long history of coal combustion for industrial purposes within the Trent Catchment. Two major input pathways can be considered, (a) fluvial dispersal of finely ground coal waste (Shepherd et al., 2009) from power stations and from the historical transport of coal along the Trent, and (b) emission of Pb from coal combustion, entering the system as diffuse atmospheric pollution. Although at present the power stations adjacent to the Trent do not fire 100% locally mined coal, it is reasonable to assume for further calculations that Pb emissions over centuries of coal combustion in the area will show a local coal signature. The median value of ^{206}Pb/^{207}Pb for Midlands coal reported by Farmer et al. (1999) is 1.185±0.005 whilst ^{208}Pb/^{207}Pb is 2.462±0.012.

(iii) Pb mineralizations/mining/smelting. The catchment area of River Dove falls within the Southern Pennine Orefield, an area heavily affected by centuries of mining. The extent of mining related pollution in other riverine systems in the Pennines can reach more than 40 km (MacKinnon et al., 2011) and as far as 70 km downstream

(Shepherd et al., 2009). Pb isotopic signatures of galenas from Derbyshire as recorded by Rohl (1996) were considered as representative for natural Pb ore ratios from Southern Pennine area. The median values are $^{206}Pb/^{207}Pb=1.182\pm0.002$ and $^{208}Pb/^{207}Pb=2.459\pm0.002$ (Rohl, 1996).

In this work non-Pennine Pb, the dominant source being the Broken Hill Mine in Australia is referred to as 'BHT' Pb for simplicity. Attempts were made to resolve the proportion of 'BHT' Pb and quantify the contribution of different end-members using the simple mixing model as per Farmer et al. (2005) [Eqn. 4].

$$Pb_{BHT}(\%) = \left| \frac{\left(\dfrac{^{206}Pb}{^{207}Pb}\right)_{ore\cdot coal} - \left(\dfrac{^{206}Pb}{^{207}Pb}\right)_{sample}}{\left(\dfrac{^{206}Pb}{^{207}Pb}\right)_{ore\cdot coal} - \left(\dfrac{^{206}Pb}{^{207}Pb}\right)_{BHTPb}} \right| \times 100 \qquad \text{Eqn. 4}$$

It is difficult to completely unravel the individual contribution of coal combustion and mining/smelting activities. Median Pb isotope ratios for local coal were slightly higher than those for Southern Pennine galena, but they both fall on the same mixing line. Moreover, if analytical errors in the current study are considered, both sources are isotopically indistinguishable (Figure 6). The dominant non-petrol end-member in every section of the study area based on spatial criteria was difficult to establish, as the area of influence of these pollution sources is likely to overlap. It seems reasonable to assume a mixture of Midlands coal and Pennine ore as a non-petrol end-member, for which an average $^{206}Pb/^{207}Pb=1.183$ was considered for further calculations. It is worth noting that such an assumed value falls within less than 1 SD of the median values reported above for the coal and ore end-members. This exercise was restrictedto those soil samples where the $^{206}Pb/^{207}Pb$ ratio is outside of the range of the Southern Pennine galena/Midlands coal end-member ($^{206}Pb/^{207}Pb=1.172-1.191$) i.e. inferred 'BHT' Pb >10%.

3.3.2. Pʙ ɪsᴏᴛᴏᴘᴇs ɪɴ ᴛᴏᴛᴀʟ ᴘᴏᴏʟ

3.3.2.1. Iꜱᴏᴛᴏᴘɪᴄ ᴄᴏᴍᴘᴏꜱɪᴛɪᴏɴ ᴀɴᴅ ꜱᴏᴜʀᴄᴇ ᴀᴘᴘᴏʀᴛɪᴏɴᴍᴇɴᴛ

The $^{206}Pb/^{207}Pb$ ratios in the collected soil samples ($^{206}Pb/^{207}Pb$=1.123-1.186, Table 2) are in agreement with the isotopic composition of soil from an upland catchment in Wales ($^{206}Pb/^{207}Pb$≈1.104-1.189, Dawson et al., 2010) and stream sediments from the River Wear catchment in northeast England which was similarly dominated in the upper catchment by mining activity and industrial-urban activity in the lower catchment ($^{206}Pb/^{207}Pb$=1.124-1.189; $^{208}Pb/^{207}Pb$=2.405-2.466, Shepherd et al., 2009). The majority of the top and subsoil dataset falls in the range $^{206}Pb/^{207}Pb$=1.160-1.180 and shows little dependence on the total Pb content in soil.

For those samples where calculations of the 'BHT' Pb contribution to the total Pb loading were made, a wide range was found from <10% to 50% (Table 2). Soils with high $^{206}Pb/^{207}Pb$ ratios cluster at one end of the data array in Figure 6, with a general trend of surface soils extending down the mixing line towards the 'BHT' Pb signature, close to the isotopic composition of London aerosols (Noble et al., 2008), Glasgow road dust (MacKinnon et al., 2011) and roadside soil (Atkinson et al., 2011). This can be taken as evidence for the relevance of traffic-related sources. According to Farmer et al. (2005), car exhaust emissions may have accounted for up to 35% of the Pb deposited in an upland catchment in rural N.E. Scotland. Some studies have suggested that roadside soils are still impacted by petrol-derived Pb even after the phasing out of leaded petrol (Bäckström et al., 2004). A number of Pb-bearing species in road dust have low solubility at typical soil pH and E_h values, and therefore are likely to persist (Barrett et al., 2010). Along with direct aerosol deposition, other pathways in which road dust could be incorporated into the alluvial soils are either from direct road drainage or drainage derived from sewage works that feed into the Trent and has been dispersed by flooding. Atkinson et al. (2011) measured $^{206}Pb/^{207}Pb$≈1.118 for a sewage farm soil from

Nottinghamshire and concluded that recent urban inputs and run-off material from roads could explain the contribution from petrol-derived Pb.

With a few exceptions, subsoils exhibited equal or higher ^{206}Pb/^{207}Pb ratios than their paired topsoils (Figure 3). Whilst Pennine ore/Midlands coal components (i.e. high ^{206}Pb/^{207}Pb ratios) are dominant in subsoil, surface soils would be a composite of these sources together with a significant contribution of non-Pennine Pb. This general trend is in agreement with the pattern of Pb isotopic changes recorded in peat deposits in the UK (Chenery et al., 2012; Farmer et al., 2005; Komárek et al., 2008; Weiss et al., 2002).

Bacon et al. (1996 and 2006) studied soil profiles from SE England and NE Scotland and found evidence for translocation of anthropogenic Pb from the surface to deeper in the soil to at least 16 cm depth. The present dataset also suggests the migration of 'BHT' Pb down the profile. Out of 19 subsoils in the dataset, 12 soils display ^{206}Pb/^{207}Pb ratios below the range for Southern Pennine ore/Midlands coal (1.172-1.191) and 5 of them have ^{206}Pb/^{207}Pb<1.162, which yields 'BHT' proportions estimated at >20% (Table 2). This provides strong evidence that 'BHT' Pb has penetrated to considerable depths (at least to 35 cm) in the soil profile. The migration rate for petrol-derived Pb was estimated by Erel (1998) at 0.5 cm/yr for Mediterranean soils, although this figure is site specific and dependent on a number of soil features (Komárek et al., 2008).

3.3.2.2. SPATIAL DISTRIBUTION OF PB IN THE TOTAL POOL

The spatial distribution of Pb and Pb isotopes throughout the study area can be split into 4 distinctive sections (Figure 2 and 5, Tables 1 and 2).

-Section I (0-55 km)

The top and subsoil samples taken from the Dove catchment reflect the presence of Pennine Pb ore. Isotopic compositions of soil profiles along this tributary are typically ^{206}Pb/^{207}Pb=1.178-1.180, similar to Southern Pennine galena signature (Rohl, 1996). Due to most soils having Pb isotope ratios within the range for Derbyshire galena, any

likely 'BHT' contribution is hard to calculate with confidence, but was estimated at <10%. Like other river systems in the UK, the Pb concentration declined with distance from the former mining area whilst the isotopic composition remains constant (Macklin et al., 1997). A rapid decrease in concentration was noted, measuring 250 mg/kg (Site 1) 4 km downstream from the edge of the Pennine Orefield (taken as the limits of the mineralised Derbyshire Carboniferous Limestone) and 80 mg/kg (Site 6) 37 km downstream from this point.

-Section II (55-80 km)

Downstream of the confluence of the Dove with the Trent, Pb concentrations in subsoils continue to decrease downstream. The $^{206}Pb/^{207}Pb$ ratios (1.158-1.175) are lower than in Dove floodplain soils, but still suggest a major Pennine ore contribution (typically >80%). By contrast, Pb loadings in topsoils increase to concentrations on average 100 mg/kg higher than the paired subsoil and 40-50% 'BHT' Pb was inferred. This probably was associated with Pb inputs deposited during flooding events and aerial deposition until 'BHT' Pb was phased out. The presence of sewage works before this stretch of river (that floods regularly) should be considered as possible point pollution sources, especially as street drainage is likely to be routed through these systems. The proximity of a major road system is also likely to have resulted in 'BHT' Pb-rich waters draining into this area before its phasing out. Due to the lower Pb concentrations in these soils, any ^{206}Pb-depleted diffuse pollution, possibly of minor relevance in terms of Pb concentration, may create a larger than expected shift in the isotopic signature. The soil profiles along this section contain typically ~50% sand, which would encourage post-depositional vertical migration of Pb and account for the lower subsoil $^{206}Pb/^{207}Pb$ ratios compared to other subsoils in the dataset.

-Section III (80-150 km)

This section encompasses various examples of anthropogenic point-source pollution of diverse nature, as suggested by the high Pb concentrations (200-1300 mg/kg) and

variable isotopic compositions across the dataset. Site 14 revealed Pb concentrations close to 400 mg/kg and a Pennine ore/Midlands coal signature ($^{206}Pb/^{207}Pb>1.175$). The fact that this site is only 7 km downstream of a 25 km-long section (Section II) of floodplain topsoils systematically showing $^{206}Pb/^{207}Pb<1.140$ strengthens the evidence for a point source of pollution. The dominant source of Pb is believed to be the River Derwent, a tributary that drains the mineralised Southern Pennine uplands and joins the River Trent 8 km upstream of site 14. Bradley and Cox (1990) found significant erosion and redeposition of mining-affected sediments in the River Derwent catchment and estimated a contemporary Pb supply of 1.8 g m^{-2} year^{-1}. However, two other minor sources located within 3 km from site 14 are also likely to contribute to produce high $^{206}Pb/^{207}Pb$ ratios in topsoils: (i) resuspension and fugitive dust associated with the largest marshalling yards in Europe, where the bulk of the traffic that was dealt with was domestic coal and ore and (ii) Pb emissions from a major power station.

The lower River Trent was extensively used for commercial navigation until the 1950s. Historical records provide evidence of improvements such as large-scale dredging of a number of sections. Where the dredgings have been unloaded, artificial riverbanks made of dredged sediment have been constructed. These would act as historical reservoirs of Pb from various sources, with possibly an important coal/ore contribution as these products were transported. This would account for the anomalous enrichment in Pb at a number of sites along this section (nos. 15-18 and 24), with loadings in the 300-1280 mg/kg range. These samples typically have $^{206}Pb/^{207}Pb=1.158-1.180$ and greater Pb concentrations in the subsoil and, suggesting that these soil profiles have been anthropogenically modified. Direct evidence for dredging and subsequent stocking was found at sites 16-18 and 24. The remaining sites along this section are considered to be naturally developed alluvial soil profiles that have remained undisturbed.

<u>-Section IV</u> (*215-230 km*)

The progressive dilution of sediment and the absence of major point-source pollution directly affecting the southern bank of the Humber Estuary results in Pb concentrations between 90-240 mg/kg. The isotopic compositions suggest very low 'BHT' Pb contributions (<20%). The slightly higher ^{206}Pb/^{207}Pb ratio at Site 26 topsoil compared to the paired subsoil could be associated with emissions from major steel works at Scunthorpe (within 10 km) that used Midlands coal.

3.3.3. Pb isotopes in labile pool

The measured labile pool showed a variable isotopic composition, with ^{206}Pb/^{207}Pb≈1.126-1.182 (Table 2) and no dependence on the concentration of the labile (E-value) and total pools. The estimated 'BHT' proportions in the labile pool reached 50% in topsoils and 35% in subsoils, thus demonstrating that 'BHT' Pb had penetrated to at least 35 cm depth. The labile ^{206}Pb/^{207}Pb was linearly correlated (R^2=0.94) with the ^{206}Pb/^{207}Pb in the total pool (the latter ratios being 0.005 higher on average) and therefore the spatial distribution of Pb isotopes in the labile fraction is similar. Section I is Pennine ore dominated, with labile ^{206}Pb/^{207}Pb>1.170 in most sampling sites regardless of depth. The ^{206}Pb/^{207}Pb ratios of the labile fraction in Section II follow the pattern of the total pool, displaying a more pronounced 'BHT' Pb signature due to the proximity of major conurbations and road systems on sand and gravel terraces. The greatest penetration of 'BHT' Pb in the labile pool was found in soil profiles from this section, which were alluvial soils with the largest 'BHT'% in topsoils and a relatively high sand content. The isotopic signatures of sites from Section III and IV reflected a mix of various sources.

3.3.4. Pb isotopes in solution pool

The ^{206}Pb/^{207}Pb ratios of pore waters (^{206}Pb/^{207}Pb≈1.125-1.176) are also correlated with ^{206}Pb/^{207}Pb in the labile (R^2=0.83) and total (R^2=0.79) pools and therefore the spatial distribution is similar. The proportion of petrol-derived Pb was estimated in some of the

pore waters and greater overall contributions were found than those in the labile and total pools (Table 2). 'BHT' Pb accounted for up to ~50% in top and subsoil pore waters. The petrol Pb contribution was the lowest (<20%) in Pennine ore-rich Section I sites and typically 30-55% in petrol Pb-rich Section II sites. The isotopic composition was independent of the total concentration of Pb in solution.

3.3.5. A COMPARISON OF ISOTOPES RATIOS IN DIFFERENT POOLS

Figure 7 shows the comparison between the $^{206}Pb/^{207}Pb$ in the total pool with the ratio in the other pools i.e. labile, non-labile and solution pools. The $^{206}Pb/^{207}Pb$ ratios were also statistically compared, exploratory analysis of the model residuals was undertaken and the data produced a symmetrical histogram with a skewness=−0.0183. The observed residuals were plotted against the fitted values for the model and were found to be independent. The ANOVA for the model (Eqn. 3) is shown in Table 3. The pool (differences in $^{206}Pb/^{207}Pb$ ratios in total, labile and pore water pools) effect was found to be highly significant ($p<0.001$). The model was refined by partitioning the Pool Sum of Squares into the two orthogonal contrasts as described in Section 2.4. The subsequent ANOVA (analysis II) shows that the Sums of Squares for the two contrasts add up to the Pool Sum of Squares in the previous analysis. All contrasts were significant. The significant difference found in the comparison of $^{206}Pb/^{207}Pb$ ratios between the total vs labile/pore water pools (model I, as stated in Section 2.4.) indicates an enrichment of 'BHT' Pb in the labile/pore water pool (Figure 7).

As described previously, Pb contamination in these alluvial soils comes from a number of different sources. Mechanisms of Pb deposition to floodplain soils in periods of flooding would include deposition in particulate form, colloid–metal complexes including clay, nanoparticulate FeO_x or DOC, or sorption of Pb^{2+} ions to in-situ soils as the flood waters drained. Once in the soil, the deposited Pb, depending on form (e.g. $PbSO_4$, PbS, $PbCO_3$, sorbed to colloids) and soil conditions, will with time undergo processes including weathering, sorption, complexation and fixation with components of the soil matrix. Thus, the Pb that enters the labile pool is either (i) potentially soluble and will contribute

to the solid – solution equilibria or (ii) over longer periods of time move into the non-labile pool through fixation processes such as occlusion or precipitation.

The statistical analysis of the $^{206}Pb^/{^{207}}Pb$ ratios undertaken confirmed that there was a significant enrichment ($p<0.001$) in 'BHT' Pb in the labile and solution pools, both in the top and subsoils, compared to their respective total pools as well as a weaker but still significant difference ($P<0.02$) between the $^{206}Pb^/{^{207}}Pb$ ratios in the labile and solution pool (Fig 8). Thus although the addition of 'BHT' Pb to petrol was phased out in 2000 in the UK, results suggest that 'BHT' Pb is still enriched within the bio-available pools of Pb in these soils. This enrichment of 'BHT' Pb in the labile/solution pools could originate from current wet (contemporaneous samples of rain water in Scotland showed $^{206}Pb^/{^{207}}Pb$ ratios as low as 1.136 (Vinogradoff et al., 2005)) and dry deposition sources - the recent UK Defra metal deposition map (DEFRA, 2007) suggests that the Trent catchment still has Pb deposition of between 10-25 g ha^{-1} yr^{-1}. Present/recent Pb inputs could come from the continued dissolution of soluble $PbSO_4$ formed by weathering of $PbSO_4 \cdot (NH_4)_2SO_4$ (Biggins and Harrison, 1978) and possibly also a number of other traffic-related Pb-bearing species that occur at minor levels such as Pb^0, Pb_3O_4, $2PbCO_3PbO(OH)_2$ (Biggins and Harrison, 1980). These compounds are poorly soluble and may remain virtually unaltered in soils for a period of time, but their weathering products may cause delayed Pb inputs to the labile pool. In addition, adsorption of recently deposited 'BHT' Pb onto amorphous FeO_x and re-release under subsequent aerobic/anaerobic cycles as those occurring in periodic flooding events (Trent catchment flood regularly) may delay some transfer into the non-labile pool, thus maintaining an enrichment of 'BHT' Pb in the labile and solution pools. However, it is likely that much of this $^{206}Pb^/{^{207}}Pb$ enrichment found in the solution phase may be sorbed onto colloids, both organic and inorganic. It is highly likely that much of the solution Pb may be associated with colloidal/nano FeO_x present in the solution phase (Hasselöv and Von der Kammer, 2008).

4. CONCLUSIONS

Alluvial soils sampled within 10m of the banks of the rivers Dove and Trent floodplain show significant spatial differences in Pb concentration and isotopic composition with strong anthropogenic influences linked to past Pb mining and smelting activity, coal mining/combustion, sewage works, canal dredging and the deposition of traffic-related atmospheric Pb. The reactive pool of Pb was found to vary between 9 and 56% of the total soil Pb and was negatively correlated with soil pH. Whilst the Southern Pennine ore and/or Midlands coal signature is dominant in the labile pools of most soils, 'BHT' Pb appears to provide substantial contributions to the elevated Pb concentrations in some samples, particularly those close to major road systems or sewage outlets. Our results demonstrated that there is widespread contribution of 'BHT' Pb in each of the measured total, labile and pore water pools in top and subsoils The occurrence of 'BHT' Pb in subsoils (35-50 cm) indicates considerable post-depositional vertical migration.

Although Pb in the different soil pools studied follows the mixing line between Pennine ore/Midlands coal and 'BHT' Pb, the isotopic composition of the labile pool and the pore water suggests that 'BHT' Pb is enriched in the labile and pore water pools compared to the total soil pool. It was suggested that (i) 'BHT' Pb is still being deposited to alluvial soils, (ii) anaerobic conditions caused by flooding may preferentially help maintain more recently deposited 'BHT' Pb within the labile pool through FeO_x disolution followed by the release and re-adsorption of Pb and (iii) much of the Pb in solution may be sorbed to colloidal FeO.

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FIGURE CAPTIONS

Figure 1: Bedrock geological map of the River Trent Catchment.

Figure 2: Study area with location of sampling sites and other sites of interest mentioned in the text. The study are has been divided into 4 distinctive sections described in Section 3.3.2.

Figure 3: Variation in a range of soil characteristics in paired topsoils and subsoils.

Figure 4: Relationship between soil pH and Pb lability expressed as %E value.

Figure 5: The spatial variation of soil pH, Pb lability (as %E) and $^{206}Pb/^{207}Pb$ in topsoils along the study area. The km=0 is taken from the edge of the Southern Pennine Orefield, taken as the limits of the mineralised Derbyshire Carboniferous Limestone.

Figure 6: $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ ratio plot for total, labile and solution pools. Also shown for comparative purposes: potential sources, mixing line between the possible end-members, ratios for UK aerosols and contaminated soils.

Figure 7: Comparison of $^{206}Pb/^{207}Pb$ isotope ratios in the total soil Pb pool with the ratio found in the labile, non labile and solution pools for each sample. A 1:1 line is depicted for reference.

Figure 8: Comparison of $^{206}Pb/^{207}Pb$ isotope ratio in the labile pool and the pore water for each sample. A 1:1 line is depicted for reference.

Table 1. Characteristics of soils and pore waters and concentrations of Pb in the total, labile and pore water pools. LOI: loss on ignition; FeO_T, FeO_A: total and amorphous free iron oxides. NPOC: non-purgeable organic carbon.

| | | | | | | | TOTAL POOL SOIL | | | | LABILE POOL | | PORE WATER | | |
| | | | | | | | LOI | FeO_T | FeO_A | Total Pb | E-value | | | Pb | NPOC |
Sect.	Site	Depth	Easting	Northing	clay %	pH	%	%	%	mg/kg	mg/kg	% E	pH	µg/L	mg/L
I	1	0-15	416400	348282	39	5.9	14	5.0	1.7	249	116	47	6.1	6.47	21
I	2	0-15	414355	343708	34	7.3	13	4.5	1.4	124	32	26	7.6	2.72	27
I	3	0-15	414400	343684	18	6.4	15	4.8	1.8	261	92	43	6.4	1.34	33
I	4	0-15	411670	342137	30	6.2	9	3.1	0.8	116	58	50	6.2	2.37	20
I	5	0-15	409983	337657	44	5.8	13	4.4	1.6	108	36	34	6.1	1.74	24
I	6	0-15	415163	331508	41	7.2	9	3.5	1.1	84	24	28	7.2	0.27	20
I	7	0-15	420771	329652	50	6.2	13	3.9	1.6	135	52	38	6.3	2.14	30
II	8	0-15	428106	326349	19	6.8	8	2.7	1.2	192	53	27	6.9	0.85	31
II	9	0-15	429380	327091	41	6.5	14	3.7	1.6	237	72	30	6.5	2.02	34
II	10	0-15	434116	327262	28	7.3	8	3.7	1.7	205	36	17	7.3	0.23	21
II	11	0-15	434259	327251	33	6.5	14	3.7	1.6	221	66	30	6.3	2.10	29
II	12	0-15	441613	327552	24	6.1	11	3.5	1.5	159	55	35	5.8	4.90	27
II	13	0-15	445390	329980	40	7.0	15	4.1	1.9	241	44	14	7.0	0.18	22
III	14	0-15	451906	333318	21	6.7	8	2.2	0.5	373	170	45	7.3	5.54	31
III	15	0-15	469183	343982	50	7.4	15	3.6	1.3	680	315	43	7.6	1.02	41
III	16	0-15	469241	344110	30	7.3	9	3.3	1.4	470	78	17	7.9	0.98	19
III	17	0-15	469201	344265	46	7.3	9	2.7	0.9	302	81	27	8.1	0.65	25
III	18	0-15	470631	346372	45	7.1	18	4.1	1.9	860	193	22	7.8	1.72	62
III	19	0-15	473453	350698	28	7.2	9	3.2	1.0	353	104	30	7.7	0.93	28
III	20	0-15	473513	350506	32	7.1	12	3.6	1.2	389	100	26	7.7	0.36	37
III	21	0-15	477078	353827	39	7.2	11	3.5	1.3	340	80	23	7.8	0.46	28
III	22	0-15	477078	353827	48	7.4	8	3.0	0.7	212	45	21	7.6	0.47	25
III	23	0-15	477024	353983	26	7.1	11	2.9	1.1	319	88	27	7.9	1.23	24
III	24	0-15	480194	359977	47	7.1	14	4.4	1.5	547	125	23	7.9	1.00	43
III	25	0-15	480194	359977	19	7.8	6	3.1	1.2	376	74	20	8.1	0.51	24
IV	26	0-15	483180	308929	33	7.7	7	2.8	1.4	90	11	12	7.9	0.34	19
IV	27	0-15	486625	322273	54	7.5	15	4.4	2.1	175	48	27	8.9	0.72	59
I	1	35-50	416400	348282	35	6.9	7	5.2	1.5	422	229	54	7.1	1.22	14
I	2	35-50	414355	343708	36	7.5	7	4.6	1.0	119	18	15	7.2	1.41	43
I	4	35-50	411670	342137	46	6.9	5	3.2	0.6	95	37	39	7.0	2.53	21
I	5	35-50	409983	337657	35	5.3	8	4.8	1.7	139	57	41	5.0	1.12	30
II	8	35-50	428106	326349	17	6.9	4	1.9	0.7	43	15	36	6.8	0.33	38
II	9	35-50	429380	327091	29	6.7	6	2.7	0.9	80	30	37	6.9	0.87	36
II	10	35-50	434116	327262	22	7.4	8	5.0	1.8	106	22	21	7.6	0.42	19
II	11	35-50	434259	327251	23	6.2	5	2.5	1.0	97	34	35	5.8	1.64	41
II	12	35-50	441613	327552	29	6.4	7	4.0	1.4	132	49	37	6.3	1.62	20
II	13	35-50	445390	329980	37	7.0	14	5.0	2.6	387	91	24	6.8	0.57	31
III	14	35-50	451906	333318	22	6.7	5	2.3	0.5	300	169	56	7.0	2.61	28
III	15	35-50	469183	343982	45	7.6	10	4.0	1.4	877	192	22	7.8	0.57	35
III	16	35-50	469241	344110	39	7.5	9	3.9	1.7	1012	159	16	7.8	0.91	18
III	17	35-50	469201	344265	37	7.6	8	3.4	1.3	592	139	23	7.8	0.42	28
III	18	35-50	470631	346372	39	7.5	14	4.5	2.2	1282	273	21	7.7	1.13	63
III	22	35-50	477078	353827	33	7.4	7	2.9	1.2	328	71	22	7.6	0.34	22
III	24	35-50	480194	359977	50	7.1	11	4.4	1.8	817	188	24	7.3	0.24	33
IV	26	35-50	483180	308929	42	7.8	7	2.3	2.0	123	12	9	7.9	0.17	24
IV	27	35-50	486625	322273	44	8.0	9	3.7	1.3	241	70	29	8.2	0.49	38

Table 2. Isotopic composition and inferred BHT-derived Pb in the total, labile, non-labile and pore water pools at each sampling site.

Sect	Site	Depth	Pb IN SOIL $^{206}Pb/^{207}Pb$	Pb IN SOIL $^{208}Pb/^{207}Pb$	Pb IN SOIL $\%Pb_{BTH}$	LABILE Pb $^{206}Pb/^{207}Pb$	LABILE Pb $^{208}Pb/^{207}Pb$	LABILE Pb $\%Pb_{BTH}$	NON LABILE Pb $^{206}Pb/^{207}Pb$	NON LABILE Pb $^{208}Pb/^{207}Pb$	NON LABILE Pb $\%Pb_{BTH}$	LABILE/NONLABILE RATIO $^{206}Pb/^{207}Pb$	LABILE/NONLABILE RATIO $^{208}Pb/^{207}Pb$	PORE WATER $^{206}Pb/^{207}Pb$	PORE WATER $^{208}Pb/^{207}Pb$	PORE WATER $\%Pb_{BTH}$
I	1	0-15	1.177	2.451	<10	1.173	2.449	10	1.181	2.452	<10	0.993	0.999	1.168	2.448	14
I	2	0-15	1.178	2.453	<10	1.171	2.450	12	1.180	2.453	<10	0.992	0.999	1.164	2.445	18
I	3	0-15	1.179	2.454	<10	1.172	2.453	10	1.184	2.456	<10	0.990	0.999	1.169	2.450	13
I	4	0-15	1.180	2.454	<10	1.175	2.452	<10	1.186	2.456	<10	0.991	0.998	1.173	2.444	<10
I	5	0-15	1.158	2.436	23	1.149	2.428	32	1.163	2.440	19	0.988	0.995	1.153	2.431	28
I	6	0-15	1.179	2.452	<10	1.167	2.447	15	1.183	2.454	<10	0.987	0.997	1.168	2.438	14
I	7	0-15	1.178	2.454	<10	1.171	2.451	11	1.182	2.455	<10	0.991	0.999	1.166	2.443	16
II	8	0-15	1.142	2.419	38	1.136	2.417	44	1.145	2.419	36	0.992	0.999	1.139	2.412	42
II	9	0-15	1.132	2.407	48	1.128	2.411	51	1.133	2.405	47	0.996	1.002	1.136	2.413	44
II	10	0-15	1.135	2.411	45	1.131	2.411	48	1.136	2.411	44	0.996	1.000	1.125	2.410	55
II	11	0-15	1.137	2.412	43	1.130	2.413	50	1.140	2.412	40	0.991	1.000	1.143	2.418	38
II	12	0-15	1.141	2.417	39	1.134	2.415	46	1.145	2.418	36	0.991	0.999	1.137	2.417	43
II	13	0-15	1.138	2.412	42	1.135	2.415	45	1.139	2.411	41	0.996	1.002	1.147	2.426	34
III	14	0-15	1.175	2.452	<10	1.172	2.452	10	1.177	2.453	<10	0.996	1.000	1.173	2.451	<10
III	15	0-15	1.169	2.447	13	1.167	2.447	15	1.170	2.447	12	0.998	1.000	1.156	2.429	26
III	16	0-15	1.159	2.436	22	1.157	2.437	24	1.160	2.436	22	0.998	1.000	1.158	2.434	24
III	17	0-15	1.168	2.446	15	1.166	2.444	16	1.168	2.446	14	0.998	0.999	1.165	2.441	17
III	18	0-15	1.161	2.437	21	1.158	2.439	24	1.162	2.437	20	0.996	1.001	1.157	2.436	24
III	19	0-15	1.166	2.443	17	1.164	2.441	18	1.166	2.443	16	0.998	0.999	1.165	2.440	17
III	20	0-15	1.164	2.442	18	1.162	2.443	19	1.164	2.441	18	0.999	1.001	1.163	2.438	19
III	21	0-15	1.163	2.441	19	1.161	2.439	21	1.164	2.442	18	0.997	0.999	1.159	2.436	23
III	22	0-15	1.178	2.455	<10	1.175	2.453	<10	1.178	2.456	<10	0.997	0.999	1.165	2.441	17
III	23	0-15	1.163	2.440	19	1.161	2.440	21	1.163	2.441	19	0.998	1.000	1.162	2.436	20
III	24	0-15	1.158	2.433	24	1.156	2.433	26	1.159	2.433	23	0.997	1.000	1.156	2.427	26
III	25	0-15	1.162	2.441	20	1.159	2.438	23	1.162	2.442	20	0.997	0.998	1.159	2.435	23
IV	26	0-15	1.171	2.454	11	1.167	2.448	15	1.172	2.455	11	0.996	0.997	1.162	2.434	20
IV	27	0-15	1.165	2.449	17	1.163	2.445	19	1.166	2.450	16	0.997	0.998	1.158	2.430	24
I	1	35-50	1.178	2.454	<10	1.175	2.455	<10	1.181	2.452	<10	0.995	1.001	1.168	2.447	15
I	2	35-50	1.178	2.453	<10	1.169	2.449	14	1.179	2.453	<10	0.991	0.998	1.161	2.443	21
I	4	35-50	1.186	2.458	<10	1.182	2.458	<10	1.189	2.458	<10	0.994	1.000	1.170	2.453	12
I	5	35-50	1.169	2.447	14	1.162	2.444	20	1.173	2.448	<10	0.990	0.998	1.162	2.442	20
II	8	35-50	1.167	2.446	15	1.152	2.433	29	1.175	2.453	<10	0.980	0.992	1.160	2.442	21
II	9	35-50	1.158	2.431	23	1.150	2.430	31	1.163	2.432	19	0.989	0.999	1.137	2.410	43
II	10	35-50	1.160	2.433	21	1.146	2.426	35	1.164	2.435	18	0.985	0.996	1.153	2.439	28
II	11	35-50	1.171	2.446	12	1.159	2.439	23	1.177	2.450	<10	0.985	0.996	1.150	2.431	31
II	12	35-50	1.175	2.453	<10	1.168	2.449	14	1.179	2.455	<10	0.991	0.998	1.159	2.436	23
II	13	35-50	1.130	2.405	50	1.126	2.407	53	1.131	2.404	49	0.996	1.001	1.134	2.416	46
III	14	35-50	1.182	2.460	<10	1.179	2.458	<10	1.185	2.462	<10	0.995	0.998	1.176	2.450	<10

III	15	35-50	1.180	2.457	<10	1.177	2.456	<10	1.180	2.457	<10	0.997	1.000	1.169	2.452	13
III	16	35-50	1.162	2.440	20	1.163	2.443	19	1.162	2.439	20	1.001	1.002	1.162	2.439	19
III	17	35-50	1.175	2.454	<10	1.173	2.453	<10	1.176	2.454	<10	0.998	0.999	1.163	2.438	19
III	18	35-50	1.164	2.440	18	1.163	2.442	19	1.164	2.439	18	0.999	1.001	1.165	2.436	17
III	22	35-50	1.157	2.437	25	1.154	2.435	28	1.158	2.437	24	0.997	0.999	1.150	2.417	31
III	24	35-50	1.169	2.448	13	1.165	2.445	17	1.171	2.449	12	0.995	0.998	1.165	2.447	17
IV	26	35-50	1.165	2.448	17	1.164	2.445	18	1.166	2.448	17	0.999	0.998	1.155	2.435	26
IV	27	35-50	1.171	2.451	12	1.169	2.450	13	1.171	2.451	11	0.998	1.000	1.165	2.438	18

Table 3: ANOVA tables for statistical analysis showing the difference in the ^{206}Pb/^{207}Pb ratio among the total, labile and pore water pools.

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Analysis I					
SoilStrat	45	0.0232053	0.00051567	32.321	$< 2.2 \cdot 10^{-16}$
Pool	2	0.0010448	0.00052238	32.741	$2.07 \cdot 10^{-11}$
Residuals	90	0.0014359	0.00001595		
Analysis II					
SoilStrat	45	0.0232053	0.00051567	32.3214	$< 2.2 \cdot 10^{-16}$
TvsPL	1	0.0009573	0.00095734	60.0041	$1.36 \cdot 10^{-11}$
PvsL	1	0.0000874	0.00008741	5.4786	0.02146
Residuals	90	0.0014359	0.00001595		

FIGURE 1

Clay, undifferentiated
Chalk
Oolite, undifferentiated
Lias, undifferentiated

Magnesian Limestone
Millstone Grit
Permian and Triassic Sandstone
Permian Mudstone

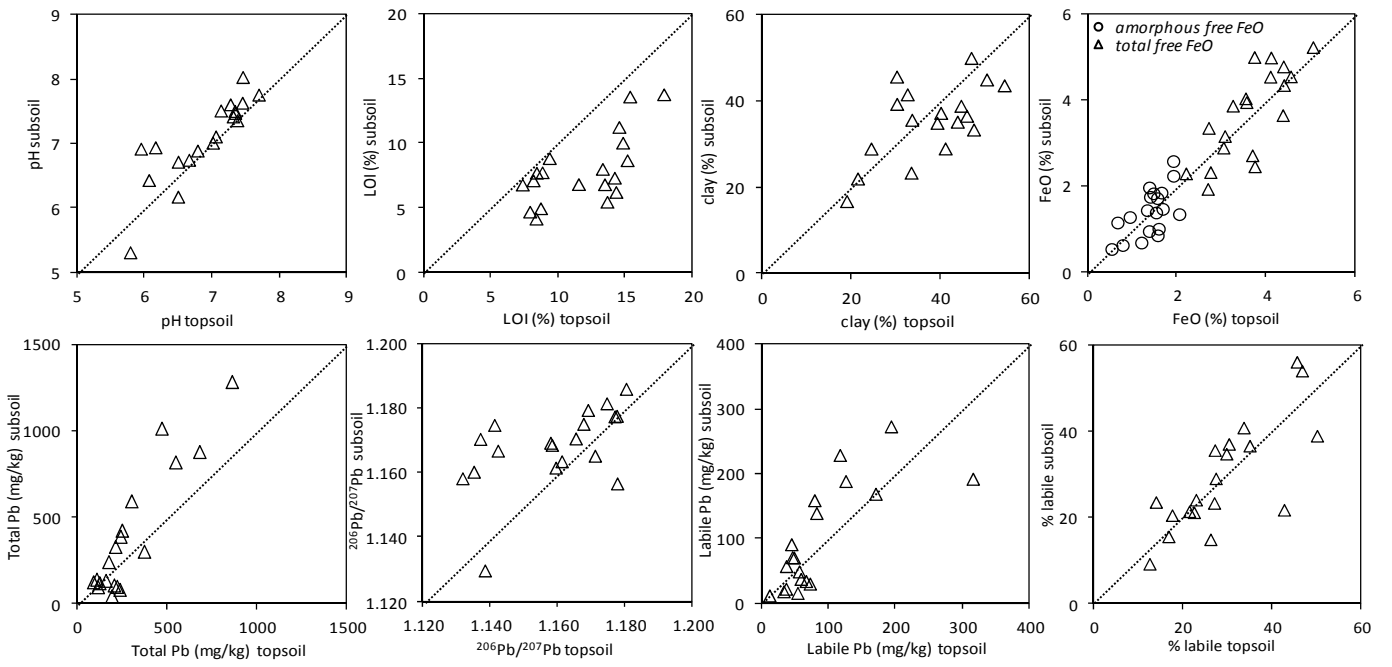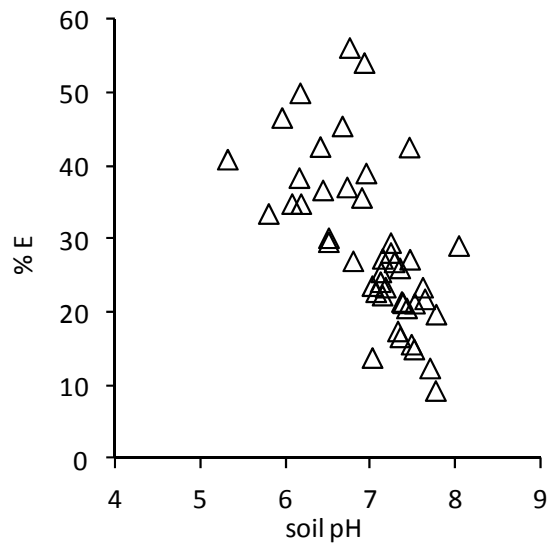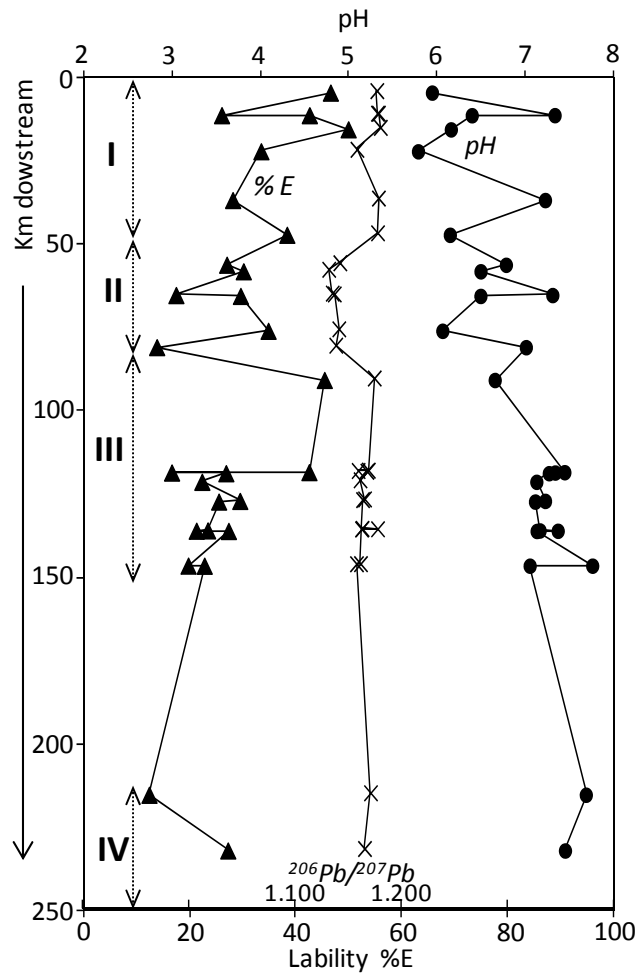Carboniferous Limestone
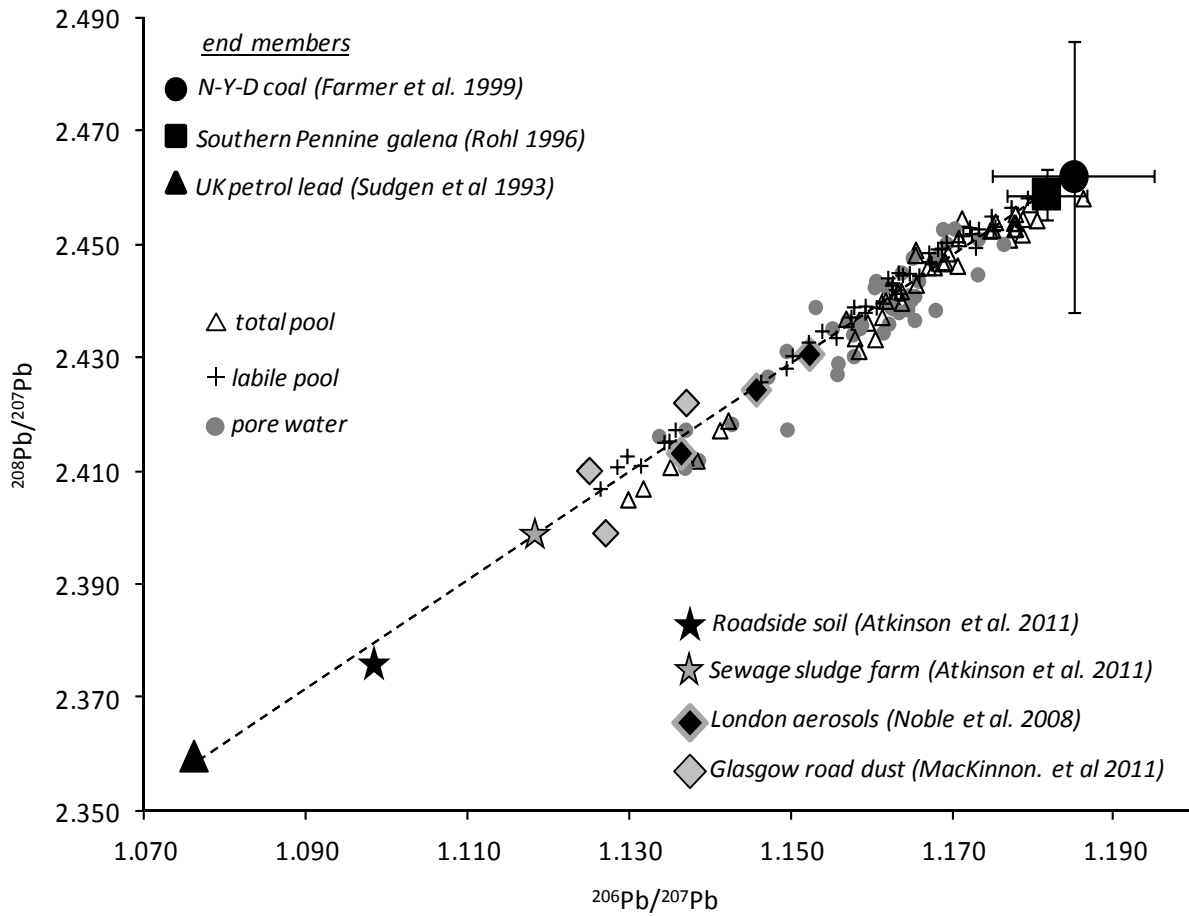Triassic Mudstone
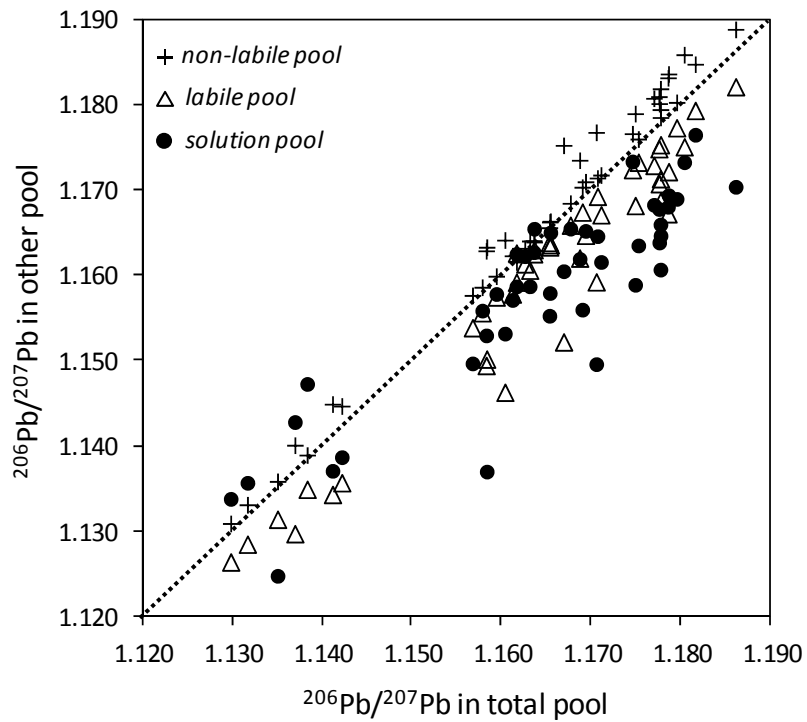Coal Measures (Westphalian)
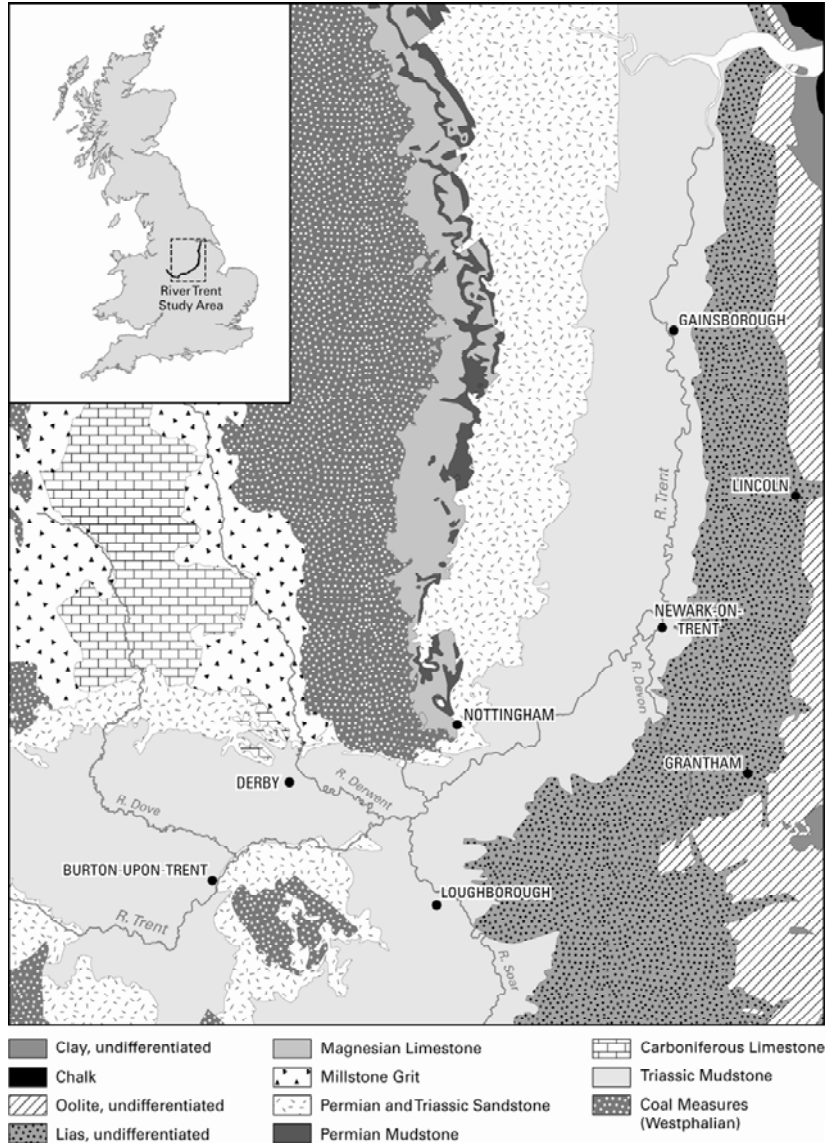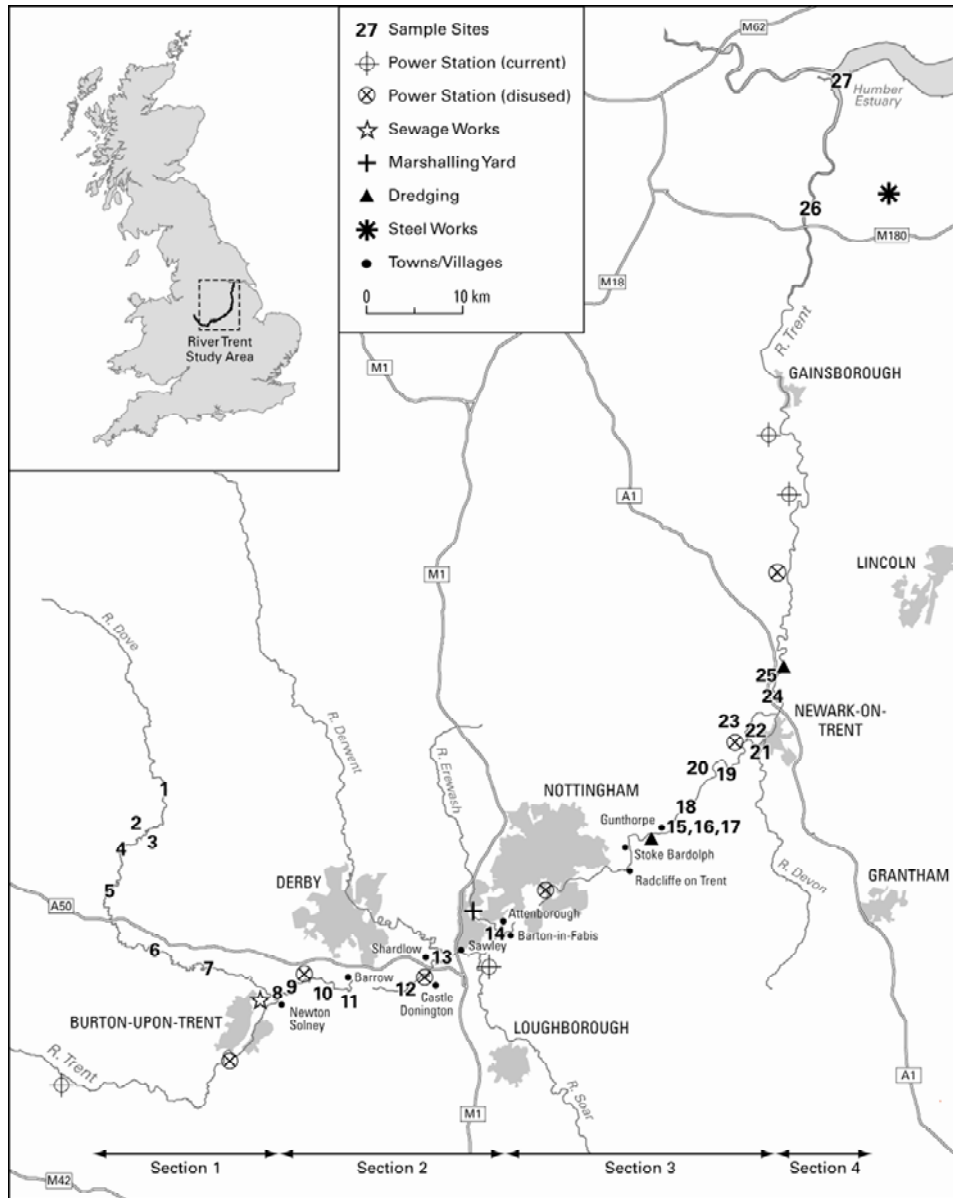
FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8