Science of the Total Environment 581–582 (2017) 782–793

Contents lists available at ScienceDirect

Science of the Total Environment

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

Arsenic bio-accessibility and bioaccumulation in aged pesticide contaminated soils: A multiline investigation to understand environmental risk

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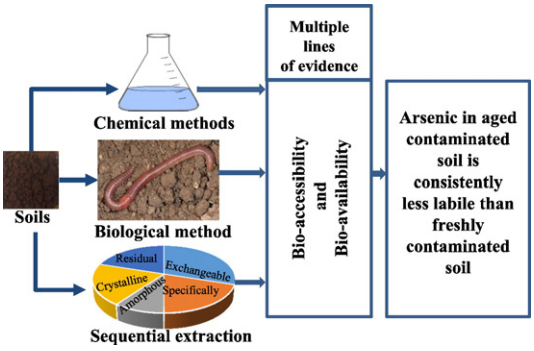
HIGHLIGHTS

- Soil ageing reduces As bio-accessibility by15%
- Soil ageing reduces As bioaccumulation by 9%
- Sequential extraction shows bio-accessibility is controlled by Fe/Al oxy-hydroxide.
- Earthworms are a complementary line of evidence reinforcing other extraction data.
- Earthworm bioaccumulation correlates with bio-accessible, and bioavailable measures.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 November 2016
Received in revised form 1 January 2017
Accepted 2 January 2017
Available online 5 January 2017

Editor: D. Barcelo

Keywords:
Contaminated soils
Holistic approach
Risk assessment
Earthworms
Physiologically based
Sequential extractions

ABSTRACT

Bio-accessibility and bioavailability of arsenic (As) in historically As-contaminated soils (cattle tick pesticide), and pristine soils were assessed using 3 different approaches. These approaches included human bio-accessibility using an extraction test replicating gastric conditions (in vitro physiologically-based extraction test); an operationally defined bioaccessibility extraction test - 1.0 M HCl extraction; and a live organism bioaccumulation test using earthworms. A sequential extraction procedure revealed the soil As-pool that controls bio-accessibility and bioaccumulation of As. Findings show that As is strongly bound to historically contaminated soil with a lower degree of As bio-accessibility (<15%) and bioaccumulation (<9%) compared with freshly contaminated soil. Key to these lower degrees of bio-accessibility and bioaccumulation is the greater fraction of As associated with crystalline Fe/Al oxy-hydroxide and residual phases. The high bio-accessibility and bioaccumulation of freshly sorbed As in pristine soils were from the exchangeable and specifically sorbed As fractions. Arsenic bioaccumulation in earthworms correlates strongly with both the human bio-accessible, and the operationally defined bioavailable fractions. Hence, results suggest that indirect As bioavailability measures, such as accumulation by earthworm, can be used as complementary lines of evidence to reinforce site-wide trends in the bio-accessibility using in vitro physiologically-based extractions and/or operationally defined extraction test. Such detailed knowledge is useful for successful reclamation and management of the As contaminated soils.

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http://dx.doi.org/10.1016/j.scitotenv.2017.01.009
0048-9697/

1. Introduction

Arsenic (As) is ubiquitous in the environment and a commonly encountered contaminant at many sites associated with former anthropogenic activity. Arsenic contamination occurs in >30% of US superfund sites (2006) and has been extensively identified as a contaminant throughout Europe (Navarro et al., 2006; Schulin et al., 2007), Asia (McCarty et al., 2011), South America (de Esparza, 2008), and Australia (Smith et al., 2006; Smith et al., 2003). Soil contamination occurs from anthropogenic sources such as mining, milling, and agricultural practices, as well as natural geochemical processes (Mandal and Suzuki, 2002; Smith et al., 1998). In Australia, As-containing pesticides were frequently used to control cattle ticks from the early 1900s to 1955 at some 1600 former cattle-dip sites in New South Wales (NSW) alone. Repeated arsenical pesticides applications (mostly as sodium arsenite) at these sites gives surrounding soil contamination of up to 5000 mg kg^{-1} (Kimber et al., 2002; Naidu et al., 2006; Niazi et al., 2011a; Smith et al., 1998). Hence, a significant proportion of dip sites investigated exceed the Australian ecological investigation level (EIL) of 20 mg kg^{-1} (NEPM, 1999) and as such, raise concerns about the potential soil-borne As risks to animal-, human-, and environmental-health.

Arsenic exposure from contaminated soils is of great concern to regulatory agencies and the broader community, because As-related health disorders have been linked to As exposure (Mandal and Suzuki, 2002). The primary pathways of human exposure to As that result in significant health effects are inhalation and oral ingestion, leading to both carcinogenic and non-carcinogenic responses (Schultz and Biksey, 2003). Over recent decades, a number of in vitro assays (IVG, PBET, Rel SBRC-I, RBALP, SBRC-G, UMB) have been developed for the assessment of contaminant bio-accessibility, where bio-accessibility is considered to be the fraction of a soil contaminant that is soluble in the gastrointestinal tract and available for absorption (Oomen et al., 2002; Rodriguez et al., 1999; Ruby et al., 1996; Ruby et al., 1999; Sarkar and Datta, 2003). These methods have been used to determine the bio-accessibility of As from a wide range of soils (Basta et al., 2001; Button et al., 2009; Juhasz et al., 2007; Juhasz et al., 2009; Kim et al., 2014; Palumbo-Roe et al., 2015; Ruby et al., 1996; Smith et al., 2011; Smith et al., 2014). Australian and New Zealand Environment and Conservation Council (ANZECC) and Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ; 2000) recommended an operationally defined extraction test for metals in soil and sediment, which have been used in several contaminant bio-accessibility assessment studies (Kashem et al., 2007; Keon et al., 2001; McCready et al., 2006; McCready et al., 2003).

Bioavailability is not a universal attribute; it can be geochemical species- and, in some cases, organism-specific (Giller et al., 1998). Moreover, bioavailability can only be measured by evaluating uptake of a metal/metalloid, and the impact on growth or activity of the target organism (Wolt, 1994). Ecosystem indicator species as a guide to bioavailability (e.g., earthworms) have proven useful in assessing soil contamination, particularly in contaminant accumulation by earthworm populations, (Langdon et al., 2001b; Langdon et al., 2003; Marino and Morgan, 1999; Morgan and Morgan, 1999) and environmental risk (Button et al., 2009; Langdon et al., 2002; Langdon et al., 1999; Langdon et al., 2003; Lee et al., 2013; Romero-Freire et al., 2015; Watts et al., 2008). However, other studies that have investigated the impact of soil contamination on soil biota, in particular earthworms (Cotter-Howells et al., 2005; Lukkari et al., 2004; Piearce et al., 2002; Van Vliet et al., 2006), suggest ecological input into contaminated land risk assessment is challenging. Hence, a holistic approach, whereby the geochemical, human and ecological aspects of contaminated land are employed to provide multiple lines of evidence in understanding risk, is required for risk assessment investigation.

It is well recognized that a fraction of total As in a soil is bio-accessible and bioavailable. Therefore, the accurate evaluation of soil As-pools or solid phase contributions in bio-accessible-, and bioavailable-As are crucial for risk assessment and/or for developing suitable remediation strategies in contaminated sites, because soil As solid-phases regulates mobility and bioavailability of As (Kim et al., 2014; Meunier et al., 2010; Niazi et al., 2011b; Palumbo-Roe et al., 2015; Ruby et al., 1999). In order to investigate solid-phase As speciation in soil, sequential extractions have been successfully applied (Arai et al., 2006; Kim et al., 2014; Li et al., 2015; Meunier et al., 2010; Niazi et al., 2011b; Parviainen et al., 2012; Wenzel et al., 2001). Sequential extractions are a relatively simple though useful method to assess As chemical forms by selectively extracting As bound to specific solid phases (Wenzel et al., 2001). However, sequential extractions require careful interpretation because the extractants are not wholly selective, they may mobilize materials from more resistant phases and carry over material from more accessible forms to be redistributed to more resistant phases (Akhurst et al., 2011; Clark et al., 2000). Moreover, knowledge of the solid phases hosting the bio-accessible As can help envisage bio-accessibility changes with changing environmental conditions that affect the stability of As-hosting phases (Liu et al., 2015; Palumbo-Roe et al., 2015).

The current study, investigates the interrelatedness of several bio-accessibility and bioavailability/bioaccumulation techniques for assessing As from several historically contaminated dip-site soils, as well as in freshly As-sorbed pristine soils of Northern Rivers, NSW, Australia. The study followed a holistic approach through the geochemical assessment as well as the application of an ecological tool (i.e., ecosystem indicator species such as earthworm accumulation) providing multiple lines of evidence for assessing As contaminated site risk. Hence, to our knowledge, this is quite different and not a commonly used approach where application of several experimental techniques in combination provide a powerful tool to delineate the bio-accessible and bioavailable As fractions and the attributing factor such as chemically-lability, -sorbed and -mineral bound As forms in the contaminated soils.

2. Materials and methods

2.1. Soil sample collection and preparation

Surface (0–30 cm) soils were collected from three As-contaminated cattle dip sites of McLeans Ridges (28°48′1.692″S and 153°23′8.734″E) and Pearces Creek (28°46′12.513″S and 153°26′40.018″E) (both kraznozem/ferralitic soil types), and Cudgen (28°15′13.944″S and 153°33′22.182″E; sandy soil type), representing different soil types and As-contamination levels in dip site soils from northern NSW, Australia. Two pristine soils were collected as controls, a ferralitic and a sandy soil, which were located in Wollongbar (28°48′36.5″S and 153°23′50.7″E) and Cudgen (28°15′11.99′S and 153°33′32.99″E), NSW, respectively. A synthetic standard soil was prepared according to OECD (Organization for Economic Cooperation and Development) guidelines (OECD, 1984) containing 10% organic matter (air-dried and finely ground sphagnum peat, 2-mm sieved), 20% kaolinite clay, 70% industrial quartz sand (>50% particles 0.05–0.2 mm). All soil samples were air-dried to a constant weight, sieved at <2 mm, and homogenized for analysis.

2.2. Soil analysis

Soils samples were characterized for pH in a 1:5 soil:water extracts and for effective cation exchange capacity (ECEC) using the method described by Rayment and Lyons (2011). The organic carbon was analyzed using an elemental analyzer (LECO IR analyzer). Particle size distributions of the soil samples were determined using the hydrometer analysis method (Klute, 1986). For elemental analysis, the soil samples were digested in 12 mL of *aqua-regia* (1/3 HNO_3-HCl, v/v) on a hotplate for 3 h at 110 °C. After evaporation to near dryness samples were reconstituted by addition of 2 mL 50% v/v nitric acid, heated at 50 °C for 30 min and then made up to 10 mL with Milli-Q (MQ) water before filtering through Whatman no. 42 filters. Samples were then diluted with MQ