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Arsenic distribution in a pasture area impacted by past mining activities

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ABSTRACT

Former mine exploitations entail a serious threat to surrounding ecosystems as after closure of mining activities their unmanaged wastes can be a continuous source of toxic trace elements. Quite often these mine sites are found within agricultural farming areas, involving serious hazards as regards product (feed/food) quality. In this work a grazing land impacted by the abandoned mine exploitation of an arsenical deposit was studied so as to evaluate the fate of arsenic (As) and other trace elements and the potential risks involved. With this aim, profile soil samples (0–50 cm) and pasture plant species (*Agrostis truncatula, Holcus annus* and *Leontodon longirostris*) were collected at different distances (0–100 m) from the mine waste dump and analyzed for their trace element content and distribution. Likewise, plant trace element accumulation from impacted grazing soils and plant trace element translocation were assessed. The exposure of livestock grazing animals to As was also evaluated, establishing its acceptability regarding food safety and animal health. International soil guideline values for As in grazing land soils (50 mg kg^{-1}) resulted greatly exceeded (up to about 20-fold) in the studied mining-affected soils. Moreover, As showed a high mobilization potential under circumstances such as phosphate application or establishment of reducing conditions. Arsenic exhibited relatively high translocation factor (TF) values (up to 0.32–0.89) in pasture plant species, reaching unsafe concentrations in their above-ground tissues (up to 32.9, 16.9 and 9.0 mg kg^{-1} in *Agrostis truncatula, Leontodon longirostris* and *Holcus annus*, respectively). Such concentrations represent an elevated risk of As transfer to the high trophic-chain levels as established by international legislation. The limited fraction of arsenite found in plant roots should play an important role in the relatively high As root-to-shoot translocation shown by these plant species. Both soil ingestion and pasture intake resulted important entrance pathways of As into livestock animals, showing quite close contribution levels. The cow acceptable daily intake (ADI) of As regarding food safety was surpassed in some locations of the study area when the species *Agrostis truncatula* was considered as the only pasture feed. Restrictions in the grazing use of lands with considerable As contents where this plant was the predominant pasture species should be established in order to preserve food quality. Therefore, the exposure of livestock animals to As via both soil ingestion and pasture consumption should be taken into account to establish the suitability of mining-impacted areas for gazing.

1. Introduction

Arsenic (As) occurs naturally in all the environmental compartments (Mandal and Suzuki, 2002). Typical As concentrations in non-contaminated soils range between 1 and 40 mg kg^{-1}, depending on the parent material (Kabata-Pendias and Pendias, 1992), but rarely exceed 10 mg kg^{-1} (Adriano, 1986). However, such restricted levels can be importantly increased in areas impacted by certain human activities. Primary anthropogenic As sources are mining activities, agricultural practices, such as the use of As-contaminated irrigation water, As-containing pesticides and herbicides, phosphate fertilizers, sewage sludge and manure, and industrial processes, including manufacture of glass/ceramics, alloys, electronics and pigments, combustion of fossil fuels for energy production and smelting (Alloway, 1995; Kabata-Pendias and Mukherjee, 2007).

Arsenic is present as a major constituent in over 200 minerals

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(Adriano, 1986), with arsenopyrite (FeAsS) being the most common one (Alloway, 1995). It is found in a wide variety of mineral deposits, in close association with many elements such as copper (Cu), lead (Pb), zinc (Zn), silver (Ag), gold (Au), tungsten (W), tin (Sn), nickel (Ni) and cobalt (Co) (Alloway, 1995; Smedley and Kinniburgh, 2002). Mining and beneficiation of these resources have generated large amounts of As-rich mine wastes, especially at historic mine sites. The transport by either wind or water of these wastes and the unconstrained leaching from them constitute a significant source of As pollution in the surrounding area. Thus, mining areas affected by long-term off-site release of As represent a serious concern for the environment and human health, particularly when used for grazing or agriculture. This situation is quite common as many former mine exploitations are located in areas where their main economic activities are livestock farming and agriculture.

Arsenic is toxic to both plants and animals, with mammals being those most seriously affected. Arsenic toxicity depends on its chemical forms. Usually, inorganic species are more toxic than organic ones (Sharma and Sohn, 2009). Both As(III) and As(V) may cause similar toxicological effects, but the former is regarded as more toxic (Kabata-Pendias and Mukherjee, 2007). Chronic exposure to inorganic As can lead humans to develop a variety of adverse health effects. Thus, its intake via food and/or water can cause skin changes or lesions such as hyperpigmentation, keratosis and ulceration, respiratory system problems, cardiovascular disease, nervous system alterations, hematological and immunological disorders, reproductive complications and cancer of different organs, namely, skin, lung and bladder, whereas its inhalation mainly impacts the respiratory and reproductive systems and the skin, including lung and skin cancer development as the primary adverse effect (Mandal and Suzuki, 2002; Basu et al., 2014).

Ingestion of contaminated food and water is the main route of As intake into the organism (Kabata-Pendias and Mukherjee, 2007; Tarvainen et al., 2013; Sharma et al., 2014). The As content of many foods such as milk, beef, pork, poultry and cereals is mainly inorganic, typically reaching values of 65–75% of the total As content (Mandal and Suzuki, 2002). The relative content of inorganic As in vegetables has been shown to be much more variable, but levels close to 100% have been also reported (Mandal and Suzuki, 2002; Smith et al., 2006). In any case, pasture and agricultural lands impacted by former mine exploitations of arsenical deposits entail an important risk of inorganic As incorporation in the trophic chain. Many studies have been devoted to evaluate the As content and distribution in food-cultivated areas affected by past mining activities (e.g., Castro-Larragoitia et al., 1997; Liu et al., 2005, 2010; Williams et al., 2009; Álvarez-Ayuso et al., 2012; Li et al., 2010, 2014; Xue et al., 2017), revealing in numerous instances As accumulation in crops at levels that fail prescribed food standards. Nevertheless, studies on mine-impacted grazing lands are much more restricted (Li and Thornton, 1993; Abrahams and Thornton, 1994; Bruce et al., 2003; Tighe et al., 2005, 2013). Some of these studies have included trial experiments with animals to assess their exposure to As. Recently, the use of soil-plant-animal transfer models in mining areas has been suggested as an useful tool to establish the exposure risks of grazing animals, and finally humans, to toxic elements (Moreno-Jiménez et al., 2011; Rodrigues et al., 2012; Martínez-López et al., 2014; Simmler et al., 2016). Both soil ingestion and herbage intake are considered the possible entrance pathways of toxic elements into livestock grazing on lands affected by mining activities. In general, the ingestion of soil has been found the dominant via for the intake of As (Abrahams and Thornton, 1994; Bruce et al., 2003; Simmler et al., 2016), although levels around the half of the element intake has been also attributed to the consumption of grass (Rodrigues et al., 2012). This variability is highly dependent on the plant species, particularly on their specific characteristics of As uptake, transport and accumulation. Although usually plants that colonize As-polluted soils show an excluder behavior (Wang et al., 2002), the presence of plants able to accumulate intermediate As levels in their aerial parts is not so uncommon (Rodrigues et al., 2012; Martínez-López et al., 2014). Furthermore, the soil physicochemical characteristics also play an important role on the soil-plant transfer of As, with pH, redox potential, phosphate content and iron and aluminum oxide content being highly influential (Adriano, 1986; Moreno-Jiménez et al., 2012). Thus, under oxic conditions the mobility of As is fairly low in acid soils with high metal oxide content (McBride, 1994), although it could be greatly increased by the presence of phosphate as this anion competes very effectively with arsenate for soil adsorption sites (Manning and Goldberg, 1996). Nevertheless, both also compete for their uptake by plant roots via phosphate transporters for which phosphate shows a higher affinity than arsenate (Tripathi et al., 2007; Zhao et al., 2009). Therefore, numerous factors can affect the soil-plant-animal transfer of As. The environmental characterization of As-polluted areas and the identification of the main factors responsible for the exposition of animals and/or humans to this toxic element are crucial to establish the suitable management options for this kind of scenarios in order to preserve product (feed/food) quality and protect public health.

The main goals of this work were to 1) perform the soil environmental characterization of a pasture area affected by the former mine exploitation of an arsenical tungsten deposit, 2) assess the accumulation of As and other trace elements by pasture plant species of this area, 3) determine their suitability for feeding grazing animals according to international legislation, and 4) evaluate the exposure of grazing animals to As via both soil ingestion and pasture consumption, establishing its acceptability regarding food safety and animal health.

2. Materials and methods

2.1. Study area

The studied mining area is placed 2 km from the south of Barruecopardo village, in the north-west of the Salamanca province (Spain), where the Barruecopardo mine is situated. During the period 1912–1983, this mine exploited the largest tungsten deposit in Spain. This exploitation took place in two phases, in which two open pits of dimensions 800 m long × 12 m wide × 20 m deep and 500 m long × 40 m wide × 90 m deep were excavated, respectively (Fig. 1). The exploited deposit is a hydrothermal vein/stockwork hosted in granitic rocks. Veins are filled with quartz and an ore mineral assemblage of scheelite ($CaWO_4$), the predominant tungsten-bearing mineral, wolframite ($(Fe,Mn)WO_4$), pyrite (FeS_2) and abundant arsenopyrite (FeAsS). Chalcopyrite ($CuFeS_2$), molybdenite (MoS_2) and cassiterite (SnO_2) also occur locally (Arribas, 1979; Sanderson, 2008). Mining activities generated large amounts of wastes mainly composed of barren rocks, sulfide minerals (mostly arsenopyrite) and their weathering products.

This mine emplacement is situated in an agricultural farming area, mainly devoted to the raising of cattle and sheep and, in a lesser extent, to cereal (rye, barley and wheat) cultivation. The climate of this area is Atlantic-continental, with long and cold winters, and short, warm and dry summers. Average seasonal temperatures vary between 5 and 8 °C in winters and 21 and 24 °C in summers. Most rainfall occurs from early autumn to mid-spring, with an annual precipitation of about 900 mm.

Previous studies have been performed in this mining area seeking for new plant species for phytoremediation (Otones et al., 2011a). Sites affected by mining activities carried out throughout the second phase of mine exploitation and not used specifically as grazing lands were employed in such studies. *Agrostis castellana* (Boiss. & Reut.) and *Scirpus holoschoenus* L. were identified as suitable species to be used in As phytostabilisation strategies.

2.2. Sampling

Soil and plant sampling was carried out in a grazing land located near a dump where mine wastes were accumulated during the first