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

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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.

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, vs 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 inter-laboratory 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 bloodstream (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

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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 physicochemical 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 to 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 min for the Swansea and London samples compared to 3000 g for 5 min 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, 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 London, Northampton, and Swansea, whilst BGS 102 and NIST 2710 were used for 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).