Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Linking selective chemical extraction of iron oxyhydroxides to arsenic bioaccessibility in soil

Barbara Palumbo-Roe[*], Joanna Wragg, Mark Cave

British Geological Survey, Environmental Science Centre, Nicker Hill, Keyworth, Nottingham NG12 5GG, UK

ABSTRACT

The relationship between As bioaccessibility using the physiologically based extraction test (PBET) and As extracted by hydroxylamine hydrochloride (HH), targeting the dissolution of amorphous Fe oxyhydroxides, is established in soils from the British Geological Survey Geochemical Baseline Survey of SW England, UK, to represent low As background and high As mineralised/mined soils. The HH-extracted As was of the same order of magnitude as the As extracted in the bioaccessibility test and proved to be a better estimate of bioaccessible As than total As (bioaccessible As − total As: r = 0.955; bioaccessible As − HH-extracted As: r = 0.974; p-values = 0.000). These results provide a means of estimating soil As bioaccessibility on the basis of the HH extraction. Further selective extraction data, using hydrochloride acid that seeks to dissolve both amorphous and crystalline Fe oxyhydroxides, indicates a decrease in the As bioaccessible fraction with the increase of the soil Fe oxyhydroxide crystallinity.

1. Introduction

Soil ingestion is typically the primary human health exposure pathway to consider for arsenic (As) contaminated soils. The health risk is related to the relative bioavailability (RBA) of the contaminant that is absorbed into systemic circulation (USEPA, 2007), which in soils is typically lower than soluble metal(loid) salts, from which oral metal toxicity values are derived. In the last decades, as a surrogate for RBA, several *in vitro* methods (IVG, PBET, Rel SBRC-I, RBALP, SBRC-G, UMB) have been developed for the determination of bioaccessibility of soil As, where bioaccessibility is considered to be the fraction of a soil contaminant that is soluble in the gastrointestinal (GI) tract and available for absorption (Ruby et al., 1996, 1999). The relationship between *in vivo* RBA and *in vitro* bioaccessibility for As documented in the studies of Basta et al., 2007; Bradham et al., 2011, 2015; Denys et al., 2012; Juhasz et al., 2007, 2009; Li et al., 2014; Rodriguez et al., 1999, has demonstrated the potential of *in vitro* assays to predict As RBA using swine, primates or rodents (Juhasz et al., 2014).

While it is well recognised that only a fraction of total As in soil is bioaccessible, understanding of which soil As pools are measured in *in vitro* tests is crucial in order to reach a broader acceptability of

in vitro tests in human health risk assessment. Moreover, knowledge of the solid phases hosting the bioaccessible As can help envisage bioaccessibility changes with environmental conditions affecting the stability of the As hosting solid phases (e.g. the mobilisation of As associated to iron (Fe) redox cycling in flooded or paddy soils (Liu et al., 2015)).

Numerous studies have successfully carried out predictive modelling of As bioaccessibility using multiple regression analysis based on soil physicochemical properties, such as the elemental composition of the soil and soil pH (Appleton et al., 2012 and references within; Cave et al., 2013; Mikutta et al., 2014). These model predictor variables can provide an insight into the phases and processes governing the bioaccessibility of As in the soils. Unsurprisingly, considering the well-known role of Fe oxyhydroxides phases in regulating As geochemical cycle, many of these studies converge in identifying Fe oxyhydroxides as key factors influencing As bioaccessibility where As is naturally enriched in soil (e.g. Appleton et al., 2012; Wragg et al., 2007). Yang et al. (2002, 2005) also indicate that soils with high Fe oxyhydroxide contents and low pH are able to sequestrate As in the lowest bioaccessible form in As (V) spiked soils.

Besides multiple regression analysis, selective/sequential chemical extractions and mineralogical analysis can help to understand As solid phase speciation and to gain a better understanding of the sources of bioaccessible As in the *in vitro* tests. Rodriguez et al., 2003 first evaluated the ability of chemical

---

extractions to measure bioavailable As from soil ingestion for 15 contaminated soils and found the strongest relationship between *in vivo* bioavailable As and As determined by soil chemical extractions for hydroxylamine hydrochloride (HH) extractant, selected to dissolve As in Fe and Mn oxyhydroxides. Smith et al. (2008), by comparing sequential extraction results pre and post As bioaccessibility assessment (using the simplified bioaccessibility extraction test (SBET)), attributed the As bioaccessible fraction to the amorphous and poorly-crystalline oxyhydroxide Fe/Al fractions in 12 long-term contaminated soils. Yet, from these and other studies (Li et al., 2015; Mikutta et al., 2014; Whitacre et al., 2013) it is highlighted that various soil fractions are found to contribute to As bioaccessibility depending on the As contamination source, but also on the type of As solid speciation analysis/chemical extractant and As bioaccessibility *in vitro* methods in use. Most of these studies also analysed a small number of samples. Clearly, further investigation is warranted in order to consolidate the above studies, especially with large datasets.

In this study we aimed to investigate how As bioaccessibility using the PBET assay is related to the Fe oxyhydroxide phase pool based on chemical extraction assessments. The investigation is carried out on a robust dataset of 94 soils selected from the British Geological Survey Geochemical Baseline Survey (G-BASE) of the Tamar catchment, SW England, UK, including both low As background and high As mineralised/mined soils.

Previous work indicates the different importance of amorphous and crystalline Fe oxyhydroxides in affecting As bioaccessibility; higher bioaccessibility of As was observed for As bound to amorphous Fe oxyhydroxides than for As associated with crystalline Fe oxyhydroxides (Kim et al., 2014). Since the transformation of amorphous Fe oxyhydroxides like ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) to more crystalline forms such as goethite (α-FeOOH) or hematite (Fe_2O_3) is a major process of soil genesis (Blume and Schwertmann, 1969), the relationship between As bioaccessibility and degree of crystallinity of Fe oxyhydroxides can be important to predict bioaccessibility changes with soil development. In this study our further objective was to discern the relationship between bioaccessible As and the ratio "amorphous Fe oxyhydroxides/amorphous and crystalline Fe oxyhydroxides" in order to obtain evidence of the effect of soil Fe oxyhydroxide degree of crystallinity on As bioaccessibility in natural soils.

2. Study area

A recent study published by the UK Department for Environment, Food and Rural Affairs (Defra) on soil "normal" background concentrations (NBCs), which include contribution from both natural and diffuse anthropogenic sources, recognises different NBCs for different regions of England called domains (Ander et al., 2013). These domains are defined as distinct areas where a distinguishable factor is recognised as controlling the concentration of an element. Arsenic has three different NBC values for the "principal" (As 32 mg kg^{-1}), "ironstone" (As 220 mg kg^{-1}) and "mineralisation" (As 290 mg kg^{-1}) UK domains, the last two domains largely exceeding the UK screening levels (32 mg kg^{-1}) for the assessment of contaminated land (DEFRA, 2014). Our study area includes part of the UK "mineralisation" domain, where the geogenic (geology and mineralisation, see Supporting information for description of the geology) and anthropogenic (associated mining activities, Dines, 1956) inputs have resulted in elevated NBC of As.

The Tamar catchment is situated in SW England (UK) and covers an area of 976 km^2 (Fig. 1). As a result of intense exploitation of metalliferous ore deposits, combined with the natural geochemical dispersion from the copper-tin-arsenic mineralisation, SW England has significant areas of As rich soils and sediments (Abrahams and

Thornton, 1987; Aston et al., 1975; Colbourn et al., 1975; Rawlins et al., 2003; Rieuwerts et al., 2014). In particular, within the catchment Devon Great Consols mine (grid reference SX 426 733) was one of the major As producers in the world in the late 1800s (Dines, 1956).

3. Material and methods

The soil samples for this study were from a comprehensive geochemical survey of soils, sediments and water in the Tamar catchment, carried out as part of the British Geological Survey G-BASE project (Johnson et al., 2005). Sites for the soil samples were selected from every second kilometre square of the British National Grid by random location within each square, subject to the avoidance of roads, tracks, railways, domestic and public gardens, and other seriously disturbed ground.

3.1. Geochemical hierarchical clustering of the tamar soils and sample selection

The 468 soil samples, part of the G-BASE survey of the Tamar catchment, were grouped using k-mean clustering of the soil geochemical variables to derive more homogeneous data subsets (clusters) for further selecting the samples for bioaccessibility testing and chemical extractions. The soil geochemical dataset from Rawlins et al. (2003) consisted of 43 major and trace elements, pH, organic carbon and available phosphorus. The data were mean centred and scaled with Euclidean distance linkage using Ward's method (Ward, 1963). The spatial distribution of the resulting distinct 5 clusters was compared against the solid geology of the area (DiGMapGB-50, Smith, 2013) to identify possible relationships between regional soil geochemical data and geology (Fig. 1). The geochemical clusters largely reflected the distribution of the principal geological formations over which soils developed and therefore also referred as geo-domains (Supporting information).

94 samples were chosen for bioaccessibility testing from the 5 clusters suggested by the k-mean clustering dendrogram. The clustering allowed the production of a reduced number of samples for further investigation, whilst ensuring that the selection of samples used for bioaccessibility testing were representative of the region under study.

3.2. Sample preparation, total elemental digestion and As bioaccessibility extraction

The 94 selected topsoils (collected from 0 to 15 cm soil depth) were sub-sampled from the archived G-BASE soil samples and sieved to < 250µm. This fraction was chosen for bioaccessibility and associated testing, as this is the upper bound of particle size that is likely to remain on the hands of children (the "at risk" receptor) and be incidentally ingested (Duggan et al., 1985).

A mixed acid ($HF/HClO_4/HNO_3$) digest with Inductively Couple Plasma-Atomic Emission Spectrometry (ICP-AES) was used to determine the major and trace elements in the < 250µm size fraction sub-samples.

The bioaccessible As concentration was determined using a modified physiologically based extraction test (PBET), based on the method first described by Ruby et al. (1993, 1996). The PBET method was a simple sequential extraction used to simulate a number of physical and chemical conditions in the human GI tract, such as transit time, pH and chemical conditions, in order to estimate the amount of As that may be absorbed after the accidental soil ingestion of 100 mg day^{-1} by a child. The methodology and the modifications have been previously described in full by Cave et al.