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Colloidal mobilization of arsenic from mining-affected soils by surface runoff

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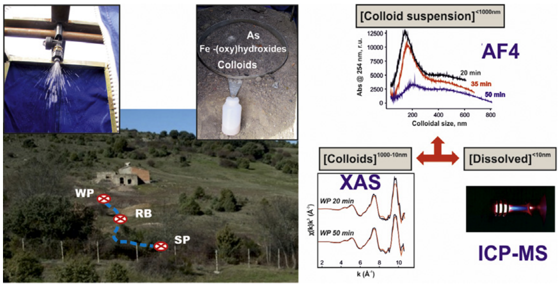
HIGHLIGHTS

- A rainfall simulation study on mine wastes was performed to evaluate As release.
- As is being mobilized as colloidal scorodite for 50 min of simulated rainfall.
- Nanometric colloidal ferrihydrite acts as As(V)-carrier phase downstream.
- Scorodite-rich wastes are releasing As by weathering and erosion processes.

GRAPHICAL ABSTRACT



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ABSTRACT

Scorodite-rich wastes left as a legacy of mining and smelting operations pose a threat to environmental health. Colloids formed by the weathering of processing wastes may control the release of arsenic (As) into surface waters. At a former mine site in Madrid (Spain), we investigated the mobilization of colloidal As by surface runoff from weathered processing wastes and from sediments in the bed of a draining creek and a downstream sedimentation-pond. Colloids mobilized by surface runoff during simulated rain events were characterized for their composition, structure and mode of As uptake using asymmetric flow field-flow fractionation coupled to inductively plasma mass spectrometry (AF4-ICP-MS) and X-ray absorption spectroscopy (XAS) at the As and Fe K-edges. Colloidal scorodite mobilized in surface runoff from the waste pile is acting as a mobile As carrier. In surface runoff from the river bed and the sedimentation pond, ferrihydrite was identified as the dominant As-bearing colloidal phase. The results from this study suggest that mobilization of As-bearing colloids by surface runoff may play an important role in the dispersion of As from metallurgical wastes deposited above ground and needs to be considered in risk assessment.

1. Introduction

Mining and smelting operations have changed the global distribution and occurrence of metal(loid)s at the Earth's surface (Rauch, 2012), and the release of metals and metalloids from mining and

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processing wastes into aquatic and terrestrial environments may threaten environmental and human health. Human activities have led to substantial As contamination in the environment (Morin and Calas, 2006), as often occurs in association with economically relevant metal ores. Accordingly, the roasting and smelting of metal ores has led to widespread environmental contamination via atmospheric emissions and deposition of waste materials (Vaughan, 2006). In Spain, there are many As-affected legacy sites affected from former mining activities. Often, As-bearing processing wastes had been dumped above ground and remain exposed to rainfall and weathering, posing a risk for adjacent water bodies (Garcia-Sanchez and Alvarez-Ayuso, 2003).

The weathering of processing sulfide-containing wastes leads to the formation of acid mine drainage (AMD). The oxidation of Fe(II) and precipitation of Fe(III) in neutralized AMD may lead to the formation of mobile colloidal carriers for As (Cheng et al., 2009). Due to their physicochemical properties, colloids may persist in aqueous suspensions over extended periods of time and act as carriers for poorly soluble metals and metalloids in surface and surbsurface environments (Kretzschmar and Sticher, 1997). The affinity of As to colloidal Fe(III) and the importance of such colloidal particles as As-mobilizing carriers in the environment has been documented (Fritzsche et al., 2011). For instance, Grosbois et al. (2011) identified different As-carriers during the transport of solid particulate matter in varying abundances according to the hydrological cycle of a river draining a former gold mine district in France. Furthermore, colloids and colloid-associated contaminants, mobilized by rainfall within ephemeral overland courses, can be transported rapidly through the vadose zone with minimal interaction with the soil matrix (Ranville et al., 2005). This can be attributed to the presence of preferential flow paths, which in turn may play a role in the solid-phase As distribution and As retention mechanism in soils, especially in locations affected by large amounts of metals released with AMD (Helmhart et al., 2012). Overall, the importance of surface runoff as compared to infiltration for As dispersion may vary with rainfall intensity and duration, vegetation cover, soil topography, as well as soil physical properties and flow conditions through soils and riverbeds. Irrespective of the mode of colloid transport, the nature and stability of As-bearing colloids in tailings and mining wastes that control the extent of As release needs to be assessed.

The combined use of spectroscopic, spectrometric and fractionation techniques offers the means to gain information on the size-dependent elemental composition of colloids, the nature of the colloidal carrier phase, and the speciation of associated contaminants. Rainfall simulation experiments on the other hand, allow to control rainfall parameters (intensity and duration) and to exclude the inherent variability associated with natural rain that increases the complexity of stormwater quality research (Bian et al., 2011). Simulated rainfall has been used to assess heavy metal contamination in urban areas (Wicke et al., 2012), but only few studies have been performed on contaminated soils under natural conditions (Fernandez-Galvez et al., 2008). To date, however, the colloid-facilitated release of As with surface runoff in mining-affected areas has not been assessed.

Asymmetric flow field-flow fractionation (AF4) is a separation technique for the characterization of colloids from natural samples (Laborda et al., 2011). When coupled to an inductively coupled plasma mass spectrometer (ICP-MS), the size-dependent elemental composition of the colloidal phases can be determined. For instance, Neubauer et al. (2013) characterized the colloid distribution in soil runoff as generated by storm events using AF4-ICP-MS. The authors showed that a colloidal fraction ranging from 0.2 to 0.45 μm was mobilized but they did not assess the speciation of the colloidal As. Direct insight into the speciation of colloidal As and Fe can be gained using X-ray absorption spectroscopy (XAS), widely used to study the speciation of As and Fe in natural samples (O'Day et al., 2004; Voegelin et al., 2007), including dispersible soil colloids (Regelink et al., 2014; Serrano et al., 2015).

In previous studies, we examined the dispersion and solid phase partitioning of As in soils and sediments affected by weathering and erosion of metallurgical processing wastes at a former mining and smelting site in Madrid province (Gomez-Gonzalez et al., 2014). In the same area, the molecular-scale speciation of As associated to colloids detached from soil extracts has previously been studied (Serrano et al., 2015). In this continuing work, we aimed at determining the extent and mode of colloidal As mobilization with surface runoff during simulated rain events. AF4-ICP-MS was used to determine the colloid size distribution and As partitioning between the dissolved and colloidal phase, and Fe and As K-edge XAS to determine the colloidal carrier phase and colloidal As speciation.

2. Materials and methods

2.1. Site description

The experiment was conducted in a sub-catchment of the Guadalix River (Madrid, Spain) at the foot of the 'Sistema Central' mountain range (40°45′34.33″ N – 3°41′07.13″ O, 929 m altitude). In the area, metal sulfides and wolframite ores in association with quartz veins were mined for tungsten extraction during the Second World War. The abandoned smelting factory along with mining wastes deposited above ground still remain at this site (Helmhart et al., 2012). The massive pile of processing wastes (approximately 6 × 6 m, 1 m-thick, 19 g As kg^{-1}), is subjected to weathering and erosion (Gomez-Gonzalez et al., 2014). The site is representative for many other legacy sites in Madrid province and other regions of Spain.

The average annual rainfall in the area reaches 705 mm and the average temperature, 13.3 °C (Spanish Agency of Meteorology, AEMET). About 188–201 mm of the annual rain precipitate in winter, 197–213 mm in spring, 85–93 mm in summer and 200–233 in autumn. Rainfall simulation tests were performed at: A) the arsenic-bearing waste pile (WP); B) the river bed (RB) of a small stream (~1 m wide) that seasonally collects surface runoff from WP; and C) the sediment that accumulates downstream in an artificial sedimentation pond (SP) (Fig. S1). During intense rainfall, a major part of runoff waters is usually retained in the sedimentation pond remaining stagnant over several days until evaporation and infiltration lead to the drying out of the pond.

Physical, chemical, and mineralogical properties of the topmost layer of soils and sediments at the experimental locations are in Table 1.

2.2. Rainfall simulation experiments

Simulation experiments were performed using the portable rainfall simulator designed by Calvo et al. (1988) and modified by Cerda et al. (1997). Single rainfall events of distilled water were applied at 28 mm h^{-1} during 60 min in each experimental location. The basic components of the simulator and the experimental conditions are described in the Supplementary Material (Figures S2 and S3).

2.3. Isolation of the colloid-suspensions in runoff

Three fractions of the runoff suspensions from the rainfall simulations were analyzed: (i) the colloid-containing suspension (CS, ≤1000 nm) obtained after centrifugation of the runoff suspension for the removal of particulate material, (ii) the solid colloids (1000–10 nm) isolated from the colloid-containing suspen-