Lead bioaccessibility in topsoils from lead mineralisation and urban domains, UK.

J D Appleton*, M R Cave, B Palumbo-Roe and J Wragg

British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

* Corresponding author: J. D. Appleton, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

Tel: +44 (0) 115 936 3207

Fax: +44 (0) 115 936 3200

E-mail address: jda@bgs.ac.uk (J. D. Appleton)

Abstract

Predictive linear regression (LR) modelling indicates that total Pb is the only highly significant independent variable for estimating Pb bioaccessibility in "mineralisation domains" located in limestone (high pH) and partly peat covered (low pH) shale-sandstone terrains in England. Manganese is a significant minor predictor in the limestone terrain, whilst organic matter and sulphur explain 0.5% and 2% of the variance of bioaccessible Pb in the peat-shale-sandstone terrain, compared with 93% explained by total Pb. Bootstrap resampling shows that LR confidence limits overlap for the two mineralised terrains but the limestone terrain has a significantly lower bioaccessible Pb to total Pb slope than the urban domain. A comparison of the absolute values of stomach and combined stomach-intestine bioaccessibility provides some insight into the geochemical controls on bioaccessibility in the contrasting soil types.

Capsule Abstract

Total Pb is the major predictor for bioaccessible Pb in topsoils from two lead mineralised areas in England.

Keywords

bioaccessibility, lead, mining, mineral processing, urban, topsoil, England, UK

1. Introduction

A significant proportion of the rural landscape in Great Britain has elevated topsoil concentrations of lead (Pb). In a study of the background concentrations of potentially harmful elements (PHEs) in soils in England, Ander et al. (2011) and Cave et al. (2012) demonstrated that 2% of the land area could be classified as being impacted by Pb mineralisation and that systematically surveyed soil samples in this domain (Figure 1) had median and 95th percentile lead concentrations of 330 mg kg^{-1} and 1900 mg kg^{-1} compared with 170 mg kg^{-1} and 790 mg kg^{-1} respectively for urban areas (DEFRA, 2012; Figure 1). The Pb content of soil is important since this PHE is toxic to humans and particularly because children absorb up to 40% to 50% into the bloodstream when ingested or inhaled (Fischbein and Hu, 2007; Grant, 2009). A number of studies have shown that relatively low concentrations of Pb in blood can lead to significant decrease in IQ of children (Bierkens et al., 2012; Isaac et al., 2012, Jakubowski, 2011; Kim et al., 2010).

The main exposure pathway for Pb in soil is via the soil ingestion pathway (Paustenbach, 2000), so it is the fraction of Pb that is absorbed into the body following soil ingestion, i.e. the bioavailable fraction, which is important for assessing human health risk. In vitro bioaccessibility testing has been developed and validated to be used as a conservative estimate of bioavailability. In general bioaccessibility tests fall into two categories: (i) those which try to closely mimic the physiological conditions in the stomach and upper intestine (Oomen et al., 2002; Wragg et al., 2011) and (ii) methods which use a simplified extraction media (Drexler and Brattin, 2007; Zia et al., 2011).

The method adopted by this study is the Unified BARGE method (UBM), which has undergone inter-laboratory trials to assess for suitability as a standard methodology (Wragg et al., 2011) and been correlated against a swine model for Pb (Caboche, 2009; Denys et al., 2012). The UBM method measures the fraction of Pb which is released from the soil into solution in the gastro-intestinal (GI) tract in a form that can potentially be absorbed into the blood stream (Wragg and Cave, 2003; Intawongse and Dean, 2006). The UBM in vitro test is a partial extraction methodology and the amount of Pb solubilised during the extraction is dependent on the how soluble the different chemical forms of Pb in the soil are in the UBM solutions. Guidelines for the use of data produced by in vitro bioaccessibility testing methods in human health risk assessment have recently been produced (Nathanail, 2009).

The bioaccessibility and hence bioavailability of Pb bound to the soil depends to a certain extent upon the properties of the soil and the source of the contaminant. Cave et al. (2011) described how soil pH, organic matter content, mineral constituents, and solid phase partitioning of PHEs and soil ageing may influence bioaccessibility of contaminants. Pb bioaccessibility studies have generally focussed on the relationships between total and bioaccessible Pb concentrations (Farmer et al., 2011; Cave et al., 2011; Appleton et al., 2012), sometimes with due consideration given to the different sources of Pb contamination (Smith et al. 2011a), mineralogy and soil chemistry (Denys et al., 2007). There are a number of studies which illustrate that the bioaccessible fraction can come from different physico-chemical components in the soil. Denys et al (2007) demonstrates that in some soil the Pb can come from cerussite ($PbCO_3$) and sulphur containing phases, whereas Beak et al. (2008) found that the mineral Birnessite, a commonly found manganese oxide mineral in soil, had a high affinity to absorb Pb.

Smith et al. (2011b) used XANES analysis of Pb speciation to demonstrate that Pb associated with Fe minerals and the organic fraction was predominantly solubilised in the gastric phase. However, during the intestinal phase of the in vitro procedure, Pb was strongly associated with formation of ferrihydrite which precipitated due to the pH (6.5) of the intestinal phase. If a linear regression model is robust, it can be used to predict bioaccessibility from soil properties so that the in vitro bioaccessibility test does not have to be carried out on every soil from a given soil region. However, this is only useful if the soil chemistry properties are already known or more economically measured than the in vitro bioaccessibility. In addition, the relative size of the coefficients of significant predictor variables can provide an insight into processes governing bioaccessibility. Multiple LR models may be very specific to a particular soil type and geochemical domain so may not be universally applicable, although this was not the case in a recent study in which no significant differences could be detected between four UK urban domains (Appleton et al., 2012).

Concentrations of Pb in topsoils from UK lead mineralisation domains are in almost all cases strongly influenced by mining and mineral processing activities. This Pb accumulation in the topsoils is mainly a result of the dispersion of (i) mineral processing waste products, and (ii) Pb in fumes from smelting in the major historical mining areas of Derbyshire, N. Pennines and Somerset (Figures 1 - 2). $^{206}Pb/^{207}Pb$ ratios of bulk soil and peat in the Rookhope (N. Pennines) area (1.18) are higher than for grass shoots (1.16) and new growth heather (1.14) (Chenery et al., 2012). The ratio in the top few cm of peat (1.16) suggests that grass accessed Pb consisting of both Pennine ore Pb (1.16 – 1.207) and long-range Pb deposition from petrol Pb (1.06 – 1.09). Outside the Pb mineralisation areas, anthropogenic contamination in urban areas produces high Pb concentrations in topsoils, the most notable of which is the London area (Figures 1 - 2).

The aim of this study is to get an overview of the bioaccessibility of lead in areas with Pb mineralization in the UK using soils collected during geochemical sampling programs and to relate this to the unspeciated total concentrations of major and trace elements in these soils. It is appreciated that total element concentrations will not pick out all the relationships between mineral phases and the bioaccessible Pb; however, they may help to predict how Pb bioaccessibility can vary in Pb mineralization and urban domains and in different soil types within the UK. Predictive regression modelling between bioaccessible Pb and a range of total elemental compositions and soil properties was executed for the Derbyshire and Rookhope Pb mineralisation areas in order to assess the potential for developing a national mineralisation domain bioaccessible Pb dataset derived from the British Geological Survey (BGS) Estimated Ambient Background Soil Chemistry dataset (Appleton, 2012). Comparisons are made with linear regression models for UK urban areas (Appleton et al., 2012).

2. Materials and methods

2.1 Sample selection

Forty nine samples were selected from the Geochemical Baseline Survey of the Environment (G-BASE) (Johnson et al., 2005) regional topsoil geochemical data set (<2 mm fraction) for the Derbyshire Pb mineralisation domain, where the principal bedrock is Carboniferous limestone. The samples selected for further preparation and bioaccessibility testing are representative of the wide range of total Pb found in this area (Figure 3). Forty eight <2 mm topsoil samples were selected from the Rookhope (Northern Pennines) Pb mineralisation domain where the principle bedrocks are Carboniferous (Namurian) shales with subsidiary siltstones and sandstones (Chenery et al., 2012). About a third of the Rookhope study area is covered with peat deposits (Figure 4). The Rookhope samples are representative of the wide range of total Pb (48 –

27586 mg kg^{-1}; Chenery et al., 2012) and soil types found in this area. Background information on mineralisation and mineral processing in the Rookhope area is available in Chenery et al. (2012).

2.2 Sample collection, preparation and determination of total concentrations

Topsoil samples in the Derbyshire area were collected from open ground at an average density of one per 2 km^2 (Johnson et al., 2005) whilst in the Rookhope area, samples were collected along a series of transects at a nominal spacing of 500 m (Chenery et al., 2012). Composite samples, based on 5 subsamples taken at the centre and four corners of a 20-m square, were collected from 5–20 cm depth. Approximately 40 chemical elements were determined in the <2 mm size fractions of the Derbyshire topsoils. Sample preparation, X-ray fluorescence analytical methods, and quality control procedures are described in Allen et al. (2011) and Johnson (2011). The Rookhope data set includes total element data for 29 major and trace elements (ICP-AES), organic matter (OM, based on loss on ignition at 450°C). Soil pH was measured by suspending soil in 0.01 M $CaCl_2$ solution in the ratio 1:2.5 (Chenery et al., 2012).

2.3 Bioaccessible lead

Samples selected for bioaccessibility testing were further sieved to <250 μm as this particle size fraction is considered to be the optimum size to adhere to children's hands (Duggan et al., 1985). The <250 μm fraction of the samples was assessed for bioaccessible Pb contents using the UBM which is a two stage in vitro physiological GI simulation, carried out according to the methodology of Caboche (2009), recently described by Denys et al. (2012). The UBM was designed to ensure adequate conservatism and robustness whilst still being applicable to a range of soil types. In

particular, this included a stomach pH of 1.2, which was based on preliminary studies where calcareous soils were found to cause difficulties in maintaining a low pH in the stomach phase (Wragg et al 2011).

The UBM validation used a juvenile swine model for Pb and other PHEs in a study of 16 different soils contaminated by mining and smelting practices, including the reference material NIST 2710 (Caboche, 2009; Denys et al., 2012). Correlation between the relative bioavailability and bioaccessibility of Pb, as part of the validation study, was highly significant, both for the gastric (stomach) and the gastro-intestinal phases. Absorption of available Pb occurs in the small intestine of the GI tract and the UBM methodology provides samples for analysis from both the 'stomach' (BS-Pb) and 'stomach and intestine' (BSI-Pb) phases. The BS-Pb is then the amount of Pb extracted during the gastric phase extraction only and the BSI-Pb is the Pb extracted from the sequential extraction of the gastric phase followed by the intestine phase; this is not the sum of the BS-Pb and the BSI-Pb. Whilst both the 'stomach' and 'stomach and intestine' phases have been shown to be correlated with animal bioavailability (Denys et al., 2012), the 'stomach' phase gives a more conservative (higher) bioaccessible fraction than the stomach and intestine due, primarily, to the low pH conditions. In addition to this, the higher pH of the 'stomach and intestine' leads to poorer reproducibility of the results (Wragg et al., 2011). The 'stomach' phase samples have been chosen as being most suitable for this study, although the relationship between BS-Pb and BSI-Pb in mineralisation and urban domains is also examined.

Chemical analysis of bioaccessibility extracts was carried out as described by Wragg et al. (2011) using a Thermo Elemental ExCell quadrupole ICP-MS instrument in combination with a Cetac ASX-510 autosampler, according to the operating conditions previously described by Watts et al. (2008). The quality control (QC) of the

bioaccessibility extractions was monitored by carrying out replicate analyses of a BGS guidance soil BGS 102 (Wragg, 2009). At present there are no certified reference materials for bioaccessible Pb, however, BGS 102 used for QC checks in this study has been the subject of an international inter-laboratory trial (Wragg et al., 2009; 2011), which has generated the reference value used in this study. Within every batch, of a maximum of 10 unknown samples, one duplicate, one quality control soil and one blank were extracted.

Replicate bioaccessibility values for BGS 102 of 14.3 ± 1.32 mg kg^{-1} (n = 7) and 14.3 ± 1.55 mg kg^{-1} (n = 9) for Rookhope and Derbyshire, respectively, were obtained for the 'stomach' phase of the UBM, which are in good agreement with consensus values of 12.8 ± 6.0 mg kg^{-1}(Wragg et al., 2011). The detection limits for the 'stomach' phase calculated as five times the average blank measurement equated to 3 mg kg^{-1}. All blank UBM extractions returned values below the method detection limits.

2.4 Statistical analysis

LR and MLR analysis in MINITAB® was used to model the relationship between bioaccessible Pb (BS-Pb <250 µm fraction) with total Pb, Al, Ca, Fe, K, Mg, Mn, P, Si, Ti, pH and organic matter (OM wt. %) in the <2 mm fraction of topsoil samples from the Rookhope area and total Pb, Al, Ca, Fe, Mg, Mn, P and Ti in the Derbyshire area (no K, Si, pH and OM data being available for the G-BASE soil samples used in this study). Soil chemistry summary statistics for Derbyshire and Rookhope are presented in Table 1.

Regression analysis, Analysis of Covariance and bootstrap resampling was carried out following the methodology described in Appleton et al. (2012). In the Rookhope area, a

subset with <10,000 mg kg^{-1} total Pb was used for MLR, after removing a sample with a large leverage (27,203 mg kg^{-1} Pb).

3. Results and discussion

3.1 Summary statistics

The mean, median and ranges of total Pb, BS-Pb, BSI-Pb and the proportion of bioaccessible Pb (the stomach bioaccessible fraction, % Pb-BSAF; stomach + intestinal % Pb-BSIAF) are listed in Table 1 together with summary statistics for the other soil chemistry variables used for MLR and LR. The spatial variation in BS-Pb in the Derbyshire samples is related to total Pb concentrations in the <2 mm fraction of surface soils (Figure 3). The soils from the Derbyshire area, underlain by Carboniferous limestones, are less acid (median pH 5.7) and with lower organic matter (median 5.1%) than the acidic (median pH 3.7) and organic matter rich (median 26% OM) soils of the Rookhope area that are underlain mainly by peat, Namurian shales and sandstones (Figure 4). Relatively high BS-Pb together with OM and S characterise the peat soils located to the east of the mouth of the Rookhope Chimney, which took poisonous Pb and S fumes from the historic Pb smelter located in Lintzgarth out of the valley bottom up onto the moor at Redburn Common (Figure 4).

The median stomach bioaccessible fraction (%Pb BSAF) ranges from 51% in Derbyshire to 67% in Rookhope which is comparable to BSAF levels recorded in urban topsoils (Appleton et al., 2012). Pb bioaccessibility data for smelter-contaminated agricultural soils in northern France have average stomach phase bioaccessibility of 58% (Pelfrêne et al., 2012) determined using the UBM, whilst peri-urban mining/smelting impacted soils in Australian and New Zealand (Smith et al., 2011a) have mean gastric phase bioaccessibility of 55% (range 27 – 95%, n = 13; determined

using the Solubility Bioavailability Research Consortium in vitro assay at pH 1.5; mean total Pb = 2051 mg kg^{-1}).

3.2 Regression analysis

The regression modelling procedures described above gave a range of statistically and geochemically appropriate LR and MLR models for bioaccessible Pb (Table 2). R^2 indicates the proportion of the variance in BS-Pb accounted for by each regression model. R^2 (adjusted) is no more than 2% lower than R^2 for models with fitted intercepts. All regression models are statistically significant ($p < 0.0005$). High intercept values may reflect the magnitude of the errors on the input parameters because least squares LR makes the assumption that all the uncertainty is associated with the y axis. Positive intercept values are theoretically impossible so, in such cases, it may be more appropriate to use models without fitted intercepts. However, in the Derbyshire, Rookhope (<10,000 mg kg^{-1} subset) and Combined Derbyshire + Rookhope models (Table 2) the intercept values are relatively low, so the difference between using models with or without fitted intercepts for estimating BS-Pb from total element concentrations will be relatively small.

3.2.1 Derbyshire

Stepwise LR using untransformed data suggests that total Pb and Ca may be significant predictors. All variables except Al are positively skewed so the SLR was repeated using log-transformed data. This indicated that only LnPb and LnMn are likely to be significant predictors of LnBS-Pb. The negative coefficient for Mn implies that Mn slightly restricts, rather than amplifies the bioaccessibility of Pb. 96.7% of the variance in BS-Pb can be explained by total Pb, whilst Mn accounts for only 0.3% of the total

variance in BS-Pb. Only Pb and Ca are significantly correlated with BS-Pb. However, LR based on log-transformed data indicates that LnMn ($P < 0.0005$) is a significant predictor together with LnPb ($P < 0.0005$), whereas LnCa ($P = 0.030$) is not.

Linear regression using Pb as the sole predictor for BS-Pb (Figure 5) indicates that the intercept (39 mg kg^{-1}) is not significant ($P = 0.260$) and not significantly different from zero (Standard Error = 34 mg kg^{-1}). The regression model with the intercept not fitted (BS-Pb = 0.508 Pb; Table 2) is the preferred model for the Derbyshire dataset.

Mn explains such a small percentage of the variance and is not a significant predictor in the other Pb mineralisation area studied (Rookhope), so it would not be appropriate to include Mn as a predictor for estimating Pb bioaccessibility in Pb mineralisation domains in England. SLR and LR of %Pb BSAF against chemical variables excluding total Pb, indicates that only Mn is significant ($p = 0.003$) and this explains 16% of the variance. The negative coefficient suggests that Mn restricts the Pb bioaccessibility, which is compatible with previous research (Hettiarachchi et al., 2000).

SLR of BSI-Pb using Pb and major element variables as potential predictors indicates that only total Pb and Ca are significant for untransformed data whilst LnPb, LnMn and LnCa are significant for Ln_e transformed data. The linear regression model for LnBSI-Pb vs. LnPb, LnMn and LnCa (LnBSI Pb = 0.913 + 1.23 LnPb - 0.403 LnMn - 0.216 LnCa) indicates that Pb explains 86% of the total variance of BSI-Pb, Mn 7% and Ca 1%. Both LnMn and LnCa have negative coefficients implying that the BSI- Pb is slightly constrained by Mn and Ca.

On average BSI-Pb is only about 0.2 of BS-Pb (Table 1). Previous studies have indicated higher factors of 0.45 (Farmer et al., 2011; Glasgow urban area), 0.30 (Barsby et al., 2012; Northern Ireland rural soils), 0.5 (Roussel et al., 2010, urban soils), and 0.36 (Pelfrêne et al., 2012; agricultural soils from N. France). BSI-Pb is generally lower

than BS-Pb due to precipitation or readsorption of dissolved Pb species at the higher pH of the intestinal phase (Sialelli et al., 2010, 2011; Smith et al., 2011a).

On average, Pb in the <250 μm fraction is about 90% of total Pb in the <2 mm fraction (Pb <250 μm = 131 + 0.88 Pb <2 mm fraction). Size fraction is probably not a very important factor for BS-Pb vs. total Pb models. At higher total Pb concentrations, grain size distribution may be an important factor in some samples, possibly reflecting the types of soils developed on different parent materials and also the influence of different types of anthropogenic contamination.

3.2.2 Rookhope

SLR using untransformed data suggests that total Pb, S, OM and pH may be significant predictors. LR confirms that these four predictors are all statistically significant explaining 86%, 2%, 5% and 1% of the total variance of BS-Pb, respectively (Table 2). S has a negative coefficient implying that bioaccessibility is restricted when a significant proportion of the Pb occurs in sulphides (or sulphates), whilst the positive coefficients for OM and pH suggests that Pb bioaccessibility is enhanced at higher levels of OM and pH. The data tend to be strongly skewed so the SLR was repeated using Ln_e transformed data which suggested that LnPb, LnFe and LnS may be significant predictors, and this is confirmed by LR. After excluding one extreme sample (27,203 mg kg^{-1} Pb), SLR of untransformed data suggests that total Pb is the only significant predictor, whilst SLR of the Ln-transformed data indicate that total Pb, Fe, S, OM and pH may be significant, although the P-values suggest that pH ($p = 0.022$) and perhaps also OM ($p = 0.003$), S ($p = 0.021$) and Fe ($p = 0.002$) may not be strongly significant predictors. LR indicates that only Pb, OM and S ($p = < 0.0005 – 0.001$) are significant predictors of BS-Pb, explaining 93%, 0.5% and 2%, respectively, of the total

variance. OM has a positive coefficient while S has again a negative coefficient (Table 2), despite OM and S being positively correlated in the Rookhope samples (R^2 0.897). This can be explained considering the sensitivity of bioaccessibility to Pb-bearing phase speciation and suggests that the presence of the primary ore mineral galena (PbS) decreases the bioaccessibility in the soil. Sulphur has a strong affinity for organic matter which explains the positive correlation between OM and S. High concentrations are present in the peaty soils of the Rookhope area. Part of this S may be due to atmospheric deposition related to Pb ore smelting, which was centred in the upland peaty sectors of the Rookhope area. SLR and LR of %Pb BSAF against chemical variables excluding total Pb, indicates that only P is significant ($p = 0.002$) and this explains 18% of the variance. The negative coefficient suggests that P restricts the %Pb BSAF which is compatible with the well known impact of P on Pb bioaccessibility in soil (Nriagu, 1974; Hettiarachchi et al., 2000).

LR of BS-Pb vs total Pb for the complete data set gives a large intercept (Table 2) and a relatively low R^2 (adjusted for number of predictors in the model) of 86%. The coefficient is only 0.39 when the intercept is not fitted. For the <10,000 mg kg^{-1} total Pb dataset the intercept is not significantly different to zero and the R^2 (adj) is 95%. The coefficient of 0.65 for the LR (intercept not fitted) is slightly higher than that for the Derbyshire mineralisation domain (0.51, Table 2).

SLR of BSI-Pb using Pb and major element variables as potential predictors indicates that only total Pb and Ca are significant based on untransformed variables, whereas total Pb, S and OM are significant for log-transformed data. The linear regression model for LnBSI-Pb vs. LnPb, LnS and LnOM (LnBSI-Pb = 2.85 + 1.15 LnPb - 1.04 LnS + 0.680 LnOM) indicates that 81% of the variance can be explained by LnPb, 3% by LnS and

4% by LnOM, similar to the LR results for BS-Pb. The LR for BSI-Pb vs BS-Pb and median values (Table 1) indicate that BSI-Pb is about half BS-Pb.

3.2.3 Comparison of LR models for mineralisation and urban domains

Analysis of Covariance was used to assess whether the AREA (Glasgow, London, Northampton, and Swansea urban areas; Derbyshire and Rookhope Pb-mineralisation areas), DOMAIN (URBAN: data for four urban areas combined; separate Derbyshire and Rookhope Pb-mineralisation areas), or DOMAIN2 (urban combined and mineralisation combined) had a substantial influence on the regression between BS-Pb and total Pb. This was achieved using the Generalised Linear Model (GLM) option in the ANOVA part of the Stat menu in MINITAB® 15 (Response = BS-Pb or LnBS-Pb; Model = AREA, DOMAIN, or DOMAIN2; and Covariate = Pb or LnPb). The Rookhope dataset comprised only those samples with <10,000 mg kg^{-1} Pb.

Results for both untransformed and transformed data revealed that AREA and DOMAIN differences are significant ($p < 0.0005$) both for transformed and untransformed BS-Pb and Pb data with R^2 (adj) values of 94-96%. However, there are not significant differences between the Urban domain (combined Glasgow, London, Northampton, and Swansea) and the Pb-mineralisation domain (combined Derbyshire and Rookhope) ($P = 0.024$ for untransformed and 0.617 for Ln-transformed BS-Pb and Pb data; R^2 (adj) 94-96%).

Whereas AREA is significant ($p < 0.005$) for the analysis of covariance based on Ln-transformed data, AREA explains only 1.2% of the variance compared with 96% explained by total Pb. When the log-transformed data for the urban domain are compared with the separate Derbyshire and Rookhope mineralisation datasets (Figure 6), DOMAIN is significant ($p < 0.005$), but explains only 0.25% of the variance

compared with 96% explained by total Pb. For the DOMAIN2 model (i.e. urban vs Pb mineralisation), DOMAIN2 explains only 0.0035% of the variance, which is not statistically significant (P = 0.617). When the Derbyshire and Rookhope (<10,000 mg kg^{-1} Pb subset) are compared using GLM, the BS vs total Pb regression models are significantly different both for untransformed and Ln-transformed data.

The 95th percentile confidence limits for the intercepts of the BS-Pb vs Pb linear models obtained by bootstrap resampling for the Derbyshire, Rookhope, Combined Derbyshire and Rookhope and Combined Urban datasets all encompass zero showing that none of them have an intercept significantly different from zero (Table 3). The median R^2 values show that all models explain between 94.5 and 98% of the variance in BS-Pb. The 95th percentile confidence limits for the slope show that there is no significant difference between the Rookhope and Derbyshire models and the Rookhope and Urban domain models. However, the Derbyshire and the combined Mineralisation domain model have significantly lower slopes than the Urban model (Table 3).

3.3 Comparison of BS-Pb and BSI-Pb relationships

The relationship between total Pb with BS-Pb and BSI-Pb for Derbyshire and the <10,000 mg kg^{-1} subset of the Rookhope data is illustrated in Figures 7 and 8. For the purposes of this study, a comparison of the absolute values of the BS-Pb and BSI-Pb provides some insight into the geochemical controls on bioaccessibility in the different domains.

BS-Pb and BSI-Pb concentrations for the Glasgow, London and Swansea urban areas are compared with data for the Derbyshire and Rookhope mineralisation-mineral processing domains in Table 4. Median BSI/BS-Pb ratios are similar for Glasgow, Swansea and Rookhope (0.43-0.47), lower for London (0.30) and substantially lower

for Derbyshire (0.17). The BSI-Pb:BS-Pb regression coefficients are highest for Rookhope (0.52), intermediate for London (0.37) and Swansea (0.42) and lowest for Derbyshire (0.20). Pb smelter contaminated urban soils in France have an average BSI/BS-Pb ratio of 0.32 (Pelfrêne et al., 2012; median soil pH 7.9) whilst the ratio is 0.36 for agricultural soils in northern France (Pelfrêne et al., 2011) and 0.36 (median) for rural soils in Northern Ireland (Barsby et al., 2012).

Pelfrêne et al. (2011) observed that *"in the near-neutral pH and the carbonate-rich environment of the intestinal phase, Pb may be stabilized in solution by processes of complexation and/or readsorption on remaining soil particles or other material present in chyme."* Marschner et al. (2006) suggested that the concentration of soluble metals in the intestinal phase is a function of the availability of (organic) ligands, including soil ligands. Marschner et al. (2006) also observed that "*the relative bioavailabilities in liver, kidney, and total uptake were highly correlated to Pb in the third fraction of the sequential extraction that is attributed to easily reducible Mn oxides. These results indicate that reductive processes in the intestine may be more relevant for Pb absorption than the initial solubilization in the acidic stomach."*

The reason why bioaccessibility is reduced in the higher pH of the BSI to a greater extent for the Derbyshire soils (Pb mineralisation area; high soil pH, low soil OM) than in the urban areas and even greater than in the low pH, high OM soils of the Rookhope area is possibly related to differences in the chemical makeup of the soils in the two regions. Differences in soil pH is unlikely to affect the overall Pb solubility as the intestine phase is buffered to pH 6.3 (± 0.5) throughout the extraction. It is well known that phosphate can stabilise and reduce the solubility of Pb in soils (Hettiarachchi and Pierzynski, 2004). Table 1 shows that the median P concentration in the Rookhope soils is a factor of 2.7 less than in the Derbyshire soils. A comparison of the solubility

of Pb in soils with the addition of phosphate (Stanforth and Qiu, 2001) shows that the solubility is markedly reduced at pH 6, which is similar to the pH of the UBM stomach and intestine extraction (6.3). The SLR modelling, does not, however, indicate P as being significant in controlling the BSI-Pb. The model of LnBSI-Pb did identify Mn as being a significant factor which reduces the BSI-Pb. Table 1 shows that the median Mn concentration in Rookhope soils is a factor of 29 less than in the Derbyshire soils. In addition Mn concentrations are a factor of c.2 less in the BSI phase compared to the BS phase indicating the possible precipitation of insoluble Mn compounds. A study of the use of manganese oxide to stabilise Pb in soils (Hettiarachchi et al., 2000) shows significant reductions in Pb bioaccessibility due to adsorption of Pb onto the manganese oxide. In the case of the Derbyshire soils it is possible that manganese is precipitated as the oxide in the higher pH environment of the stomach and intestine extract which then co-precipitates the soluble Pb from solution thereby reducing its absolute bioaccessibility. Fe is known to have a role in controlling the bioaccessibility of some elements such as Pb (Smith 2011b, Beak et al., 2008) and in particular As (Palumbo-Roe et al 2005, Wragg et al., 2007). The apparent lack of control of BS-Pb or BSI-Pb by total Fe in the Derbyshire and Rookhope areas does not indicate that no species of Fe is a controlling factor. Speciation analysis would be needed to evaluate this fully. Soil mineralogy studies might also help to elucidate the chemical and mineralogical controls on Pb bioaccessibility in these different soil types.

4. Conclusions

1. Linear regression analysis of the topsoil data for the Derbyshire and Rookhope Pb-mineralisation areas indicate that total Pb is the only highly significant independent variable for estimating the bioaccessibility of Pb.

2. Total Pb explains >90% of the variability of BS-Pb. It is possible that the low pH (1.2) of the gastric solution masks some of the impacts of soil mineralogy on Pb bioaccessibility or high Pb concentrations exceed the adsorption capacities of soil components (OM and/or oxyhydroxides).
3. Analysis of covariance indicates that Derbyshire and Rookhope BS-Pb vs total Pb relationships are significantly different, whilst bootstrap resampling shows that LR confidence limits overlap for Derbyshire and Rookhope and Rookhope and the Urban domain but the Derbyshire samples have a significantly lower BS-Pb to Pb slope than the Urban soils.
4. Validation of the relationships reported in this study by comparable studies in other Pb-mineralisation areas of the UK should be carried out.
5. The results of this study draw broad conclusions on the bioaccessibility of Pb in Pb-mineralisation domains in England. Results of this study can be used for preliminary environmental assessment but should not be used to replace bioaccessibility testing at individual sites because local conditions may significantly influence Pb-bioaccessibility.

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TABLES

Table 1 Summary statistics for topsoil data

		Derbyshire	Rookhope	Rookhope (<10,000 mg kg^{-1} subset)
Total Pb (mg kg^{-1} in <2 mm fraction)	Range	171 - 10470	151 – 27203	151 – 8513
	Mean	1710	1840	1300
	Median	775	662	656
BS-Pb (mg kg^{-1} in < 250 µm fraction)	Range	51 – 5765	75 – 8565	75 – 5937
	Mean	895	1010	849
	Median	386	464	458
BSI-Pb (mg kg^{-1} in < 250 µm fraction)	Range	4 – 1416	20 – 6002	20 – 3574
	Mean	172	507	390
	Median	67	182	179
% Pb-BSAF	Range	25 – 79	22 – 91	22 – 91
	Mean	51	65	66
	Median	51	66	67
% Pb-BSIAF	Range	2 – 17	6-55	6-55
	Mean	9	28	28
	Median	9	29	30
pH	Range	4.2 – 7.3**	2.9 – 7.4	2.9 – 7.4
	Mean	5.6**	3.9	3.9
	Median	5.7**	3.7	3.7
OM (wt. %)	Range	3.3 – 8.9**	3.7 – 96.1	3.7 – 96.1
	Mean	5.5**	39.8	40.6
	Median	5.1**	24.1	26.2
Al (mg kg^{-1})	Range	43907 – 68770	1653 – 111018	1653 – 111018
	Mean	58643	30630	31045
	Median	59248	29631	29634
Ca (mg kg^{-1})	Range	2073- 118569	215 – 153998	215 – 83350
	Mean	12045	9821	6754
	Median	5861	1510	1414
K (mg kg^{-1})	Range	2791 – 6925**	375 – 38906	375 – 38906
	Mean	4309**	6973	7033
	Median	4290**	5573	5732
Fe (mg kg^{-1})	Range	24129 – 73297	1349 – 210300	1349 – 210300
	Mean	39285	23626	22644
	Median	36858	11430	11197
Mg (mg kg^{-1})	Range	2412- 25933	265 – 4979	265 – 4567
	Mean	6659	1607	1535
	Median	4825	1452	1439
Mn (mg kg^{-1})	Range	465 – 8520	10 – 13133	10 – 13133
	Mean	2180	919	850
	Median	1704	59	58
P (mg kg^{-1})	Range	786 – 4189	145 – 1664	284 – 1664
	Mean	1855	702	714
	Median	1658	609	609
S (mg kg^{-1})	Range	938 – 2882**	367 – 8601	367 – 4363
	Mean	1501**	1756	1611
	Median	1376**	1051	989
N		49	48	47

**Summary statistics for 18 NSI soils samples (Rawlins et al., 2012) located on Carboniferous limestone in the Derbyshire area – no pH, OM, K or S data available for G-BASE soil samples analysed in this study; BS-Pb = bioaccessible Pb (stomach phase); BSI-Pb = bioaccessible Pb (combined stomach and intestine phase); %Pb-BSAF = relative bioaccessibility for stomach phase; %Pb-BSIAF = relative bioaccessibility for stomach +intestine phase

Table 2 Least squares linear regression models for bioavailable lead

Dataset	N	Intercept[1]	Model formula (*MLR models in italics*)	R^2
Derbyshire (D)				
All samples	49	F	*BS-Pb = 136 + 0.502 Pb - 0.0455 Mn*	98%
All samples	49	F	BS-Pb = 39 + 0.501 Pb	98%
All samples	49	NF	BS-Pb = 0.508 Pb	98%
Rookhope (R)				
All samples	48	F	*BS-Pb = -708 + 0.562 Pb – 0.855 S + 32.6 OM + 225 pH*	95%
All samples	48	F	BS-Pb = 362 + 0.352 Pb	86%
Pb <10000 mg kg^{-1}	47	F	*BS-Pb = 25.2 + 0.672 Pb – 0.242 S + 8.38 OM*	95%
Pb <10000 mg kg^{-1}	47	F	BS-Pb = 2.2 + 0.651 Pb	95%
Pb <10000 mg kg^{-1}	47	NF	BS-Pb = 0.652 Pb	95%
Combined D + R				
All samples	96	F	BS-Pb = -12.7 + 0.696 Pb	97%
All samples	96	NF	BS-Pb = 0.694 Pb	97%
Combined D + R + urban				
All samples <10000 mg kg^{-1}	240	F	BS-Pb = 3.4 + 0.612 Pb	94%
All samples <10000 mg kg^{-1}	240	NF	BS-Pb = 0.613 Pb	95%

[1] F = fixed; NF = not fixed; all units mg kg^{-1} except OM (wt.%) and pH

Table 3 Bootstrapped regression summaries for Total Pb (x values) and Stomach phase Bioaccessible Pb (y axis)

Dataset	Regression statistic	2.5th %tile	median	97.5 %tile
Derbyshire (D)	intercept	-34.3	37.6	98.5
Rookhope (S)	intercept	-54.4	3.9	90.7
Mineralisation domain (DS)	intercept	-24.6	59.1	126.5
Urban domain (GLNS*)	intercept	-100.0	-34.8	0.18
Derbyshire (D)	R^2	0.964	0.980	0.994
Rookhope (S)	R^2	0.871	0.945	0.982
Mineralisation domain (DS)	R^2	0.917	0.950	0.976
Urban domain (GLNS)	R^2	0.899	0.957	0.987
Derbyshire (D)	slope	0.447	0.502	0.578
Rookhope (S)	slope	0.538	0.648	0.723
Mineralisation domain (DS)	slope	0.474	0.539	0.621
Urban domain (GLNS)	slope	0.630	0.691	0.819

GLNS = urban data for Glasgow, London, Northampton and Swansea (Appleton et al., 2012)

Table 4 Summary of the stomach (BS) and stomach + intestine (BSI) bioaccessible Pb data and regression statistics for urban and Pb mineralisation domains

		Urban domain			Pb-mineralisation domain	
		Glasgow	London	Swansea	Derbyshire	Rookhope
BSI-Pb/BS-Pb	Min	0.03	0.14	0.11	0.04	0.17
	Max	0.60	0.49	0.52	0.27	0.63
	Mean	0.43	0.29	0.40	0.17	0.42
	Median	0.47	0.30	0.43	0.17	0.44
n		27	50	24	49	47
Regression coefficient		na	0.37	0.42	0.20	0.52
R^2		na	0.98	0.78	0.93	0.93
	Source of data	Farmer et al., 2011	BGS	BGS	BGS	BGS

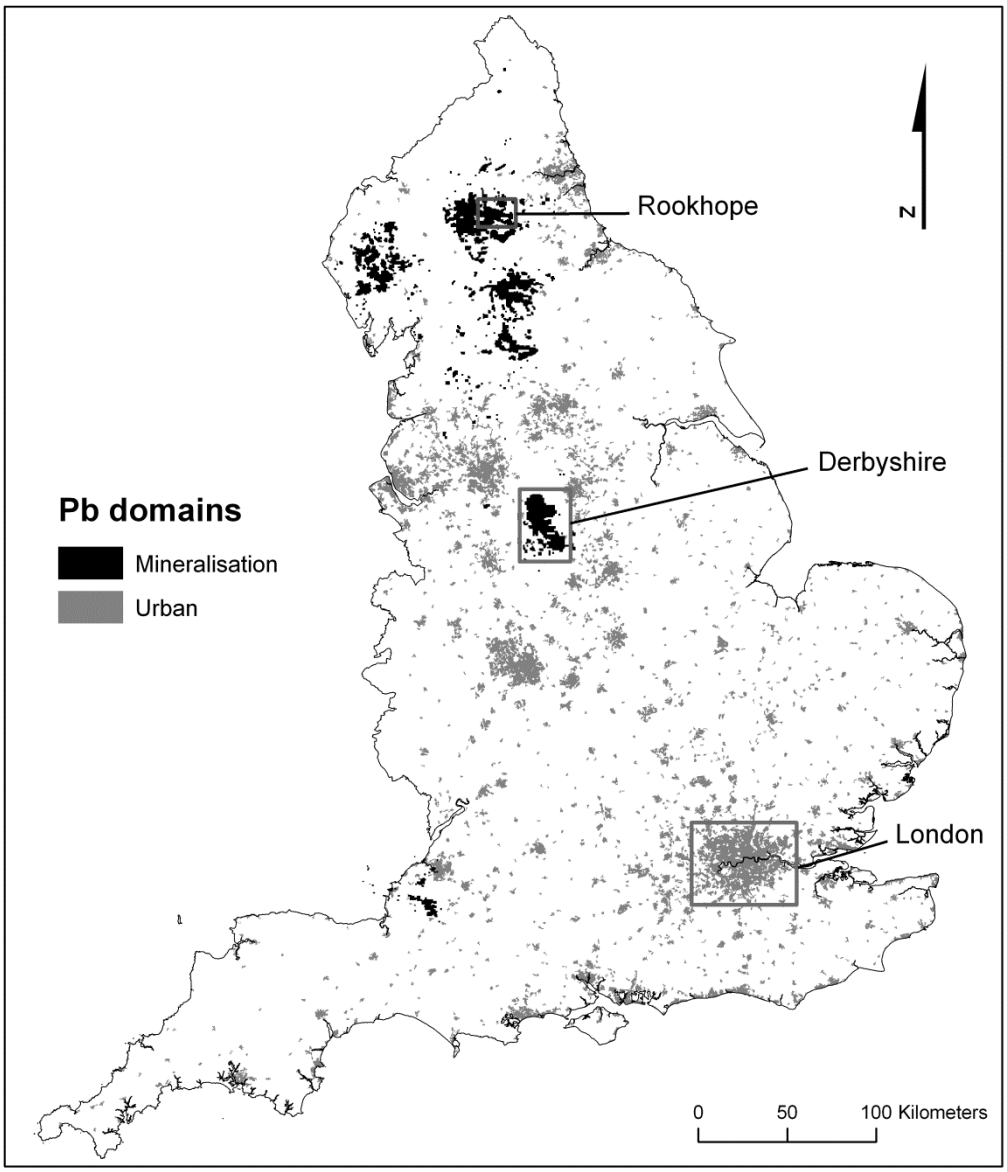

Figure 1 Lead domain map for England (Urban domain derived from Ordnance Survey Strategi ® data © Crown copyright and database right 2012))

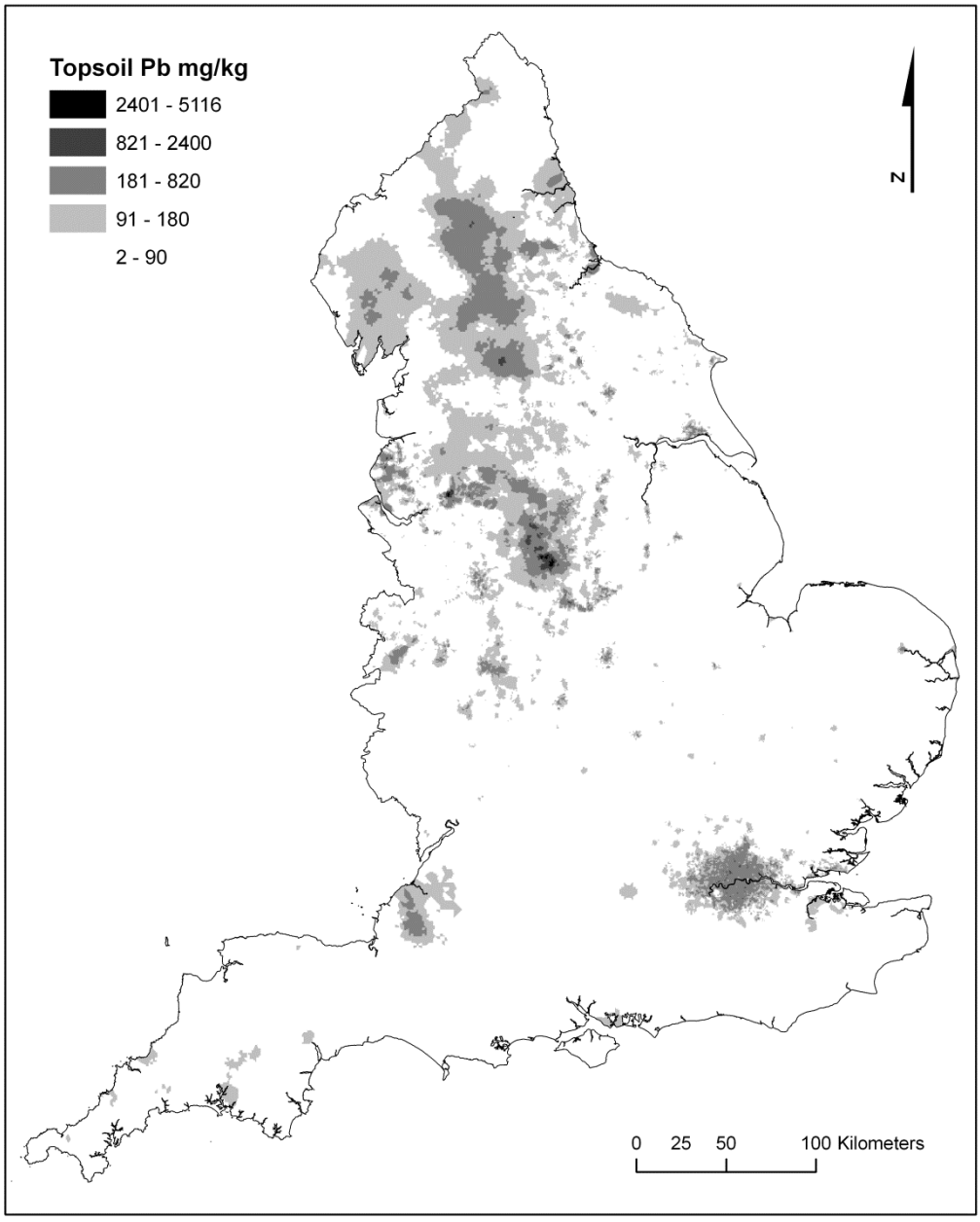

Figure 2. Estimated total Pb in English topsoils (Geometric mean for 500 m grid squares derived from nearest five BGS G-BASE and NSI (XRFS) topsoil data; class intervals of 180, 820 and 2400 mg/kg are Normal Background Concentrations for Principal, Urban and Mineralisation Pb Domains; DEFRA, 2012)

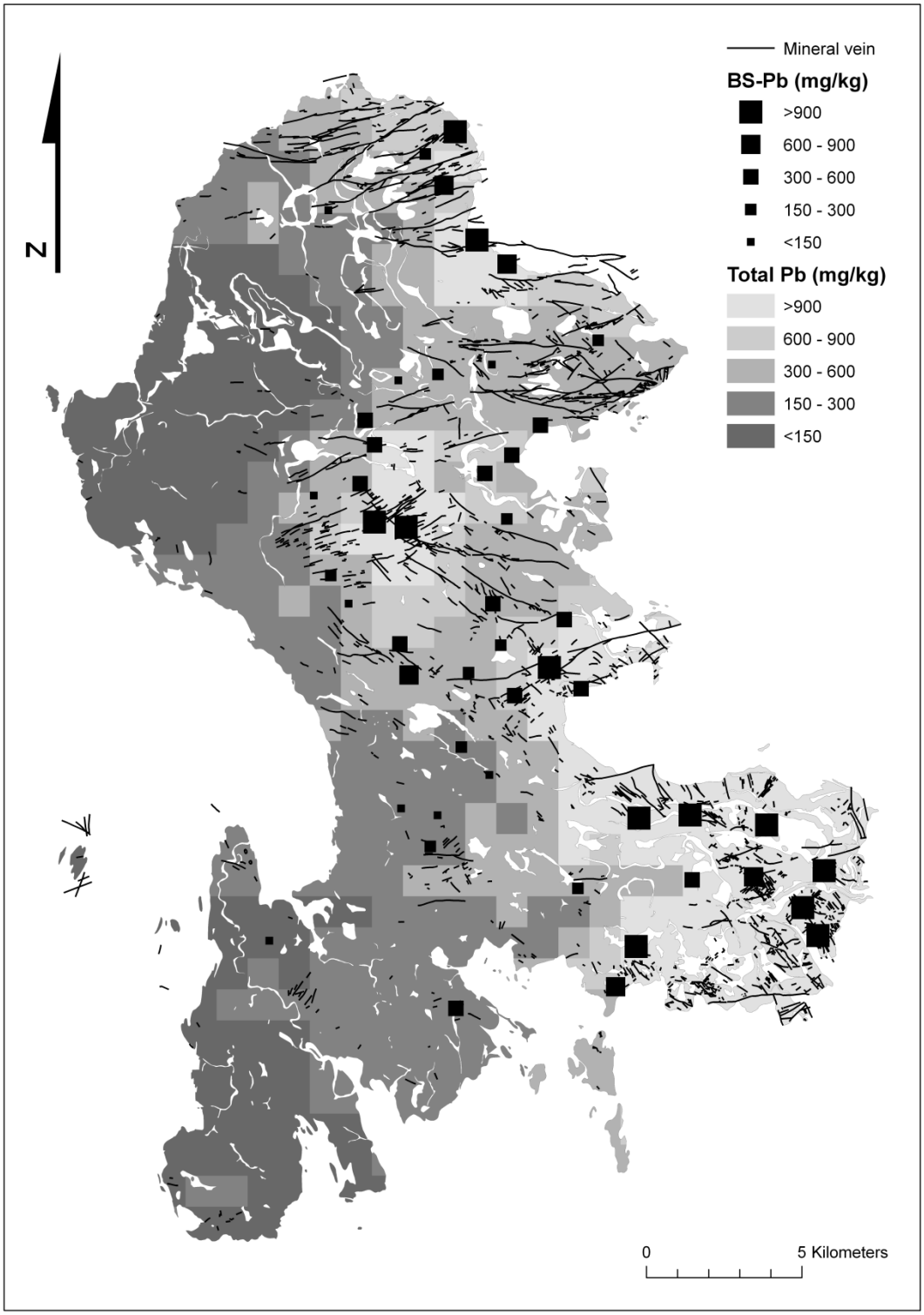

Figure 3. Bioaccessible (stomach phase) Pb in <250 µm fraction of topsoil samples (this study) and mineral veins (BGS DiGMapGB-50 data) in Derbyshire area overlain on estimated Total Pb data for Carboniferous (Dinantian) limestone terrain interpolated from G-BASE rural topsoil chemistry data

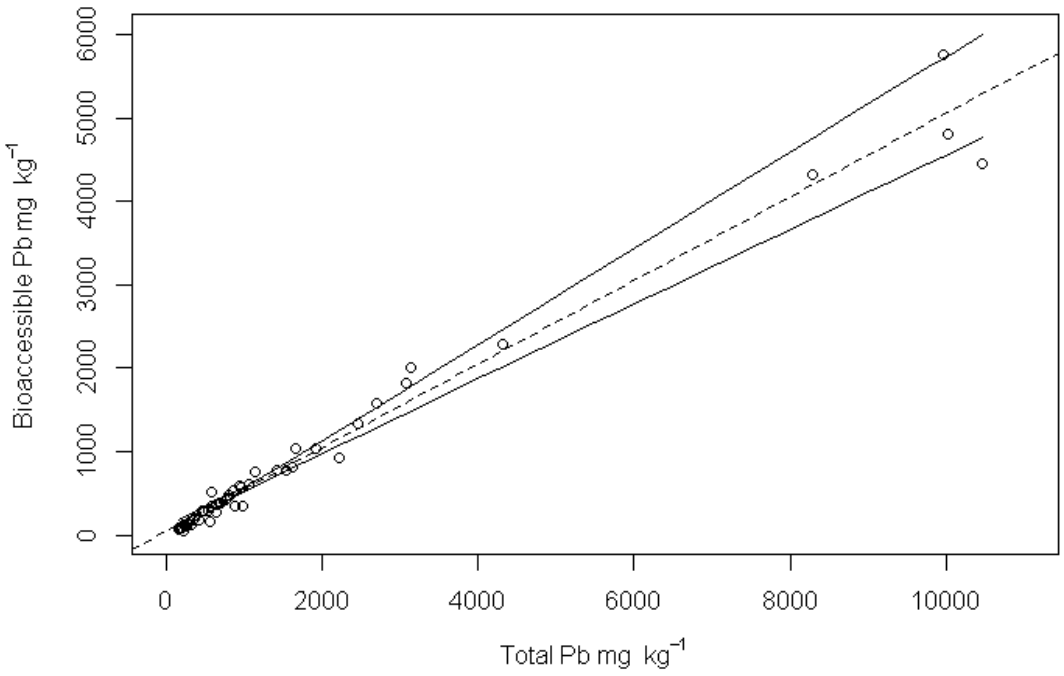

Figure 4. Bioaccessible (stomach phase) Pb in <250 µm fraction of topsoil samples from Rookhope mineralisation domain (Mineral veins and simplified geology derived from BGS DiGMapGB-50 data; extent of peat from BGS Parent Material Map v4; interim data).

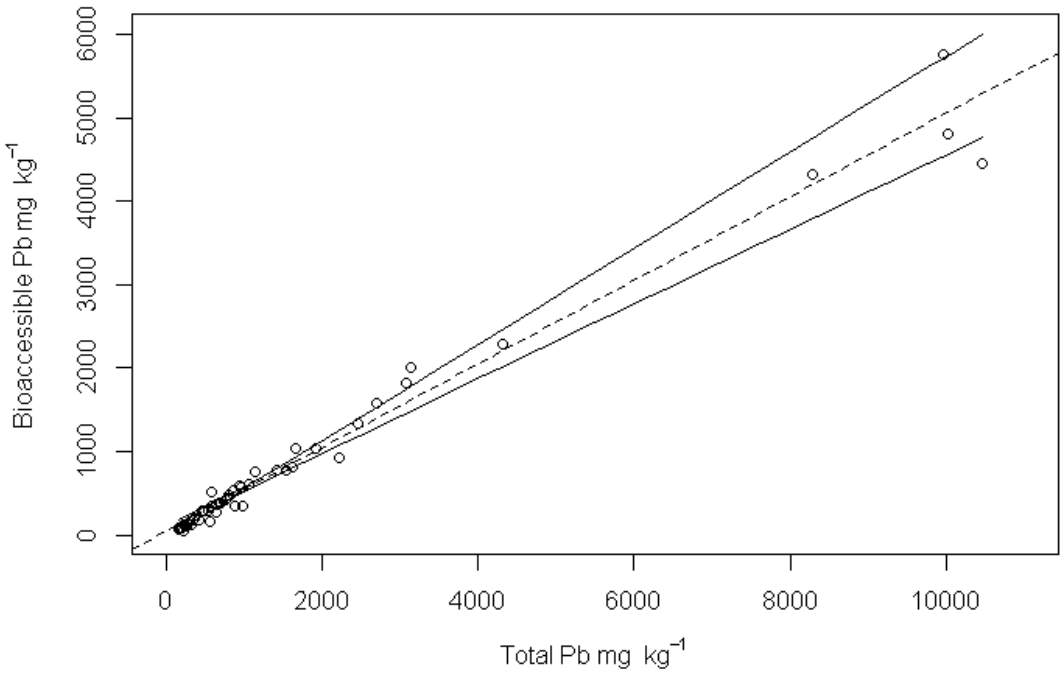

Figure 5. Fitted line plot for relationship between total Pb (<2 mm fraction) and BS-Pb (<250 μm fraction): all Derbyshire data (n=49; solid lines = 95% confidence limits)

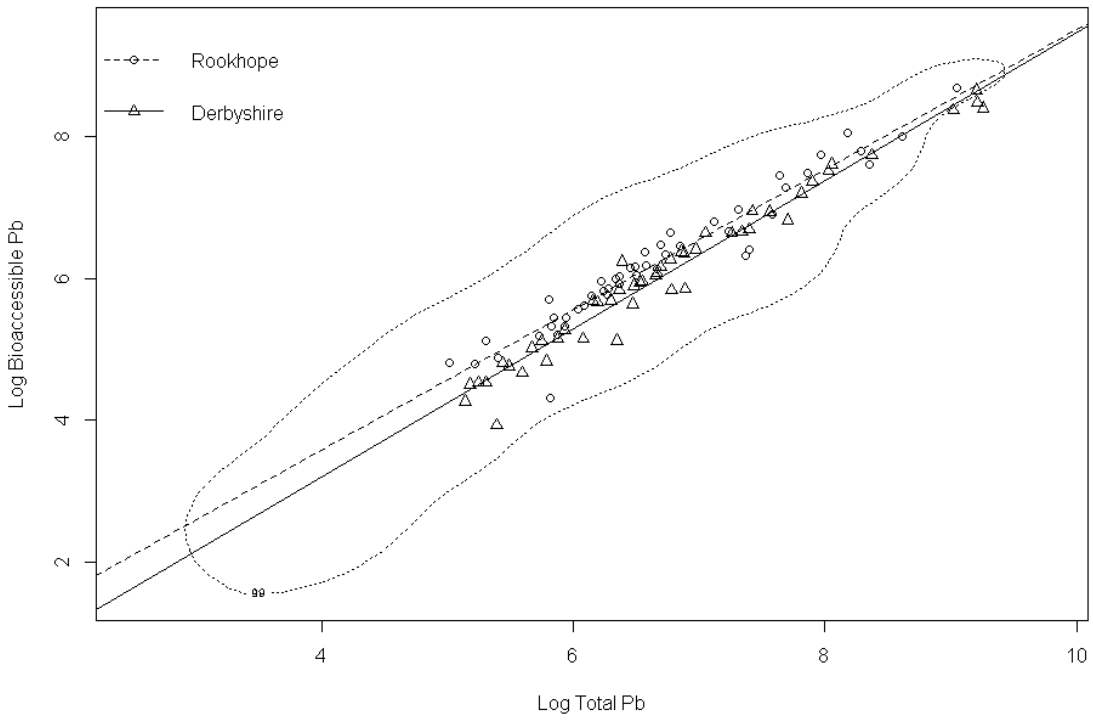

Figure 6. Relationship between Ln total Pb (<2 mm fraction) and Ln BS-Pb (<250 µm fraction) in topsoils from urban areas (99% of samples fall within dotted line) compared with the Derbyshire (triangles and solid regression line) and Rookhope (circles and dashed regression line; <10,000 mg kg^{-1} Pb subset) Pb-mineralisation domains

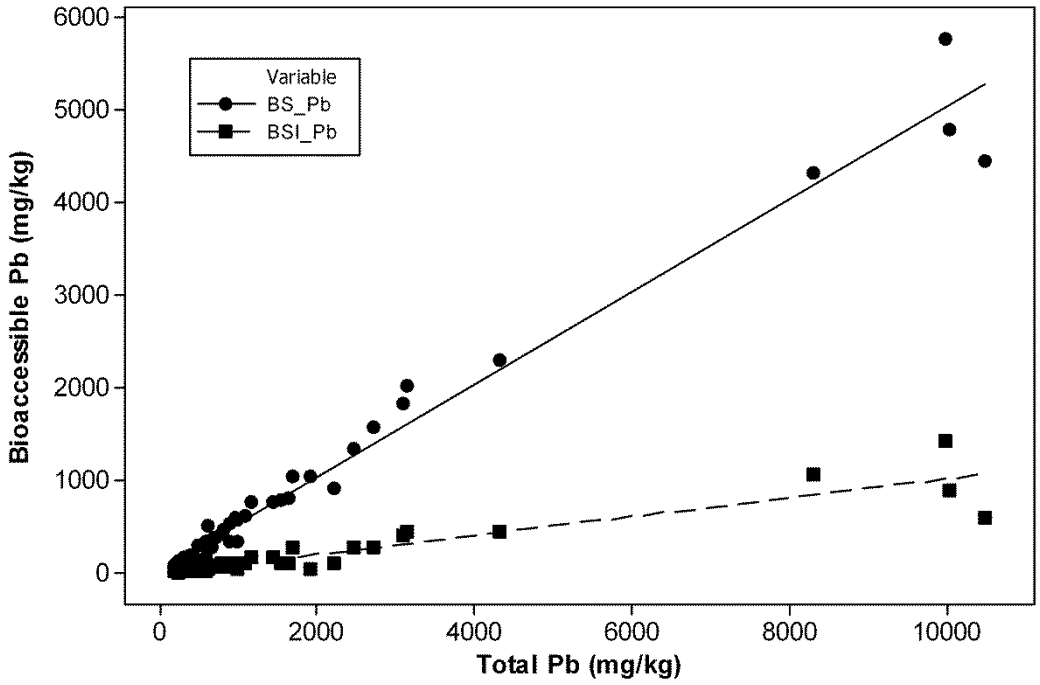

Figure 7. Relationship between BS-Pb (solid line) and BSI-Pb (dashed line) in <250µm fraction with total Pb in <2 mm fraction of soil samples from the Derbyshire Pb mineralisation domain

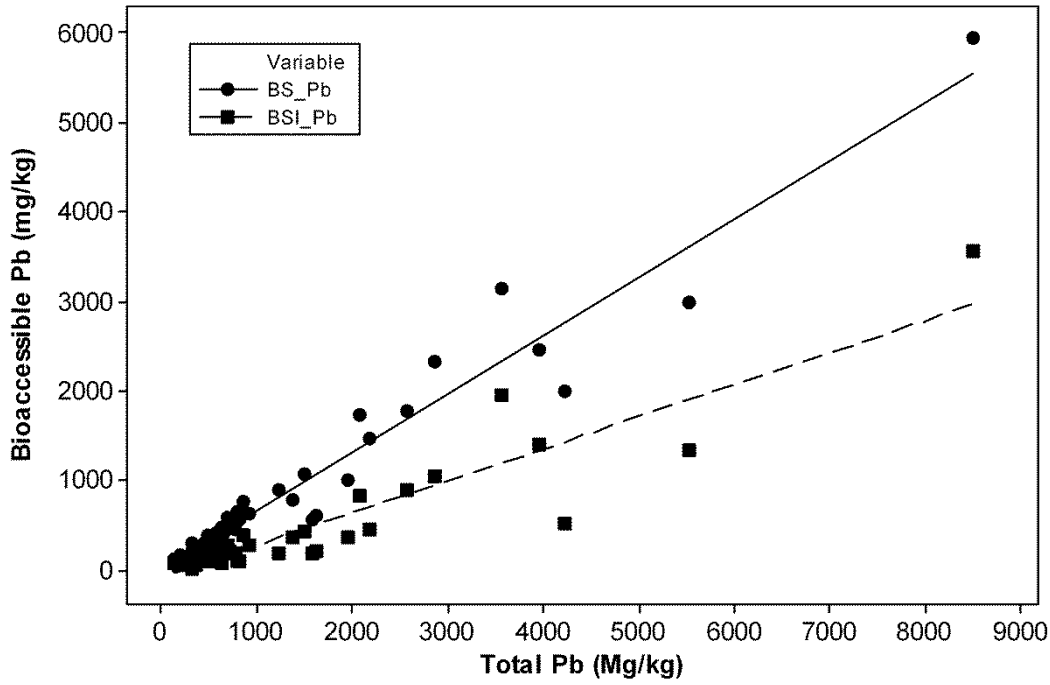

Figure 8. Relationship between total Pb (< 2 mm soil fraction) with BS-Pb (solid line) and BSI-Pb (dashed line in <250 μm fraction for Rookhope Pb mineralisation domain (<10,000 mg-kg^{-1} Pb subset)