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Spread and partitioning of arsenic in soils from a mine waste site in Madrid province (Spain)

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HIGHLIGHTS

- A scorodite-rich mining waste at an old smelting factory in Madrid is described.
- Scorodite-rich mining wastes act as an acute point source of As pollution in soils.
- Arsenic extraction and XANES analyses show ferrihydrite as an As scavenger in soils.

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ABSTRACT

The formation of scorodite is an important mechanism for the natural attenuation of arsenic in a wide range of environments. It is dumped on site by metallurgical industries to minimize arsenic release. However, the long-term stability of these deposits is unclear. Sequential As extractions and synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy were used to determine both As and Fe speciation in a small catchment area affected by a scorodite-rich waste pile at an abandoned smelting factory. Our results indicate that this deposit behaves as an acute point source of As and metal pollution and confirms the strong association of As(V) with Fe(III) oxide phases, highlighting the important role of ferrihydrite as an As scavenger in natural systems. In this seasonally variable system, other trapping forms such as jarosite-like minerals also play a role in the attenuation of As. Overall, our results demonstrate that scorodite should not be considered an environmental stable repository for As attenuation when dumped outside because natural rainfall and the resulting runoff drive As dispersion in the environment and indicate the need to monitor and reclamate As-rich mine deposits.

1. Introduction

Manufacturing, agricultural and mining activities have the global budget of metal(loid)s at the earth's surface, leading to accumulations that are greater than the natural background and to their spread through leaching and/or runoff, potentially polluting soils and water bodies (Serrano et al., 2009). Currently, mines are typically designed to mitigate their potential environmental impacts, but the extracted mineral deposits of former mines often remain where they were dumped outside after mining activity was stopped (Moreno-Jimenez et al., 2010). Abandoned mine wastes that contain high sulfide concentrations are of particular concern because of the formation of acid mine drainage (AMD), thus becoming an active and harmful point source of As and other metals to the environment. Additionally, the negative impacts of AMD may persist over time in association with the by-products from the exploitation of polymetallic sulfide deposits, such as waste piles and residues from smelting processes.

Scorodite, ferric arsenate and arsenical ferrihydrite are forms of natural arsenic attenuation that occur in a range of environments and are common precipitates used by metallurgical industries to minimize As release into the environment (Paktunc et al., 2008). The low solubility of scorodite limits the dissolution of As in acid mine-drainage at many mine sites, thus the formation of scorodite is a desired arsenopyrite secondary weathering phase (Flemming et al., 2005). However, Robins (1987, 1988) questioned the long-term stability of all ferric arsenate compounds because of the possible carbonation of the Fe contained within them. In general, both adsorption on clay minerals and scorodite mediation slow down the release of As into the environment, but erosion can induce the transport of As minerals, thus accelerating the mobilization and dispersion of As downstream (Craw et al., 2000). Moreover, incongruent scorodite dissolution is promoted by high pH.

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Thus, any source of alkalinity, through the addition of liming materials or even simply circum-neutral rainwater, may cause an increase in the rate of As release from scorodite to the soil solution.

Helmhart et al. (2012) studied in the same area, the effect of preferential flow on the spatial distribution and chemical speciation of As, Cu and Zn at a pedon-scale. They found that As was leaching into the subsoil from the surface of a small, dry riverbed that seasonally collects acidic surface runoff from a waste pile mainly composed of scorodite [$FeAsO_4 \cdot 2H_2O$]. The authors described the accumulation of As bound to masses of ferrihydrite within macropores in the subsoil underneath the riverbed. Additionally, Cu and Zn were also detected at high concentrations within the subsoil. High concentrations of metal(loid)s within the downstream soils would indicate their continuous remobilization from the waste pile and the potential for their entry into the water system. Further research is required to determine whether natural, intermittent rainfall effectively induces the spread of metal(loid) contamination and to elucidate the mechanisms by which metals are retained within soils. Knowledge of the mechanisms that control the release, mobility, and natural attenuation of contaminants is crucial to minimize the risks and consequences associated with mine wastes (Johnson and Hallberg, 2005; Cheng et al., 2009).

In this paper, we examine the spread of As, Cu and Pb, as well as the speciation of As, both at depth and along a small riverbed that collects surface runoff. The source of metal(loid) contamination is a waste pile, rich in scorodite, located at an abandoned mine in Madrid province (Spain). The occurrence of As along the creek system and its transformation to As–Fe oxyhydroxide compounds are presented.

2. Materials and methods

2.1. Experimental site, sample collection and analyses

The experiment was conducted in a shrubland situated in the upper portion of a small sub-catchment of the Guadalix River (Madrid, Spain), which feeds into the Madrid Tertiary Detrital Aquifer. Arsenopyrite [FeAsS] and scorodite [$FeAsO_4 \cdot 2H_2O$] are found in association with the sulfide-bearing pegmatite outcrops in this area (Recio-Vazquez et al., 2011). The site includes an abandoned smelting factory at which arsenopyrite that was encapsulated in quartz was processed for the extraction of wolfram during the Second World War. The mining wastes, which contain up to 19 g kg^{-1} of As and currently remain where they were dumped on the soil surface (Recio-Vazquez et al., 2011; Helmhart et al., 2012), are subject to erosion and weathering processes (Fig. 1).

Undisturbed soil cores (5 cm in diameter) were collected from the following experimental sampling locations: the arsenic-bearing waste pile (WP) [A site], along the riverbed (RB) of a small stream (~1 m wide) that seasonally collects surface runoff from the WP [B and C sites], the sediment that accumulates downstream in an artificial pond (SP) [D site], and a soil sample from a flat area of land on an adjacent farm that receives the excess runoff that overflows the pond during intense rain events [E site] (Fig. 1). These soil cores served to assess the depth of contamination and the gradient with distance from the point source of metal pollution (WP). Cores were collected to a depth of 60 cm at the waste pile and riverbed sampling locations [A, B and C cores], while a 30 cm deep core was collected from the pond [D core]. Bulk soil samples were collected at the farm from the 0-to-15 cm depth because of the rock content in the shallow farm soil (at sampling point E). All cores and soil samples were transported to the laboratory and sectioned at 15-cm intervals. Each soil section was air-dried, sieved (2-mm mesh), and homogenized prior to analysis. Previous spectroscopic experiments have revealed the absence of Fe(II) or As(III) in the waste pile as well as in the riverbed and soil layers.

Texture was determined by the pipette method after removing soil organic matter (Gee and Bauder, 1982). Soil pH and electrical conductivity were measured in deionized water (1:5 m/m suspension). Total organic carbon (TOC) was determined by wet digestion (Walkley and Black, 1934). Exchangeable bases (Ca, Mg, Na and K) were extracted with 1 M NH_4OAc (at pH 7) (Thomas, 1982), and exchangeable Al was extracted with 1 M KCl (Barnhisel and Bertsch, 1982). The Ca, Mg, Na, K, and Al concentrations in the extracted solutions were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) on a Perkin-Elmer OPTIMA 4300DV. All the chemicals used for

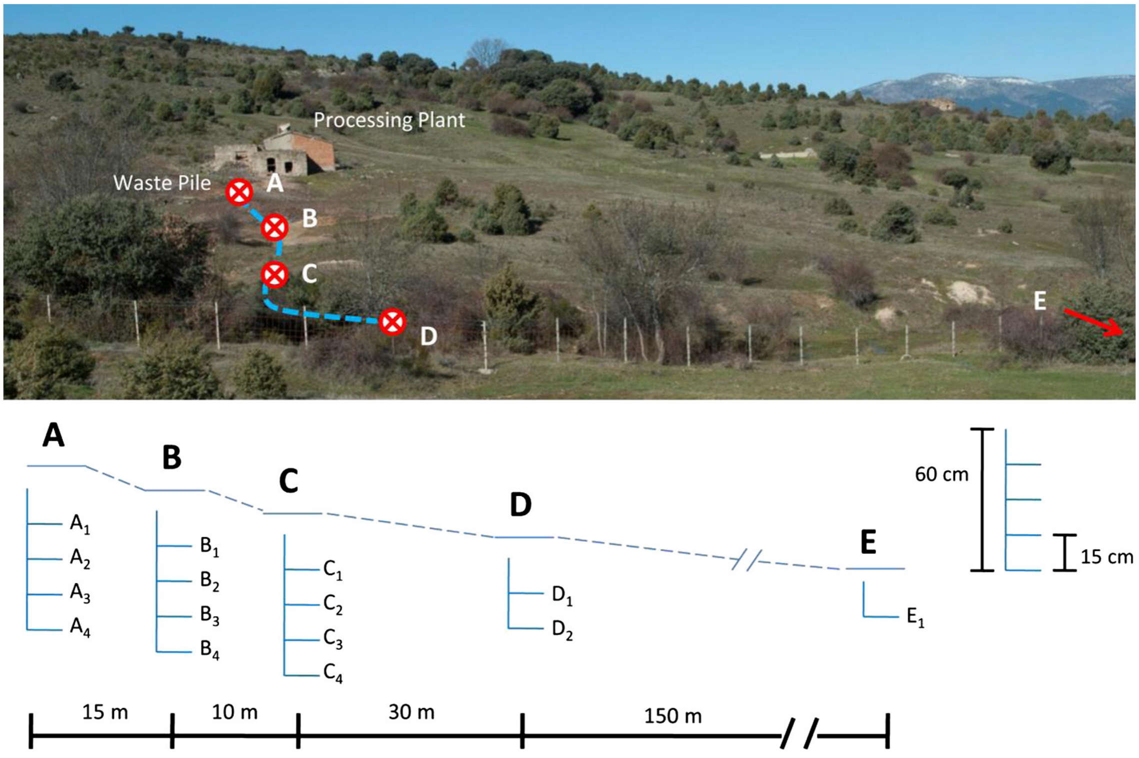

Fig. 1. Location of the study area and the relative positions of the sampling locations.