



Assessing the environmental availability of heavy metals in geogenically contaminated soils of the Sierra de Aracena Natural Park (SW Spain). Is there a health risk?



M.B. Rivera^a, M.I. Giráldez^{b,c}, J.C. Fernández-Caliani^{a,c,d,*}

^a Department of Geology, Faculty of Experimental Sciences, University of Huelva, Spain

^b Department of Chemistry, Faculty of Experimental Sciences, University of Huelva, Spain

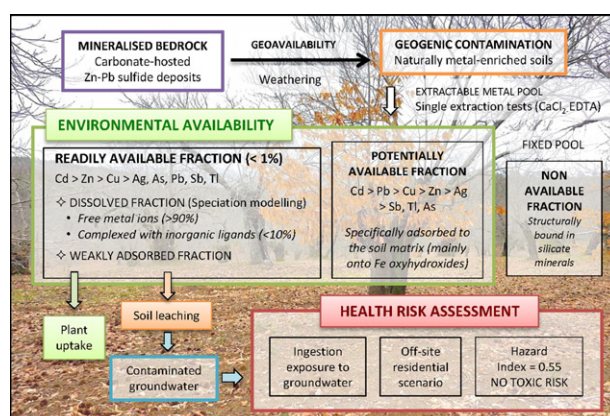
^c International Campus of Excellence for Environment, Biodiversity and Global Change (CeiCambio), Spain

^d Centre for Research in Sustainable Chemistry (CIQSO), Spain

HIGHLIGHTS

- Naturally occurring heavy metals in a Mediterranean forest soil was investigated.
- Environmental availability of trace metals was assessed by single extraction tests.
- Factors controlling metal availability, speciation and leaching were discussed.
- Groundwater ingestion is the most likely exposure scenario for potential health risk.

GRAPHICAL ABSTRACT



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ABSTRACT

Soil developed on mineralised bedrock areas of the Sierra de Aracena Natural Park (SW Spain) is geochemically characterised by naturally high levels of heavy metals and metalloids (notably Zn, Pb, Ag and Cd, but also As, Sb, Cu and Tl). To assess environmental availability, geochemical speciation and potential health risk of such geogenic trace elements, 24 randomly selected soil samples were subjected to one-step extraction procedures (0.01 M CaCl₂ and 0.05 M EDTA), aqueous speciation modelling, and site-specific risk analysis. Metal fraction available for plant uptake or leaching to groundwater was found to be negligible (<1%) due to the low activity of dissolved and exchangeable ions in soil solution, as predicted from the CaCl₂ extracts. Based on modelling calculations, free metal ions, primarily Cd²⁺ and Zn²⁺, were the dominant species in solution over the soil pH range of 5.8 to 7.8. For most metals, the EDTA-extractable fraction generally accounted for <5% suggesting that a limited reservoir of trace elements, mainly bound to Fe oxy-hydroxides, could be potentially available. The results of the health risk assessment for ingestion exposure to groundwater affected by soil leaching revealed that the hazard quotients of heavy metals are within the acceptable risk level. The cumulative hazard index (HI =

Abbreviations: ADD, average daily dose; ASTM, American Society for Testing and Materials; CEC, cation exchange capacity; CHEAQS, Chemical Equilibria in Aquatic Systems; DTPA, diethylene-triamine-pentaacetic acid; EC, electrical conductivity; EDS, energy dispersive x-ray spectroscopy; EDTA, ethylene-diamine-tetraacetic acid; FAAS, flame atomic absorption spectrometry; HI, hazard index; HQ, hazard quotient; ICP, inductively coupled plasma; ICP-MS, inductively coupled plasma-mass spectrometry; ISO, International Organization for Standardization; LOI, loss on ignition; PCA, principal component analysis; RBCA, risk-based corrective action; RSD, relative standard deviation; SEM, scanning electron microscopy; TC, total carbon; TIC, total inorganic carbon; TOC, total organic carbon; USEPA, United States Environmental Protection Agency; XRD, X-ray diffraction; XRFs, X-ray fluorescence spectrometry.

* Corresponding author at: Dept. Geología, Facultad de Ciencias Experimentales, Campus de El Carmen, Universidad de Huelva, 21071 Huelva, Spain.

E-mail address: caliani@uhu.es (J.C. Fernández-Caliani).

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0.55) fell below the regulatory threshold value of 1.0, even in the worst-case scenario being evaluated, leading to the conclusion that no toxic effects are expected to humans under the conditions and assumptions of the assessment.

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1. Introduction

Soil pollution with anthropogenic trace metals and metalloids has been the focus of increasing research in the last few decades due to their potentially toxic effects on the environment and human health (e.g. Jung and Thornton, 1996; Bech et al., 1997; Cabrera et al., 1999; Loska et al., 2004; Sharma et al., 2007; Fernández-Caliani, 2012; Morgan, 2013; Li et al., 2014). By contrast, soils that contain elevated levels of trace elements derived from geological sources have received scant attention, even though they provide some fascinating topics to study.

Although naturally occurring or geogenic heavy metals are normally present in soil at levels that are regarded as trace ($<1000 \text{ mg kg}^{-1}$), relatively immobile and rarely toxic (Adriano, 2001), they may pose a potential risk to the environment, as reported in some geogenically contaminated regions of Europe and the USA (Rapant et al., 2008). However, while anthropogenically polluted soils are subject to data collection and evaluation, exposure and toxicity assessment, and risk characterisation (Adamo et al., 1996), the environmental and health risks of naturally heavily contaminated soils are seldom considered (Lottermoser, 2002).

It is generally agreed that total metal concentration alone is a poor indicator of environmental risk arising from soil contamination (Cui and Du, 2011), because it does not provide predictive insights on mobility, bioavailability, and fate of the contaminants (Houba et al., 1996; Gupta et al., 1996; D'Amore et al., 2005; Degryse et al., 2009). Knowledge of metal partitioning and speciation is, therefore, of particular interest to determine geochemically reactive pools as a better indication of potential risk of toxic metal(loid)s entering the biosphere and the possible negative effects on groundwater quality (Rao et al., 2008; Rodrigues et al., 2010a).

Environmental availability is determined by an available amount of the total content in soil, including both the actual and potential fractions of metals which can be dissolved from the soil matrix in the pore water (Kim et al., 2015). The application of single chemical extraction procedures to polluted or naturally contaminated soils is the more usual approach to predicting the mobility and availability of trace elements in relation to plant uptake (phytoavailability) and their migration in a soil profile, which is often linked with groundwater contamination issues (Rauret, 1998; Sahuquillo et al., 2003; Rao et al., 2008).

The principal extraction reagents used to measure actually available metal contents are the weak neutral salt solutions of CaCl_2 , NaNO_3 and NH_4NO_3 , which provide the best relationship between soil extractable trace metal and plant tissue accumulation. The mobile fraction assessed by these unbuffered mild extractants is considered to simulate the proportion of the total soil metal pool that may be available for plant uptake, and play a key role in many transfer pathways (Degryse et al., 2003; Menzies et al., 2007; Madejón et al., 2011).

A significant number of studies (e.g. Novozamsky et al., 1993; Houba et al., 1996; Sahuquillo et al., 2003; Pueyo et al., 2004; Meers et al., 2007; Ettler et al., 2007; Ruiz et al., 2009; Rodrigues et al., 2010b; Kim et al., 2015) have proposed a 0.01 M CaCl_2 solution as the most suitable extractant for speciation modelling and analytical determinations using ICP techniques. The reason is that its ionic strength matches that of the soil solution, the low salt concentration reduces the analytical interferences, and the reagent does not modify soil pH during extraction. The release of metals electrostatically weakly bound onto soil particles is promoted by ion exchange with Ca^{2+} ions.

The potentially available metal fraction is usually assessed after a single extraction by chelating agents, such as the widely used EDTA

and DTPA extractants (e.g. Lindsay and Norvell, 1978; Quevauvillier et al., 1998; Sun et al., 2001; Sahuquillo et al., 2003). These complexing agents dissolve not only the exchangeable metal fraction but, critically, also the element fraction forming organic matter complexes, the element fraction fixed on Fe and Mn oxy-hydroxides, and elements bound to carbonates (Ure, 1996; Rauret, 1998). The fraction extractable by 0.05 M EDTA is composed of those ions present in the soil solution that are potentially able to move into the plant root system (Sahuquillo et al., 1999; Madejón et al., 2009), and reflects the metal availability in both the short-term and relatively long-term (Ure, 1996).

The soils of the Sierra de Aracena Natural Park (Andalusia, Spain) are a striking example of pedochemical enrichment with geologically-sourced and potentially harmful trace elements (Ag, As, Cd, Cu, Pb, Sb, Tl, and Zn), which become a hot spot of environmental concern. A recent study by Rivera et al. (2015) has provided strong evidence that such metal(loid)s were released by weathering from carbonate-hosted sulphide deposits and accumulated in the surface soil layer, thus reaching extremely large concentrations that are well beyond the normal ranges given in the literature for unpolluted soils (Alloway, 2013). The area offers an exciting opportunity for conducting an environmental risk assessment of naturally heavily contaminated soils in a Mediterranean forest ecosystem, based on the available pools of environmentally sensitive trace elements.

The goals of this paper were threefold: 1) to quantify the actually available (mobile) and potentially available (mobilisable) fractions of metals and metalloids in naturally occurring soil; 2) to understand the factors controlling their mobility, (bio)availability, and leachability to the groundwater; and 3) to assess whether geogenic trace elements pose a potential risk to public health for ingestion exposure to groundwater contaminated by soil leaching.

2. Site description and soil sampling

The area of interest lies within the Sierra de Aracena Natural Park, in the south-west corner of Spain (Fig. 1). It is geologically located in the low to medium-grade zone of the Aracena Metamorphic Belt (Díaz-Azpiroz et al., 2004, and references therein), a tectono-metamorphic terrain that outlines the boundary between the geotectonic zones (Ossa-Morena Zone and South-Portuguese Zone) of the southern branch of the Iberian Variscides.

The study area (about 20 km^2) is situated at an elevation between 750 and 950 m a.s.l., and has a sub-humid Mediterranean climate characterised by high rainfall (mean annual precipitation is over 1000 mm) that provides favourable weather conditions for growing chestnut trees (*Castanea sativa* Mill.). Eutric Cambisol is the dominant soil type with minor occurrences of Chromic Luvisol (Junta de Andalucía, 2005).

The soil derived from metavolcanic and metacarbonate rocks enclosed in a volcano-sedimentary sequence that overlies a carbonate horizon of Lower Cambrian age. The soil parent materials are regarded as an important metallotect for sedimentary exhalative Zn-Pb-(Ag) deposits, with sphalerite, galena and pyrite being the dominant ore minerals (Fernández-Caliani et al., 1989; Arribas et al., 1990). The carbonate-hosted sulphide mineralisations were subjected to intensive supergene alteration leading to the formation of gossans and karst-fill deposits in places. The carbonate bedrock is highly fractured and constitutes a complex karst hydrogeologic environment, which is a vital strategic groundwater resource for the region.

Surface soil samples (0–20 cm depth) were collected at 24 locations of the survey area (Fig. 1) following a stratified random sampling

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