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Arsenic solid-phase speciation and reversible binding in long-term contaminated soils

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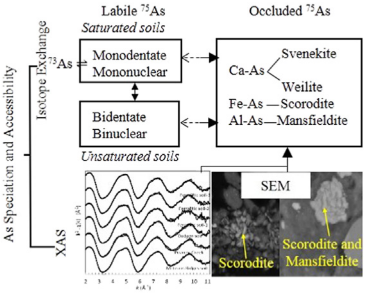
HIGHLIGHTS

- Isotope Exchange (IE) and XAS techniques combined are a powerful analytical tool.
- IE and XAS delineate chemically-labile As-forms, -sorbed and/or –free precipitates.
- Aging time is an important factor in determining the labile As in soil.
- SEM analysis confirms free precipitates of Al-, and Fe-arsenates.

GRAPHICAL ABSTRACT



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ABSTRACT

Historic arsenic contamination of soils occurs throughout the world from mining, industrial and agricultural activities. In Australia, the control of cattle ticks using arsenicals from the late 19th to mid 20th century has led to some 1600 contaminated sites in northern New South Wales. The effect of aging in As-mobility in two dip-site soil types, ferralitic and sandy soils, are investigated utilizing isotopic exchange techniques, and synchrotron X-ray adsorption spectroscopy (XAS). Findings show that historic soil arsenic is highly bound to the soils with >90% irreversibly bound. However, freshly added As (either added to historically loaded soils or pristine soils) has a significantly higher degree of As-accessibility. XAS data indicates that historic soil arsenic is dominated as Ca- (svenekite, & weilite), Al-(mansfieldite), and Fe- (scorodite) like mineral precipitates, whereas freshly added As is dominated by mineral adsorption surfaces, particularly the iron oxy-hydroxides (goethite and hematite), but also gibbsite and kaolin surfaces. SEM data further confirmed the presence of scorodite and mansfieldite formation in the historic contaminated soils. These data suggest that aging of historic soil-As has allowed neoformational mineral recrystallisation from surface sorption processes, which greatly reduces As-mobility and accessibility.

1. Introduction

Arsenic (As) is a highly toxic and carcinogenic element, which

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means that As-soil contamination is a major environmental threat (Smith et al., 1998; Mandal and Suzuki, 2002), where it may cause several adverse health effects, even at very low concentrations (Chen and Ahsan, 2004; Yuan et al., 2007; Smith and Steinmaus, 2009). However, arsenic is ubiquitous, and arsenic contamination occurs in more than 30% of "US superfund sites" (Delemos et al., 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., 2008). Surface soil contamination may arise from natural processes, but the major source of elevated As contamination of soils is through anthropogenic activities such as mining, milling, and agricultural practices (Smith et al., 1998; Mandal and Suzuki, 2002).

In Australia, cattle ticks jeopardised the beef and dairy industries, and tick eradication through a cattle-dipping program using arsenicals (sodium arsenite) as the major pesticide commenced in the early 1900s; the use of As continued up to 1955 (Kimber et al., 2002). Consequently, over 1600 dip sites were constructed, mostly in northern New South Wales (NSW) (Smith et al., 1998; Edvantoro et al., 2003). The historical application of arsenical pesticides and waste disposal in the vicinity of the abandoned dip-baths resulting in As contamination of surrounding soils up to 5000 mg kg^{-1} have been reported (McLaren et al., 1998; Smith et al., 1998, 1999; Kimber et al., 2002; Naidu et al., 2006; Niazi et al., 2011a). A soil contamination study of 12 cattle dip sites reported that 80% of soils had arsenic concentrations from 1 to 1000 mg kg^{-1}, whereas the remaining 20% were from 1000 to 4540 mg kg^{-1} (Van Zwieten et al., 2003). Hence, a significant proportion of dip sites investigated exceed the Australian ecological investigation level (EIL) of 20 mg kg^{-1} (NEPM, 1999).

Limited research suggests that As in most dip-sites exists in readily and/or potentially available forms presenting a significant environmental and health risk (McLaren et al., 1998; Smith et al., 1998, 2006; Niazi et al., 2011b). Consequently, farming and housing development around the contaminated sites are restricted. However, site-specific and accurate evaluations of As chemical forms in these contaminated soils is crucial for risk assessment, and for developing suitable remediation strategies. Arsenic solid-state speciation affects bioavailability and arsenic mobility in the environment (Paktunc et al., 2003; Arai et al., 2006; Meunier et al., 2010; Niazi et al., 2011b; Kim et al., 2014). Hence, although total-As concentrations provide an indication of soil contamination, these are an unreliable indicator of potential bioavailability or mobility. Consequently, to predict the environmental mobility/availability of arsenic, it is important to understand the interactions of arsenic with soil minerals, as this will influence the mobility and availability via adsorption, co-precipitation and mineral structural incorporation (Ruby et al., 1999; Meunier et al., 2010; Niazi et al., 2011b; Kim et al., 2014).

1.1. Radionuclide experiments with soil

The applications of radionuclides (e.g. ^{73}As) as radiotracers are important in understanding trace element behaviour in soils, where isotopic exchange techniques have been used in agricultural studies (Echevarria et al., 1998; Gérard et al., 2000; McDowell et al., 2001; Tye et al., 2002; Zhang et al., 2006; Clark et al., 2011). Isotope exchange does not occur with arsenic in strongly bound forms in soil, and for this reason the dynamics of available arsenic can be predicted from the isotope exchange results. Such studies enable the potentially mobile or 'bio-accessible' proportion of the element, that is weakly bound by the soil and is available in a soil system, to be identified (often referred to as the 'labile pool') (Lopez and Graham, 1970, 1972). Similarly radiotracer techniques are applicable to environmental studies for estimating the mobile fraction, where such techniques are often superior to chemical extractions, because of the operationally defined nature of extraction techniques (Payne et al., 2001, 2004).

1.2. X-ray absorption spectroscopy (XAS) studies of soil

X-ray absorption spectroscopy (XAS) allows a determination of oxidation state and chemical binding of trace elements in soils (Paktunc et al., 2003; Cances et al., 2005; Arai et al., 2006; Meunier et al., 2010; Niazi et al., 2011b; Parviainen et al., 2012; Gomez-Gonzalez et al., 2014). Many authors have successfully used XAS to investigate As at former arsenical processing plants (Cances et al., 2005), As(V) mineral surface associations (Arai et al., 2006; Kappen and Webb, 2013; Gomez-Gonzalez et al., 2014), links between soil composition, mineralogy, and As bio-accessibility (Meunier et al., 2010), solid-phase speciation and phyto-availability of historically contaminated soils (Niazi et al., 2011b), and As attenuation mechanisms in the vadose-zone (Parviainen et al., 2012).

In the present study, an evaluation of the arsenic solid-state speciation and lability in several historically contaminated dip-site soils of Northern Rivers, NSW, Australia is provided. We use a combination of isotope exchange techniques and XAS, which were not applied in previous studies (Paktunc et al., 2003; Cances et al., 2005; Arai et al., 2006; Meunier et al., 2010; Niazi et al., 2011b; Parviainen et al., 2012; Gomez-Gonzalez et al., 2014). Hence, to our knowledge, this is the first study where application of several experimental techniques in combination are used to provide a sufficiently powerful tool in delineating chemically-labile, -sorbed, -mineral bound, and various oxidation states in As-contaminated dip-site soils.

2. Materials and methods

2.1. Soil sampling

Surface (0–30 cm) soils were collected from three As-contaminated cattle dip sites (McLeans Ridges, Pearces Creek and Cudgen), representing different soil types and contamination levels in northern NSW, Australia. Two pristine soils were collected as controls, a kraznozem/ferralitic and a sandy soil, which were located in Wollongbar and Cudgen, NSW, respectively. A number of soil cores were collected from each of the sites, which were mixed together to make a composite soil sample for the site. A synthesized 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 thoroughly homogenized for analysis.

2.2. Soil analysis

The soils were characterized for pH in 1:5 soil:water extracts and for effective cation exchange capacity (ECEC) using the method described by Rayment and Lyons (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). Total major and trace elements were analyzed via inductively coupled plasma mass spectrometry (using a Perkin Elmer ELAN DRCe ICP-MS to avoid over estimations of As content from polyatomic species; e.g., ArCl at 75 amu) following a microwave assisted *aqua-regia* digestion. A DPTA (Diethylenetriaminepenta-acetic