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Anthropogenic and geogenic impacts on arsenic bioaccessibility in UK topsoils

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HIGHLIGHTS

► Total As is only significant predictor for estimating anthropogenic bioaccessible As.
► Total As explains 75–92% of the variance of anthropogenic bioaccessible As.
► Total As, P and pH predict geogenic (ironstone) bioaccessible As.
► Total As explains 40% of the variance of ironstone bioaccessible As.
► Anthropogenic bioaccessible As fraction is double that of ironstone soils.

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ABSTRACT

Predictive linear regression (LR) modelling between bioaccessible arsenic (B-As) and a range of total elemental compositions and soil properties was executed in order to assess the potential for developing a national B-As dataset for the UK. LR indicates that total arsenic (As) is the only highly significant independent variable for estimating B-As in urban areas where it explains 75–92% of the variance. The broad compatibility of the London, Glasgow and Swansea regression models suggests that application of these models to estimate bioaccessible As in UK soils impacted by diffuse anthropogenic urban contamination and non-ferrous metal processing should be relatively accurate. In areas dominated by Jurassic ironstones and associated clays and limestones, total As, P and pH are significant, accounting for 53, 14 and 5%, respectively, of the B-As variance. Models based on total As as the sole predictor in the combined Jurassic and Cretaceous sedimentary ironstones datasets explain about 40% of the B-As variance. The median As bioaccessible fraction (%As-BAF) is 19 to 28% in the anthropogenic contamination impacted urban domains, but much lower (5–9%) in geogenic terrains dominated by ironstones. 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 substantial proportion of the landscape of the UK has naturally elevated topsoil concentrations of total arsenic (As) which exceed the Soil Guideline Value (SGV), a threshold used in the preliminary assessments for land contamination (DEFRA-EA, 2002). Inorganic As SGVs for residential, allotment and commercial land uses are 32, 43 and 640 mg kg^{-1}, respectively (Martin et al., 2009). Approximately 1300 km^2 of the land surface of England underlain by ironstone and about 2200 km^2 of land impacted by mineralisation have topsoil As >32 mg kg^{-1} (Ander et al., 2012).

The main exposure pathway for As in soil is *via* soil ingestion (Paustenbach, 2000; DEFRA 2002; Bacigalupo and Hale, 2012), therefore, from a human health perspective, it is not the total amount of As in the soil but the fraction that is absorbed into the body during soil ingestion *i.e.* the bioavailable fraction, that is important for assessing human health risk. The measurement of the bioavailability of As in soil requires *in vivo* testing using humans or animal surrogates, a time consuming, costly and ethically challenging process. However, *in vitro* bioaccessibility testing has been developed and validated specifically to provide a conservative estimate of bioavailability (Basta et al., 2007; Caboche, 2009; Denys et al., 2012; Juhasz et al., 2007a). The *in vitro* bioaccessibility assay estimates the fraction of As 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). Guidelines for the use of data produced by *in vitro* bioaccessibility testing methods in human health risk assessment have recently been produced in order to assist the risk assessment and regulatory communities (Nathanail, 2009).

The bioaccessibility and hence bioavailability of any contaminant bound to the soil depend upon the soil type, properties of the soil, particle size, the contaminant and the manner by which the contaminant has entered the soil (Palumbo-Roe et al., 2005; Selinus, 2005; Juhasz et al., 2007a,b; Wragg et al., 2007; Meunier et al., 2011a,b;

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Mingot et al., 2011). Cave et al. (2011) have described how specific properties of soil, such as pH, organic matter content, mineral constituents, solid phase partitioning of As and soil ageing may influence bioaccessibility of As and other contaminants. A number of workers have successfully carried out multiple linear regression (MLR) modelling of the bioaccessible As content of soils 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; Juhasz et al., 2007b, 2008). Sarkar et al. (2007) used the element composition, pH, clay content and cation exchange capacity and Cave et al. (2007) used spectral properties derived from near infra-red spectra of the soils. If a 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, site specific investigations would have to be carried out. In addition, the model predictor variables and the relative size of their coefficients can provide an insight into the processes governing the bioaccessibility of As in the soils. However, the model is useful only 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. Furthermore, the MLR models tend to be very specific to particular soil types and parent materials (PMs), so cannot be applied universally and due consideration is required of the uncertainties of bioaccessibility models based on small numbers of analyses.

The British Geological Survey (BGS) holds extensive geochemical data and archives of soils collected under the Geochemical Baselines (G-BASE) Project (Johnson et al., 2005). If MLR or linear regression (LR) models could be set up using the soil geochemical data as predictor variables and As bioaccessibility data from selected *in vitro* bioaccessibility testing of soils, it would then, theoretically, be possible to predict the As bioaccessibility at a national scale and produce As bioaccessibility maps.

In this feasibility study, predictive regression modelling between bioaccessible As and a range of total elemental compositions and soil properties was executed for (1) the anthropogenically contaminated London (Scheib et al., 2011), Swansea (Marchant et al., 2011) and Glasgow (Broadway et al., 2010; Farmer et al., 2011) urban areas and (2) geogenic As associated with middle Jurassic ironstones and associated soil parent materials in the English East Midlands (Wragg et al., 2007) and Cretaceous ironstones in eastern England (Breward, 2007) and their associated soil parent materials (PMs). The objective was to assess the potential for developing bioaccessible As datasets derived from the BGS National and Urban Soil Chemistry datasets (Appleton et al., 2008; BGS, 2009; Appleton, 2011; Appleton and Adlam, 2012).

2. Geogenic and anthropogenic sources of arsenic in England and Wales

In central England concentrations above the residential As SGV (32 mg kg^{-1}) stretch from the Humber Estuary in the north all the way to the Bristol Channel in the southwest (Fig. 1; Appleton et al., 2008; Rawlins et al., 2012). The majority relate to early Jurassic calcareous ironstones of the Northampton Sand and Marlstone Rock formations (Wragg et al., 2007). The most northern part of the feature relates to the Lower Cretaceous Claxby and Lower Jurassic Frodingham ironstones (Palumbo-Roe et al., 2005; Breward, 2007) which occur in predominantly mudstone sequences. In sedimentary rocks, As is usually associated with iron and clay minerals, sulphides, organic matter and phosphates and as a consequence tends to be enriched in sedimentary ironstones, mudstones and coals. The association with phosphates is due to the chemical similarity between the PO_4^{3-} and AsO_4^{3-} anionic groups, while a strong association with sedimentary iron oxides is mainly due to the very low solubility of $FeAsO_4$ and also strong affinity for Fe oxyhydroxides (Cornell and Schwertmann, 2003).

Anthropogenic sources of As include coal combustion, sulphide ore roasting and smelting, pig and poultry sewage and some phosphate fertilisers (Reimann and Caritat, 1998). The largest cluster of elevated total As concentrations can be seen throughout the south-west of England, which are related to Cu–Sn mineralisation associated with granite intrusions as well as the legacy of mining and mineral processing in the area, including arsenic refining (Klinck et al., 2005; Palumbo-Roe and Klinck, 2007). For the majority of urban areas, As concentrations are low and below the SGV (Flight and Scheib, 2011), although higher total As concentrations have been recorded in the urban topsoils from Swansea, Northampton, Scunthorpe, Corby, Sheffield, Manchester and Hull (Flight and Scheib, 2011; Scheib et al., 2011). The concentration of total As in Swansea topsoils is above the SGV for almost the entire conurbation, largely due to the city's industrial legacy of non-ferrous smelters processing copper (Cu), As, lead (Pb), zinc (Zn), silver (Ag) and tin (Sn) (Marchant et al., 2011). Mining of Jurassic ironstones occurred within and close to the Corby, Northampton, Scunthorpe and Wellingborough urban centres, but only Corby and Scunthorpe had major iron foundries.

3. Materials and methods

3.1. 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 forty nine samples from London were selected to cover a range of total As and Pb concentrations, but data for three samples were not used in this study because the extremely high Pb concentrations meant that the As determinations were not reliable due to an XRF analytical interference. Twenty five topsoils from the Swansea urban area (Morley and Ferguson, 2001; Marchant et al., 2011) were selected to represent the wide range of total As and As/Fe ratios. Data for regression modelling in the Glasgow area is for the G-BASE samples reported in Broadway (2008), Broadway et al. (2010) and Farmer et al. (2011) which were originally selected to provide a range of total Cr, Pb or As concentrations. Only nine of the 21 bioaccessible As concentrations reported by Broadway in his PhD thesis (Broadway, 2008) were above the limit of detection of the ICP-AES analytical method (5 mg kg^{-1}).

The Northampton urban area is underlain by the Middle Jurassic ironstones of the Northampton Sand Formation (NSF) and associated Upper Lias Clays and Great Oolite Group limestones. The soil geochemical data set, containing 276 samples and consisting of 43 major and trace elements, pH, organic carbon and available phosphorus (Olsen method) was subjected to hierarchical clustering. The data were mean centred and scaled with Euclidean distance linkage using Ward's method. The resulting dendrograms suggested the existence of 4 distinct clusters in the Northampton data. A total of forty nine were chosen for further preparation and bioaccessibility testing. Twenty four topsoils with a range of relatively high total As were selected to represent the Cretaceous Claxby ironstone and associated ferruginous clays and sandstones in Lincolnshire.

3.2. Sample collection, preparation and determination of total concentrations

Topsoil samples from the Glasgow, London, Northampton and Swansea urban areas were collected from open ground on a 500 m grid at a density of approximately 4 samples per km^2; samples for the Lincolnshire (Claxby) rural area in eastern England were collected at a density of approximately 1 sample per km^2. 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 the 5–20 cm depth. Approximately 40 chemical elements were determined in the <2 mm size fraction of