Modelling lead bioaccessibility in urban topsoils based on data from Glasgow, London, Northampton and Swansea, UK.

J D Appleton, M R Cave, 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 between bioaccessible Pb and a range of total elemental compositions and soil properties was executed for the Glasgow, London, Northampton and Swansea urban areas in order to assess the potential for developing a national urban bioaccessible Pb dataset for the UK. LR indicates that total Pb is the only highly significant independent variable for estimating the bioaccessibility of Pb. Bootstrap resampling shows that the relationship between total Pb and bioaccessible Pb is broadly the same in the four urban areas. The median bioaccessible fraction ranges from 38% in Northampton to 68% in London and Swansea. Results of this study can be used as part of a lines of evidence approach to localised risk assessment but should not be used to replace bioaccessibility testing at individual sites where local conditions may vary considerably from the broad overview presented in this study.

Capsule Abstract

Total Pb is the only significant predictor for bioaccessible Pb in topsoils from four urban areas in the UK.

Keywords

bioaccessibility, lead, urban, topsoil, UK

1. Introduction

A significant proportion of the urban landscape in Great Britain has elevated topsoil concentrations of lead (Pb; Rawlins et al., 2005; Thums et al., 2008; Broadway et al., 2010; Farmer et al., 2011; Flight and Scheib, 2011). In a study of the background concentrations of potentially harmful elements (PHEs) in soils in England, Cave et al. (2012) and Ander et al. (2012) used a classification based on the ratio of built to open space to show that 4% of the land area could be classified as Urban and that systematically surveyed soil samples in this category (n=7529) had median and 95th percentile lead concentrations of 170 mg kg^{-1} and 790 mg kg^{-1} respectively.
The lead content of soil is important since it is toxic to humans and particularly because children tend to more readily absorb lead than do adults: children absorb up to 40% into the bloodstream from ingested or inhaled lead, versus 5-15% in adults. A number of studies have shown that relatively low concentrations of lead in blood can lead to significant decrease in IQ of children (Bierkens et al., 2012; Huang 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). Therefore, from a human health perspective, it is not the total amount of Pb in the soil but the fraction that is absorbed into the body following soil ingestion, i.e. the bioavailable fraction that is important for assessing human health risk. The measurement of the bioavailability of PHEs in soil requires in vivo testing using humans or animal surrogates, a time consuming, costly and ethically challenging process. However, a surrogate for bioavailability, a class of in vitro test known as bioaccessibility testing has been developed and validated specifically for this purpose

and is available to be used as a conservative estimate of bioavailability. The development of bioaccessibility testing methods for Pb in soil has recently been comprehensively reviewed (Zia et al., 2011). In general the bioaccessibility tests fall into two categories: (i) those which try to closely mimic the physiological conditions in the stomach and upper intestine (Cave et al., 2003; DIN, 2000; 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 key point regarding these tests is that they need to be validated against a human or animal model. Although there is still some discussion over the relative merits of the different methodologies (Zia et al., 2011), the method adopted by this study is the Unified BARGE method (UBM) which has undergone interlaboratory trials (Wragg et al., 2011) and been validated against a swine model for Pb (Caboche, 2009; Denys et al., 2012). The fraction of a PHE assessed in an in vitro bioaccessibility assay is that 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 (Paustenbach, 2000; Wragg and Cave, 2003; Intawongse and Dean, 2006). To assist the risk assessment and regulatory communities, 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 any contaminant bound to the soil depends upon the soil type, properties of the soil, the contaminant and the manner by which the contaminant has entered the soil (Selinus, 2005). Cave et al. (2011) have described how specific properties of soil, such as pH, organic matter content, mineral

constituents, solid phase partitioning of PHEs and soil ageing may influence bioaccessibility of priority contaminants of concern. A number of workers have successfully carried out multiple linear regression (MLR) modelling of the bioaccessible PHE content of soils, specifically arsenic (As), using their physico-chemical properties, such as the elemental composition of the soil and soil pH as the predictor variables (Yang et al., 2002; Klinck et al., 2005; Tang et al., 2007). Pb bioaccessibility studies have generally focussed on the relationships between total and bioaccessible Pb concentrations (Farmer et al., 2011; Cave et al., 2011) sometimes with due consideration given to the different sources of Pb contamination (Smith et al. 2011). Modelling of PHE bioaccessibility gives rise to two advantageous outcomes: (i) if the 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; and (ii) the predictor variables chosen for the model and the relative size of their coefficients can provide an insight into the processes governing the bioaccessibility of PHE in the soils. The first option is only useful if the soil properties used for prediction of bioaccessibility are already known or are more easily and cheaply measured than the in vitro bioaccessibility test. One drawback that is highlighted in a number of the studies is that the MLR models are very specific to a particular soil type and cannot be applied universally.

Elevated concentrations of Pb in UK urban topsoils are in almost all cases related to human activities, especially the burning of fossil fuels. This Pb accumulation is likely a result of (i) car combustion/exhausts (pre-unleaded fuels) and the denser and slow flowing traffic in inner cities and/or (ii) disposal of ash from coal burning stoves and fires during the pre-gas central heating era in domestic gardens, especially in the older,

inner parts of the cities. In most urban areas of the UK, the highest background Pb concentrations occur in the central, historically older areas (Flight and Scheib, 2011; Appleton and Adlam, 2012) with much lower Pb concentrations characterising the more recently urbanised areas (Scheib et al., 2011). Heavy industry such as smelting and coal fired power stations have also contributed to the dispersion of Pb in urban areas. In Swansea, for example, urban soils have been contaminated as a result of the city's industrial legacy of non-ferrous smelters processing copper, arsenic, lead, zinc, silver and tin (Marchant et al., 2011). The highest average Pb concentrations have been recorded in the urban topsoils from Swansea, Derby, London, Hull, Manchester, Sheffield, and Wolverhampton (Flight and Scheib, 2011; Scheib et al., 2011).

In this feasibility study, predictive regression modelling between bioaccessible Pb and a range of total elemental compositions and soil properties was executed for the Glasgow, London, Northampton and Swansea urban areas in order to assess the potential for developing a national urban domain bioaccessible Pb dataset derived from the British Geological Survey (BGS) Urban Soil Chemistry dataset (Appleton, 2011).

2. Materials and methods

2.1 Sample selection

In order for the predictive regression models to be robust, it is necessary to ensure that the samples used for bioaccessibility testing are representative of the region under study. The samples from London were selected primarily to cover the wide range of total Pb concentrations, whilst those from Swansea and Northampton were selected to represent a range of Pb and As concentrations; the results of the As bioaccessibility in UK urban soils will be published in a separate paper. Data for regression modelling in the Glasgow area is for the G-BASE samples reported in Broadway et al. (2010) and

Farmer et al., (2011) which were originally selected to provide a range of total Cr, Pb or As concentrations. Summary statistics for all the samples from the four urban areas are reported in Flight and Scheib (2011).

2.2 Sample collection, preparation and determination of total concentrations

Topsoil samples were collected from open ground on a 500 m grid at a density of approximately 4 samples per km^2 (Flight and Scheib, 2011). At each site, composite samples, based on 5 sub-samples 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 and <250 μm size fractions of the topsoils. Sample preparation, X-ray fluorescence analytical methods, and quality control procedures are described in Allen et al. (2011) and Johnson (2011).

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 (BS-Pb) contents using the Unified BARGE Method (UBM) which is an in vitro physiological GI simulation based on a methodology previously described by Oomen et al. (2002). The methodology was modified in order to ensure adequate conservatism and robustness whilst still being physiologically based and applicable to the different soil types found in a range of different countries. In particular this resulted in a reduction in stomach pH from 1.5 to 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. Minor operational differences in the method occurred between the

extraction of the Northampton samples and those from Swansea and London. The differences are as follows:

- The initial stomach phase pH for the Swansea and London samples was fixed at 1.2, whereas for the Northampton samples the initial stomach phase pH was not fixed; and
- The speed and length of time which the samples were spun at during the separation stage (4500 g for 15 minutes for the Swansea and London samples compared to 3000 g for 5 minutes for the Northampton samples).

The UBM procedure for the Northampton samples was carried out according to the methodology previously described in full by Roussel et al. (2010), Wragg et al. (2009 and 2011), Broadway et al. (2010) and Pelfrene et al. (2010) and for the Swansea and London samples according to the validated methodology of Caboche (2009) which has been recently described by Denys et al. (2012). The UBM validation used a Juvenile swine model for As, cadmium (Cd) and Pb 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 As, Pb and Cd was highly significant, both for the gastric and the gastro-intestinal phases, the slopes of the regression were not significantly different from 1 (based on 95% confidence interval) and the intercepts of the regression were not significantly different from zero.

Absorption of available PHEs occur in the small intestine of the GI tract and the UBM methodology provides samples for analysis from both the ‘stomach’ and ‘stomach and intestine’ phases, equating to gastric and intestine compartments. 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). Taking these points into consideration the 'stomach' phase samples have been chosen as being most suitable for this study.

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 an international standard reference material (SRM), NIST 2710 and a BGS guidance soil BGS 102 (Wragg, 2009). At present there are no certified reference materials for bioaccessible Pb, however, the three soils used for QC checks in this study have been the subject of an international inter-laboratory trial (Wragg et al., 2009; 2011), which has generated the reference values 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. BGS 102 was the QC material used for the London, Northampton, and Swansea, whilst BGS 102 and NIST 2710 were used for the Glasgow.

For the London sample batch (n = 8), replicate bioaccessibility values for BGS 102 were in good agreement with the consensus values (Wragg et al., 2009; 2011). The 'stomach' phase value of 15.2 ± 6.6 mg kg^{-1} is in agreement with the consensus value of 12.8 ± 6.0 mg kg^{-1}.mg kg^{-1}. For Swansea and Northampton (n = 15), replicate bioaccessibility values for BGS 102 were within the consensus values, with 'stomach' phase values of 17.6 ± 5.9 mg kg^{-1} (Wragg et al, 2011). The value obtained for Pb in

the NIST 2710 reference material for the Glasgow samples (n = 4) was 3691 ± 416 mg kg^{-1} for the 'stomach', which was in good agreement with consensus value of 3785 ± 469 mg kg^{-1} for this material (Farmer et al, 2011).

The method detection limits were calculated as five times the average blank measurement (n=25). The calculated detection limits for the 'stomach' phase used for this study 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 micron fraction) with total Pb, Al, Fe, K, Mg, Mn, Na, P, Si, Ti (and sometimes also pH, TOC, and Olsen-P) in the <2mm fraction of topsoil samples. Soil chemistry summary statistics for London and Swansea are presented in Tables 3-4 and published elsewhere for Glasgow (Farmer et al., 2011) and Northampton (Cave et al., 2003).

Regression analysis in this study was carried out in the following stages:

i. Use Pearson correlation coefficients between dependent variable (BS-Pb) and potential independent soil chemistry variables (Pb, major elements, and soil pH, TOC and Olsen-P when data is available) to select those independent variables with the strongest linear relationship with BS Pb.

ii. For each data set, use the exploratory MLR procedures of stepwise linear regression and best subset regression to identify the most important independent variables, bearing in mind that these procedures have limitations when the sample size (n) is < 5 times the number of independent variables (i.e. Glasgow and Swansea datasets). Repeat the MLR analysis after removing independent variables from the

model if the b-coefficients were not significant and/or the ANOVA p-value for an independent variable was >0.05. The objective was to generate models which are geochemically and mineralogically justifiable. Residuals plots were used to assess whether residuals were approximately normally distributed. In other cases subsets were used after removing samples with large leverages and/or large standardised residuals. Modelling stomach bioaccessible Pb from total element concentrations in topsoils requires the application of regression models between BS-Pb in the <250 μm fraction with total Pb and other chemical variables in the <2 mm fraction of topsoils.

iii Differences in the fit of linear regressions from different data sets were assessed using a bootstrap resampling routine programmed in the R statistical programming language (R Development Core Team, 2011). In simple terms, this involves taking a random sample of data pairs from the original data set, recalculating the regression statistics and repeating the process a number of times to produce a distribution of values for each test statistic. The method resampled with replacement the data pairs for the data sets under study producing LR slope and intercept data for each resampled trial. The resampling was carried out 1000 times and median and 95th percentile confidence limits were calculated on the intercept, slope and regression line fit.

3. Results and discussion

3.1 Summary statistics

The mean, median and ranges of total Pb, stomach bioaccessible Pb (BS-Pb) and the proportion of stomach bioaccessible Pb (the bioaccessible fraction, % Pb-BAF) for the four urban areas are listed in Table 1. Median soil pH is 5.4, 6.8 and 6.4 for Glasgow (G), London (L) and Northampton (N), respectively; no pH data is available for the Swansea (S) soil samples. The median bioaccessible fraction ranges from 38% in

Northampton to 68% in Swansea and London, similar to average bioaccessibility of 49% recorded in urban park soils in Xiamen (Luo et al., 2012a), 59% in Hong Kong urban soils (Luo et al., 2012b), 46-60% in the urban green area soils of Torino (Italy) and Sevilla (Spain) (Madrid et al., 2008) and 48±12% in roadside soils from Torino (Sialelli et al., 2011). Pb bioaccessibility data for peri-urban contaminated soils in Australian and New Zealand (Smith et al., 2011) is mainly for shooting range and mining/smelting impacted soils so it is not comparable with the UK urban bioaccessibility data.

3.2 Regression analysis

The linear regression modelling procedures described above were followed leading to the production of 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 a maximum of 2% lower than R^2 for models with fitted intercepts. All regression models are statistically significant ($p < 0.005$). In least square linear regression, the method makes the assumption that all the uncertainty is associated with y axis. As a consequence, high intercept values may reflect the magnitudes of the errors on the input parameters. Positive intercept values are theoretically impossible so in such cases it may be more appropriate to use models without fitted intercepts. However, in the majority of cases (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.

Linear regression modelling of the soil data for the Glasgow, Northampton and Swansea areas indicate that total Pb is either the only significant independent variable or where

there is another statistically significant independent variable (Si), then this accounts for a very small proportion of the total variance, compared with total Pb. Total Pb accounts for 62% and 95%, respectively in the MLR models for Glasgow and Northampton, whilst Si accounts for only 9% and 1%, respectively in these two urban areas.

Stepwise LR on the London dataset indicates that Total Pb, Sn, Ba, Co and SiO_2 may be significant predictors but P-values imply that SiO_2 is only marginally significant. This is confirmed by the MLR results for these variables which indicate that total Pb explains 95% of the total variance in BS-Pb. Sn and Co are not significantly correlated with either BS-Pb or total Pb and there is no logical reason to expect that any of the significant variables identified by SLR is likely to control BS-Pb, apart from Total Pb. Furthermore, the proportion of the total variance controlled by these other predictors is very small (0.3 to 0.8%) MLR modelling for the combined GLNS and LNS datasets shows that Si is not a significant predictor when all samples are used, although it is statistically significant for the < 2000 mg kg^{-1} Pb subsets, but in this case explains only 0.7% and 0.08% respectively of the variance for the GLNS and LNS datasets. As a consequence, LR modelling of BS-Pb was restricted to its relationship with total Pb.

The LR models for bioaccessible lead in the London urban area (such as illustrated in Figure 1) have slightly higher Pb coefficients (0.68-0.69) than the models for the Glasgow (0.52) and Northampton (0.47) areas (Table 2). The log-probability plot for Pb in London soils indicates that there is an inflexion point at about 2000 mg kg^{-1} total Pb so additional regression modelling was carried out using only those samples with < 2000 mg kg^{-1}, as this is more likely to represent the normal level of background

contamination within the London urban area. Samples with concentrations > 2000 mg kg^{-1} possibly reflect isolated anomalous high Pb contamination incidents.
The Pb coefficient for the <2000 mg kg^{-1} subset of the London samples is almost the same as for the whole dataset (Table 2). Additional regression models for subsets with <1500 mg kg^{-1} and <1000 mg kg^{-1} Pb have similar Pb coefficients (0.70 and 0.75 respectively) to the <2000 mg kg^{-1} model (0.68). Fitted models with positive intercepts are not theoretically feasible and likely to result from y-axis (BS-Pb) uncertainty, so it would be more appropriate to use models without fitting the intercept. Using either to predict BS-Pb gives virtually the same result.

Analysis of Covariance was used to assess whether the urban AREA (GLAS, LOND, NORT, SWAN) 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; Model = AREA; and Covariate = Pb). Results for the full GLNS combined dataset indicate that AREA differences are not significant (p = 0.105) whilst AREA is significant (p <0.005) for the <2000 mg kg^{-1} Pb subset of the GLNS data but explains only 2% of the variance compared with 88% explained by total Pb. When GLM is applied to a < 2000 mg kg^{-1} Pb subset of the combined London-Northampton-Swansea data, AREA is not significant (p 0.036) and controls only 0.2% of the variance compared with 95% controlled by Pb. The scatter plots in Figures 1 and 2 compare the 95th percentile confidence limits obtained by the bootstrap resampling for each individual data set compared to the combined data (Figure 1 for all data and Figure 2 for the <2000 mg kg^{-1} data subset). Whilst the analysis of the covariance test suggests that the Glasgow BS-Pb vs. total Pb regression model has a significantly lower slope than the London

Swansea and Glasgow model, the confidence intervals in Figures 1-2, however, show that the Glasgow data has higher scatter than the other data sets but, in both Figure 1 and Figure 2, the confidence region of the LR overlaps with the confidence region of the combined data sets. The overall conclusion is that the BS-Pb relationship with total Pb content of soils is broadly the same for the four locations studied (Figure 3). $^{206}Pb/^{207}Pb$ ratios of bioaccessible Pb are very similar to soil Pb, irrespective of the total Pb concentration in the Glasgow area suggesting that the source of Pb, which is a mixture of alkyl Pb petrol additives and Pb from indigenous ores and coal, is less important than the overall soil total Pb concentration and the soil phases with which the Pb is associated (Farmer et al., 2011). Pb isotope and CISED (Chemometric Identification of Substrates and Element Distributions; Cave et al., 2004) studies currently underway at the BGS should provide a more detailed explanation of Pb sources and bioaccessibility in London soils.

3.3 Comparison of models based on <2 mm and <250 µm fractions

Summary statistics for the <2mm and <250 µm fractions of the London samples (Table 3) show that median Pb is very similar in the <2mm (927 mg kg^{-1}) and <250 µm (1023 mg kg^{-1})fractions, whilst mean Pb is c. 8% higher in the <250 µm fraction. Mean Si and Fe are c. 18% higher in the <2mm fraction and mean Al and Mg are 10 and 25%, respectively, higher in the <250 µm fraction. The closed array (100%) effect will impact on these relationships (Reimann et al., 2008). LR models for BS-Pb vs Pb (<2mm) and Pb (<250 µm) are only slightly different both when all the data are used (Figure 4) and also when they are based on <2000 mg kg^{-1} Pb subsets (Figure 5).

Mean Pb and Si in the Swansea urban samples are 3% and 9% higher, respectively, in the <250 μm fraction whilst mean Ca and Fe are 25% and 10% higher in the <2mm fraction (Table 4).

LR models for BS-Pb vs Pb (<2mm) and Pb (<250 μm) are significantly different (95% CI; data not presented here) when all the data are used but not significantly different (95% CI limits overlap, Figure 5) when they are based on the <2000 mg kg^{-1} subset. However, differences in models for the whole Swansea data set are strongly influenced by one high Pb sample which exerts a large leverage, so these apparent differences may not be all that significant.

These results suggest that in the London and Swansea areas, size fraction is not an important factor for BS-Pb vs. total Pb models, especially when total Pb is < 2000 mg kg^{-1}. 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.

3.4 Pb bioaccessibility mapping

The combined Glasgow-London-Northampton-Swansea (GLNS) model (BS-Pb = 0.687 total Pb) was used to produce an estimated BS-Pb map from a topsoil Total Pb map of the London urban area created by interpolating log transformed total Pb data to a 100m grid using an IDW algorithm (Appleton, 2011; Appleton and Adlam, 2012). The GLNS model was selected as this is the average for the four studied urban areas that will be applied to the BGS Urban Soil Chemistry dataset (Appleton, 2011) in order to produce a bioaccessible Pb dataset covering 23 urban areas in the UK. The origin and mineralogy

of the soils can impact on the bioaccessibility of Pb so bioaccessible Pb concentrations estimated using this model should be treated with some caution. However, the broad compatibility of the Glasgow, London, Northampton and Swansea regression models suggests that bioaccessible Pb in UK urban soils estimated using the GLNS model should be relatively accurate. The resultant bioaccessible Pb map (Figure 6) shows that an extensive part of central London is characterised by estimated BS-Pb concentrations greater than 200 mg kg^{-1}. Most of the areas with <100 mg kg^{-1} BS-Pb are not classified as urban by the British Ordnance Survey 1:250,000 scale *Strategi* data, being mainly large parks or agricultural land.

4. Conclusions

1. Linear regression analysis of the topsoil data for the Glasgow, London, Northampton and Swansea urban areas indicate that total Pb is the only highly significant independent variable for estimating the bioaccessibility of Pb.
2. Although analysis of covariance indicates that only the Glasgow data are significantly different from the other three urban areas, bootstrap resampling shows that LR confidence limits overlap and that the relationship between total Pb and BS-Pb is broadly the same for the four urban areas.
3. The Pb LR coefficients for the <2000 mg kg^{-1} subsets of the London and Swansea samples are almost the same as for the whole dataset. Models based on the < 2000 mg kg^{-1} subset, are likely to better represent the 'normal' level of ambient background contamination in the urban domains of the UK, as these appear to principally reflecting the impacts of leaded petrol and coal ash. Localised anomalously high Pb concentrations will reflect the impact of point source contamination.

4. The relationship between total element concentrations in the <2mm fraction and the <250 μm fraction of the London and Swansea topsoils suggest that size fraction is not an important factor for BS-Pb vs. total Pb models, especially when total Pb is < 2000 mg kg^{-1}. Grain size distribution may be an important factor at very high total Pb concentrations, probably reflecting the influence of the type of anthropogenic contamination.
5. The broad compatibility of the LR models for the four urban areas studied here suggests that bioaccessible Pb in UK urban soils estimated using the combined GLNS model should be relatively accurate. Validation of the relationships reported in this study by comparable studies in other urban areas of the UK should be carried out.
6. The results of this study draw broad conclusions on the bioaccessibility of Pb in the urban environment in the UK. These results should not be used to draw conclusions about the bioaccessibility of Pb in other areas of the UK (e.g. in the Pb mineralised area of Derbyshire). These results can be used as part of a lines of evidence approach to localised risk assessment but should in no way be used to replace bioaccessibility testing at individual sites where local conditions may vary considerably from the broad overview presented in this study. A lines of evidence approach means that no single piece of evidence should be solely relied on to make a decision about health risks. This data can, however, be used alongside other investigations and considerations to inform a site-specific risk evaluation.

Acknowledgements

This paper is published with the permission of the Director of the British Geological Survey (Natural Environment Research Council). The contribution of all BGS staff

involved in the collection and analysis of samples from the G-BASE survey is gratefully acknowledged. Andreas Scheib (BGS) tested some of the LR and MLR models. The Glasgow data were obtained as part of the PhD research of A. Broadway, University of Edinburgh. Andrew Tye (BGS) and four anonymous reviewers are thanked for suggesting useful improvements to an earlier version of this paper.

References

Allen, M.A., Cave, M.R., Chenery, S.R.N., Gowing, C.J.B., Reeder, S., 2011. Sample Preparation and Inorganic Analysis for Urban Geochemical Survey Soil and Sediment Samples, in: Johnson, C., Demetriades, A., Locutura, J., Ottesen, R.T. (Eds.), Mapping the Chemical Environment of Urban Areas. Wiley-Blackwell, Oxford, pp. 28-46.

Ander, E.L., Cave, M.R., Johnson, C.C., Palumbo-Roe, B., 2012. Normal background concentrations of contaminants in the soils of England. Available data and data exploration. British Geological Survey, Keyworth, Nottingham.

Appleton, J.D., 2011. User Guide for the British Geological Survey Urban Soil Chemistry Dataset. British Geological Survey, Keyworth, Nottingham.

Appleton, J.D., Adlam, K.A.M., 2012. Geogenic control on soil chemistry in urban areas: A novel method for urban geochemical mapping using parent material classified data. Applied Geochemistry 27, 161-170.

Bierkens, J., Buekers, J., Van Holderbeke, M., Torfs, R., 2012. Health impact assessment and monetary valuation of IQ loss in pre-school children due to lead exposure through locally produced food. Science of the Total Environment 414, 90-97.

Broadway, A., Cave, M.R., Wragg, J., Fordyce, F.M., Bewley, R.J.F., Graham, M.C., Ngwenya, B.T., Farmer, J.G., 2010. Determination of the bioaccessibility of chromium in Glasgow soil and the implications for human health risk assessment. Science of the Total Environment 409, 267-277.

Caboche, J., 2009. Validation d'un test de mesure de bioaccessibilité. Application à quatre éléments traces métallique dans les sols: As, Cd, Pb et Sb, Science Agronomique. L'Institut National Polytechnique de Lorraine, Nancy, p. 348.

Cave, M.R., Johnson, C.C., Ander, E.L., Palumbo-Roe, B., 2012. Methodology for the determination of normal background contaminant concentrations in English soils. British Geological Survey, Keyworth, Nottingham.

Cave, M.R., Milodowski, A.E., Friel, E.N., 2004. Evaluation of a method for Identification of Host Physico-chemical Phases for Trace Metals and Measurement of their Solid-Phase Partitioning in Soil Samples by Nitric Acid Extraction and Chemometric Mixture Resolution. Geochemistry: Exploration, Environment, Analysis 4, 71-86.

Cave, M.R., Wragg, J., Denys, S., Jondreville, C., Feidt, C., 2011. Oral Bioavailability, in: Swartjes, F. (Ed.), Dealing with Contaminated Sites: From Theory towards Practical Application. Springer, Dordrecht, pp. 287-324.

Cave, M.R., Wragg, J., Palumbo, B., Klinck, B.A., 2003. Measurement of the Bioaccessibility of Arsenic in UK soils. Environment Agency, London.

DIN, 2000. Soil Quality - Absorption availability of organic and inorganic pollutants from contaminated soil material. Deutsches Institut fur Normung e. v., Berlin.

Denys, S., Caboche, J., Tack, K., Rychen, G., Wragg, J., Cave, M., Jondreville, C., Feidt, C., 2012. In Vivo Validation of the Unified BARGE Method to Assess the

Bioaccessibility of Arsenic, Antimony, Cadmium, and Lead in Soils. Environ Sci Technol 46, 6252-6260.

Drexler, J.W., Brattin, W.J., 2007. An in vitro procedure for estimation of lead relative bioavailability: With validation. Human and Ecological Risk Assessment 13, 383-401.

Duggan, M.J., Inskip, M.J., Rundle, S.A., Moorcroft, J.S., 1985. Lead in Playground Dust and on the Hands of Schoolchildren. Science of the Total Environment 44, 65-79.

Farmer, J.G., Broadway, A., Cave, M.R., Wragg, J., Fordyce, F.M., Graham, M.C., Ngwenya, B.T., Bewley, R.J.F., 2011. A lead isotopic study of the human bioaccessibility of lead in urban soils from Glasgow, Scotland. Science of the Total Environment 409, 4958-4965.

Flight, D.M.A., Scheib, A.J., 2011. Soil Geochemical Baselines in UK Urban centres: The G-BASE Project, in: Johnson, C., Demetriades, A., Locutura, J., Ottesen, R.T. (Eds.), Mapping the Chemical Environment of Urban Areas. Wiley-Blackwell, Oxford, pp. 186-206.

Huang, P.-C., Su, P.-H., Chen, H.-Y., Huang, H.-B., Tsai, J.-L., Huang, H.-I., Wang, S.-L., 2012. Childhood blood lead levels and intellectual development after ban of leaded gasoline in Taiwan: a 9-year prospective study. Environment International 40, 88-96.

Intawongse, M., Dean, J.R., 2006. In-vitro testing for assessing oral bioaccessibility of trace metals in soil and food samples. Trac-Trends in Analytical Chemistry 25, 876-886.

Isaac, C.P.J., Sivakumar, A., Kumar, C.R.P., 2012. Lead Levels in Breast Milk, Blood Plasma and Intelligence Quotient: A Health Hazard for Women and Infants. Bulletin of Environmental Contamination and Toxicology 88, 145-149.

Jakubowski, M., 2011. Low-Level Environmental Lead Exposure and Intellectual Impairment in Children - the Current Concepts of Risk Assessment. International Journal of Occupational Medicine and Environmental Health 24, 1-7.

Johnson, C.C., 2011. Understanding the Quality of Chemical Data from the Urban Environment – Part 1: Quality Control Procedures, in: Johnson, C., Demetriades, A., Locutura, J., Ottesen, R.T. (Eds.), Mapping the Chemical Environment of Urban Areas. Wiley-Blackwell, Oxford, pp. 61-76.

Kim, D.-S., Yu, S.-D., Lee, E.-H., 2010. Effects of blood lead concentration on intelligence and personality in school children. Molecular & Cellular Toxicology 6, 19-23.

Klinck, B., Palumbo, B., Cave, M.R., Wragg, J., 2005. Arsenic dispersal and bioaccessibility in mine contaminated soils: a case study from an abandoned arsenic mine in Devon, UK. British Geological Survey, Keyworth, Nottingham.

Luo, X.-S., Ding, J., Xu, B., Wang, Y.-J., Li, H.-B., Yu, S., 2012a. Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils. Science of the Total Environment 424, 88-96.

Luo, X.-s., Yu, S., Li, X.-d., 2012b. The mobility, bioavailability, and human bioaccessibility of trace metals in urban soils of Hong Kong. Applied Geochemistry 27, 995-1004.

Madrid, F., Biasioli, M., Ajmone-Marsan, F., 2008. Availability and bioaccessibility of metals in fine particles of some urban soils. Archives of Environmental Contamination and Toxicology 55, 21-32.

Marchant, B.P., Tye, A.M., Rawlins, B.G., 2011. The assessment of point-source and diffuse soil metal pollution using robust geostatistical methods: a case study in Swansea (Wales, UK). European Journal of Soil Science 62, 346-358.

Nathanail, C.P., 2009. Professional Practice Note: Reviewing human health risk assessment reports invoking contaminant oral bioavailability measurements or estimates. Chartered Institute for Environment and Health, London.

Oomen, A.G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, C., Schoeters, G., Verstraete, W., Van de Wiele, T., Wragg, J., Rompelberg, C.J.M., Sips, A., Van Wijnen, J.H., 2002. Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. Environmental Science & Technology 36, 3326-3334.

Paustenbach, D.J., 2000. The practice of exposure assessment: A state-of-the-art review (Reprinted from Principles and Methods of Toxicology, 4th edition, 2001). Journal of Toxicology and Environmental Health-Part B-Critical Reviews 3, 179-291.

Pelfrene , A., Waterlot, C., Mazzuca, M., Nisse, C., Bidar, G., Francis, D., 2010. Assessing Cd, Pb, Zn human bioaccessibility in smelter contaminated agricultural topsoils (northern France). Environmental Geochemistry and Health 33, 477-493.

R Development Core Team, 2011. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

Poggio, L., Vrscaj, B., Schulin, R., Hepperle, E., Marsan, F.A., 2009. Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy). Environmental Pollution 157, 680-689.

Rawlins, B.G., Lark, R.M., O'Donnell, K.E., Tye, A.M., Lister, T.R., 2005. The assessment of point and diffuse metal pollution of soils from an urban geochemical survey of Sheffield, England. Soil Use And Management 21, 353-362.

Rawlins, B.G., McGrath, S.P., Scheib, A.J., Breward, N., Cave, M., Lister, T.R., Ingham, M., Gowing, C., Carter, S., 2012. The advanced soil geochemical atlas of England and Wales. British Geological Survey, Keyworth, Nottingham.

Reimann, C., Filzmoser, P., Garrett, R.G., Dutter, R., 2008. Statistical Data Analysis Explained. Applied Environmental Statistics with R. Wiley, Chichester.

Roussel, H., Waterlot, C., Pelfrene, A., Pruvot, C., Mazzuca, M., Douay, F., 2010. Cd, Pb and Zn oral bioaccessibility of urban soils contaminated in the past by atmospheric emissions from two lead and zinc smelters. Archives Environmental Contamination and Toxicology 58, 945-954.

Scheib, C., Flight, D., Lister, T.R., Scheib, A., Breward, N., 2011. London Earth: As in topsoils. G-BASE summary interpretation. British Geological Survey, Keyworth, Nottingham.

Selinus, O., 2005. Essentials of Medical Geology Impacts of the Natural Environment on Public Health. Elsevier Academic Press, Burlington.

Sialelli, J., Davidson, C.M., Hursthouse, A.S., Ajmone-Marsan, F., 2011. Human bioaccessibility of Cr, Cu, Ni, Pb and Zn in urban soils from the city of Torino, Italy. Environmental Chemistry Letters 9, 197-202.

Smith, E., Weber, J., Naidu, R., McLaren, R.G., Juhasz, A.L., 2011. Assessment of lead bioaccessibility in peri-urban contaminated soils. Journal of Hazardous Materials 186, 300-305.

Tang, X.-Y., Zhu, Y.-G., Shan, X.-Q., McLaren, R., Duan, J., 2007. The ageing effect on the bioaccessibility and fractionation of arsenic in soils from China. Chemosphere 66, 1183-1190.

Thums, C.R., Farago, M.E., Thornton, I., 2008. Bioavailability of trace metals in brownfield soils in an urban area in the UK. Environmental Geochemistry and Health 30, 549-563.

Watts, M.J., Button, M., Brewer, T.S., Jenkin, G.R.T., Harrington, C.F., 2008. Quantitative arsenic speciation in two species of earthworms from a former mine site. Journal of Environmental Monitoring 10, 753 -759.

Wragg, J., 2009. BGS Guidance Material 102, Ironstone Soil, Certificate of Analysis. British Geological Survey, Keyworth, Nottingham.

Wragg, J., Cave, M., Taylor, H., Basta, N., Brandon, E., Casteel, S., Denys, S., Gron, C., Oomen, A., Reimer, K., Tack, K., Van de Wiele, T., 2009. Interlaboratory Trial of a Unified Bioaccessibility Procedure, Open. British Geological Survey, Keyworth, Nottingham.

Wragg, J., Cave, M.R., 2003. In-vitro Methods for the Measurement of the Oral Bioaccessibility of Selected Metals and Metalloids in Soils: A Critical Review. Environment Agency, London.

Wragg, J., Cave, M.R., Basta, N., Brandon, E., Casteel, S., Denys, S., Gron, C., Oomen, A., Reimer, K., Tack, K., Van de Wiele, T., 2011. An Inter-laboratory Trial of the Unified BARGE Bioaccessibility Method for Arsenic, Cadmium and Lead in Soil. Science of the Total Environment 409, 4016-4030.

Yang, J.K., Barnett, M.O., Jardine, P.M., Basta, N.T., Casteel, S.W., 2002. Adsorption, sequestration, and bioaccessibility of As(V) in soils. Environmental Science & Technology 36, 4562-4569.

Zia, M.H., Codling, E.E., Scheckel, K.G., Chaney, R.L., 2011. In vitro and in vivo approaches for the measurement of oral bioavailability of lead (Pb) in contaminated soils: A review. Environmental Pollution 159, 2320-2327.

TABLES

Table 1 Summary statistics for topsoil data grouped by urban area

		Total Pb (mg kg^{-1} in <2 mm fraction)			BS-Pb (mg kg^{-1} in < 250µm fraction)			% Pb-BAF		
	N	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
Glasgow	21	133-1709	836	648	46-1575	418	365	20-92	49	45
London	49	99-13557	1736	927	50-8581	1203	672	26-101	68	68
London (Pb <2000 mg/kg)	37	99-1863	698	507	50-1334	478	331	44-87	68	68
Northampton	49	27-335	85	66	4-185	37	26	15-57	39	38
Swansea	25	90-6766	821	510	55-4762	563	464	49-92	70	68
Swansea (Pb <2000 mg/kg)	24	90-1366	574	471	55-734	388	396	49-92	70	67

Table 2 Least squares linear regression models for bioavailable lead

Dataset	N	Intercept[1]	Model formula (*MLR models in italics*)	R^2
GLASGOW (G)				
All samples	21	F	*BS-Pb = -1648 + 0.629 Pb + 0.00632 Si*	71%
All samples	21	F	BS-Pb = -57 + 0.568 Pb	62%
All samples	21	NF	BS-Pb = 0.515 Pb	86%
LONDON (L)				
All samples	49	F	BS-Pb = -1.6 + 0.694 Pb	96%
Pb < 2000 mg/kg	37	F	BS-Pb = 9.5 + 0.671 Pb	94%
Pb < 2000 mg/kg	37	NF	BS-Pb = 0.680 Pb	98%
NORTHAMPTON (N)				
All samples	49	F	*BS-Pb = -72 + 0.536 Pb + 0.000247 Si*	96%
All samples	49	F	BS-Pb = -7.69 + 0.523 Pb	95%
All samples	49	NF	BS-Pb = 0.465 Pb	97%
SWANSEA (S)				
All samples	25	F	BS-Pb = -7.6 + 0.694 Pb	99%
All samples	25	NF	BS-Pb = 0.691 Pb	99%
Pb <2000 mg/kg	24	F	BS-Pb = 64 + 0.564 Pb	88%
Pb <2000 mg/kg	24	NF	BS-Pb = 0.703 Pb	98%
Combined GLNS				
All samples	144	F	BS-Pb = -34 + 0.695 Pb	96%
All samples	144	NF	BS-Pb = 0.687 Pb	96%
Pb < 2000 mg/kg	131	F	BS-Pb = 5.4 + 0.624 Pb	88%
Pb < 2000 mg/kg	131	NF	BS-Pb = 0.619 Pb	93%
Combined LNS				
All samples	123	F	BS-Pb = -12.7 + 0.696 Pb	97%
All samples	123	NF	BS-Pb = 0.694 Pb	97%
Pb < 2000 mg/kg	110	F	BS-Pb = -5.8 + 0.672 Pb	95%
Pb < 2000 mg/kg	110	NF	BS-Pb = 0.666 Pb	97%

[1] F = fixed; NF = not fixed

Table 3 Summary statistics for major elements (oxide wt. %) in <2mm and <250 µm fractions of topsoils from London urban area (n = 49)

Variable	Mean	Minimum	Median	Maximum
Al_2O_3 < 2mm	7.7	4.1	7.0	14.1
Al_2O_3 <250 µm	8.3	4.5	7.7	13.6
CaO < 2mm	2.6	0.4	2.2	6.0
CaO <250 µm	2.5	0.2	1.9	5.9
Fe_2O_3 < 2mm	5.1	1.4	4.9	13.0
Fe_2O_3 <250 µm	4.3	1.4	4.1	10.3
MgO < 2mm	0.9	0.2	0.8	1.8
MgO <250 µm	1.0	0.3	1.0	1.8
SiO_2 < 2mm	60.7	32.0	62.0	78.0
SiO_2 <250 µm	51.5	28.4	52.2	69.0

Table 4 Summary statistics for major elements (mg kg^{-1}) in <2mm and <250 µm fractions of topsoils from Swansea urban area (n = 25)

Variable	Mean	Minimum	Median	Maximum
Al < 2mm	46129	26979	46023	73002
Al <250 µm	45198	25392	45494	67183
Ca < 2mm	19691	357	6718	102488
Ca <250 µm	15529	357	5360	73328
Fe < 2mm	49504	24549	41684	118828
Fe <250 µm	46323	26158	37977	132466
Mg < 2mm	4053	1809	3619	11459
Mg <250 µm	4005	1809	3619	12665
Si < 2mm	199035	106943	197074	282068
Si <250 µm	221134	128425	213886	316159

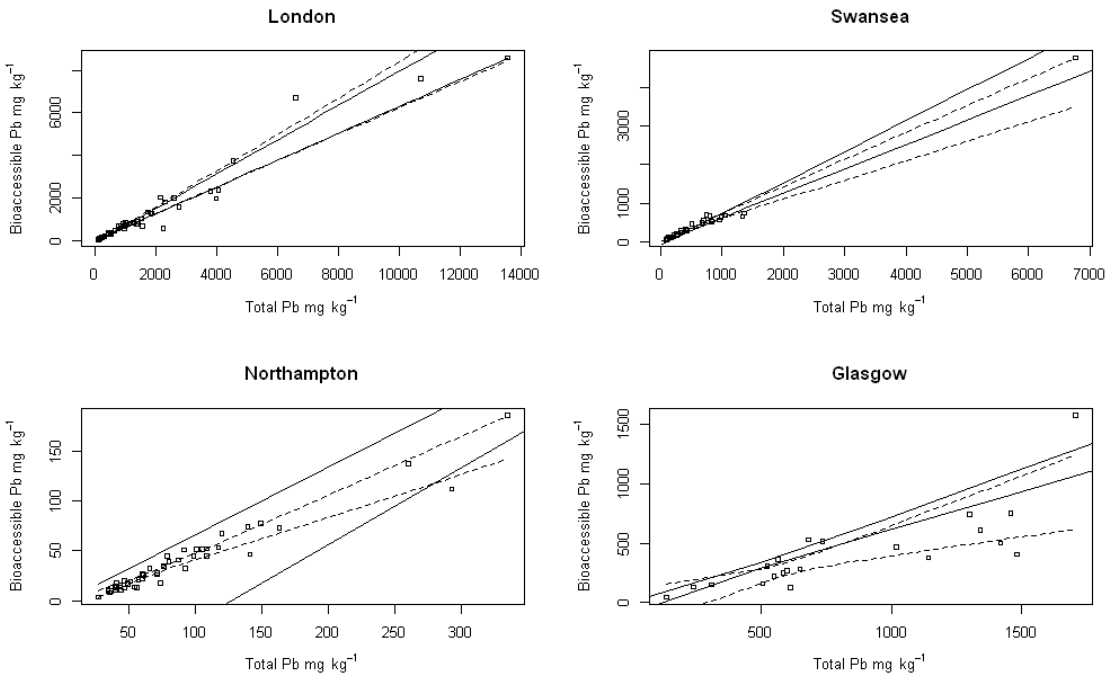

Figure 1 Scatterplot for relationship between total Pb (mg kg^{-1} in <2mm fraction) and bioaccessible Pb (<250 micron fraction) for London Swansea, Northampton and Glasgow. Solid lines show the 95th percentile confidence limits for all data combined and dotted lines show the 95th confidence interval for the individual data sets

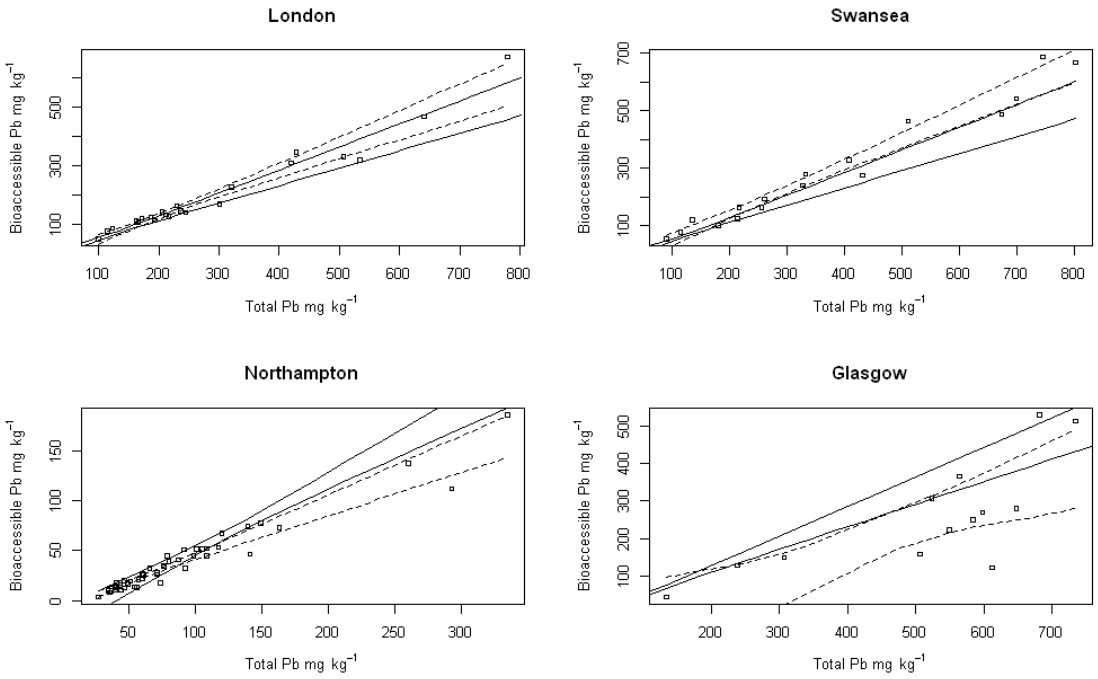

Figure 2 Scatterplot for relationship between total Pb (<2mm fraction) and bioaccessible Pb (<250 micron fraction): <2000 mg kg^{-1} Pb subset for London Swansea, Northampton and Glasgow. Solid lines show the 95th percentile confidence limits for all data combined and dotted lines show the 95th confidence interval for the individual data sets

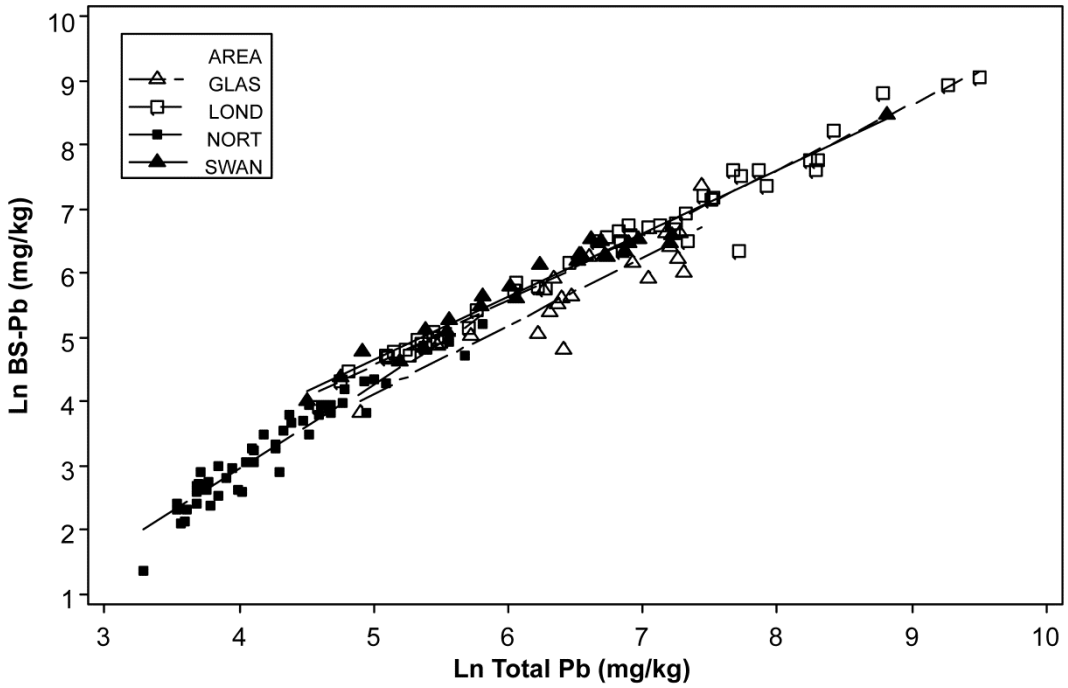

Figure 3 Relationship between Ln total Pb (<2 mm fraction) and Ln bioaccessible Pb (<250 μm fraction) in topsoils from Glasgow, London, Northampton and Swansea urban areas with corresponding regression

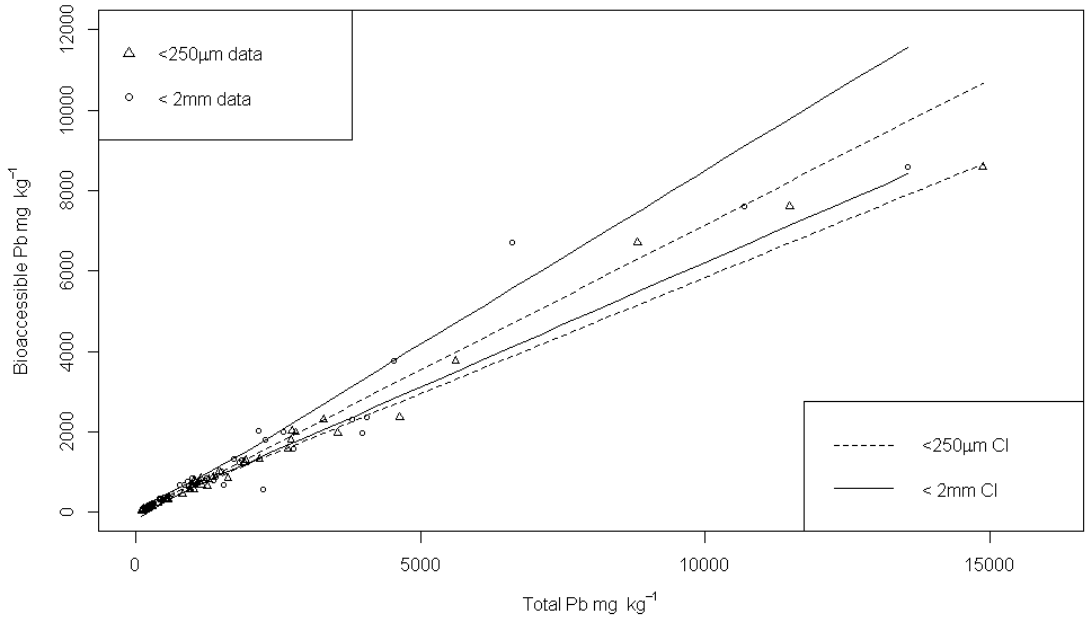

Figure 4 Scatterplot for relationship between total Pb in <2mm and <250 micron fractions and bioaccessible Pb in <250 µm fraction of London topsoils.

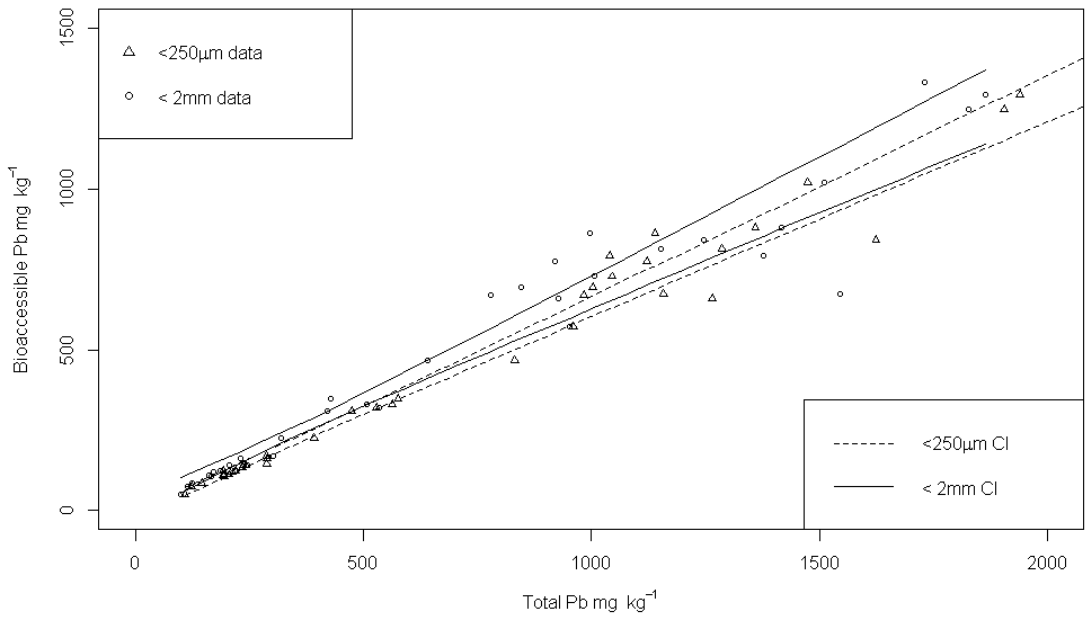

Figure 5 Scatterplot for relationship between total Pb in <2mm and <250 micron fractions and bioaccessible Pb in <250 µm fraction of London topsoils with <2000 mg/kg total Pb.

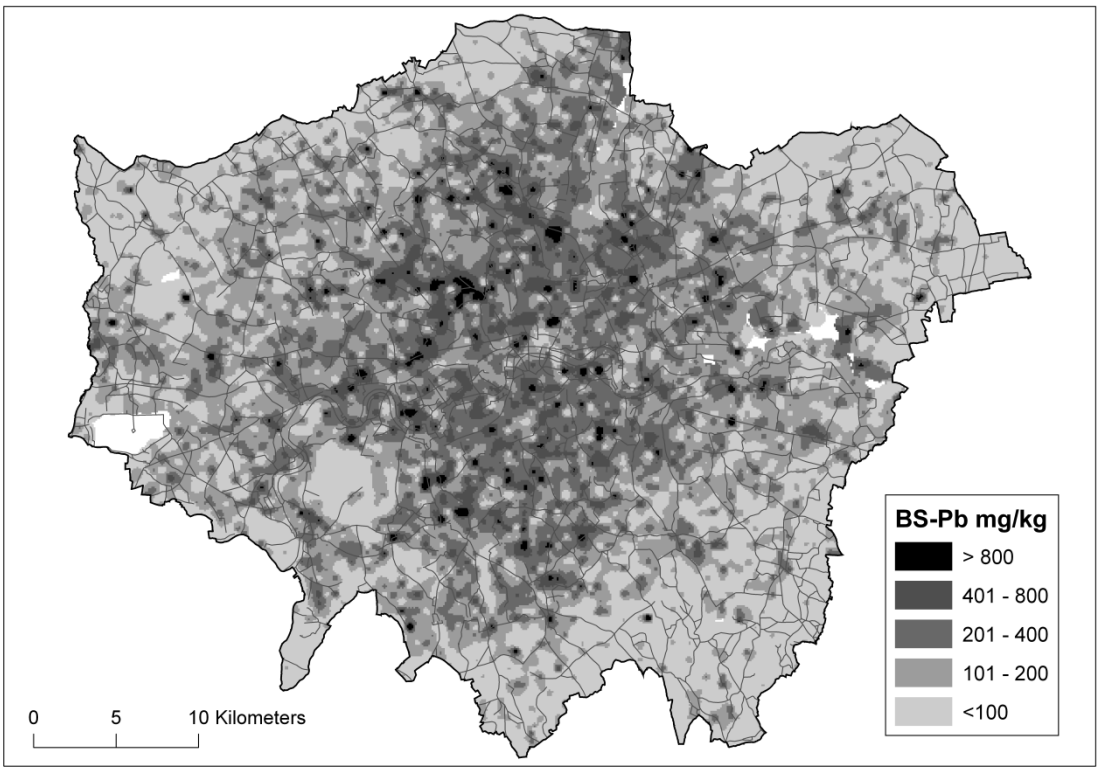

Figure 6 Estimated bioaccessible Pb in topsoils in the Greater London area (solid lines = motorways, major (A, B) and minor roads; Ordnance Survey Strategi data © Crown copyright 2012)