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Long-term ongoing impact of arsenic contamination on the environmental compartments of a former mining-metallurgy area

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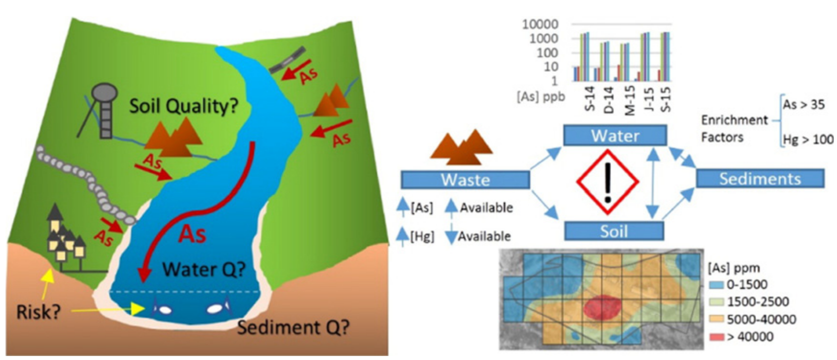
HIGHLIGHTS

- 40-years abandoned As- and Hg-rich waste promoted soil pollution.
- As showed greater mobility and dispersion than Hg.
- Waste stock-piled and highly polluted soil affected water and groundwater quality.
- River sediments were severely enriched in As and Hg.

GRAPHICAL ABSTRACT



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ABSTRACT

Arsenic and mercury are potentially toxic elements of concern for soil, surficial and ground waters, and sediments. In this work various geochemical and hydrogeological tools were used to study a paradigmatic case of the combined effects of the abandonment of Hg- and As-rich waste on these environmental compartments. Continuous weathering of over 40 years has promoted As and Hg soil pollution (thousands of ppm) in the surroundings of a former Hg mining-metallurgy site and affected the water quality of a nearby river and shallow groundwater. In particular, the high availability of As both in soils and waste was identified as one of the main determinants of contaminant distribution, whereas the impact of Hg was found to be minor, which is explained by lower mobility. Furthermore, potential additional sources of pollution (coal mining, high natural backgrounds, etc.) discharging into the study river were revealed less significant than the contaminants generated in the Hg-mining area. The transport and deposition of pollutants within the water cycle has also affected several kilometres downstream of the release areas and the chemistry of stream sediments. Overall, the environmental compartments studies held considerable concentrations of Hg and As, as remarkably revealed by the average contaminant load released in the river (several tons of As per year) and the accumulation of toxic elements in sediments (enrichment factors of As and Hg above 35).

1. Introduction

Mining and industrial activities commonly promote waste accumulation and contaminant leaching. These processes have proved

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especially significant after the closure of heavy industries in the last decades of the 20th century. In this regard, various studies have addressed the effects of the uncontrolled disposal and abandonment of toxic waste exposed to weathering and erosion on soil, sediments and (ground)water (Hudson-Edwards et al., 1997; Lefebvre et al., 2001; Foulds et al., 2014). Contaminants with high toxicity and complex geochemical behaviour, such as Potentially Toxic Elements (PTEs), particularly arsenic (As), are relevant as they require costly remediation treatments (Bhattacharya et al., 2007; Bundschuh et al., 2013; Smedley and Kinniburgh, 2002). In addition, with respect to underground mining, the excavation of wells and galleries modifies hydrogeological conditions and may generate mine drainage with a high contaminant load that affects other environmental compartments, such as soils and sediments (Moreno-Jiménez et al., 2010; Chakraborti et al., 2013).

Asturias (northern Spain) is a region with a long history of mining and metallurgical activity linked to coal and metals. Consequently, the current landscape holds many brownfields (Gallego et al., 2016), which are affected by both organic contaminants and PTEs such as heavy metals and metalloids. Hg and As pollution in particular has been detected at several sites linked to former Hg mining and metallurgy activity (Loredo et al., 1999, 2006). These sites have been examined in various studies (Sierra et al., 2011; Ordóñez et al., 2011; Sierra et al., 2013; Ordoñez et al., 2014). However, little attention has been paid to the overlapping and concurrent effects caused by this sort of pollution in the environmental compartments; i.e. soil pollution caused by waste disposal, contamination of surficial and ground waters, and effects on the sediments of the rivers crossing the areas affected. The overlapping effects are especially relevant given the complexity of the hydrogeological conditions in former mining areas, the presence of other possible sources of contamination, and the occurrence of naturally high geochemical backgrounds. In addition, knowledge of the mechanisms that regulate the release and mobility of contaminants at this type of site is essential for the design of strategies aimed to minimise environmental risk (Haffert and Craw, 2008; Rieuwerts et al., 2014). In this context, a paradigmatic site in terms of contamination is El Terronal, which has been described in depth in a previous study (Gallego et al., 2015), and it is also of particular environmental concern (even notable atmospheric emissions of Hg have been reported in Loredo et al., 2007). The site is located in an area affected by other sources of pollution and it is also very close to the San Tirso River, where high concentrations of As have been detected (Ordoñez et al., 2014).

The aims of this study were the following; i) to identify and quantify the main pollutants in the area, specifically in the river, over a period longer than a hydrological year; ii) to perform a comprehensive study of the complex relationships between waste disposal, soil, sediments, water run-off and groundwater pollution; iii) to evaluate the mobility and chemical speciation of the main pollutants found; and iv) to differentiate between possible sources of pollutants (underground mining drainage, surface run-off, coal vs. Hg mining, etc.).

2. Study area

The study area (San Tirso River valley) is located around 2 km NE of the town of Mieres, situated in the region of Asturias in northern Spain (Fig. 1a). The climate in the zone is oceanic with mild temperatures (yearly average 12.5 °C). Regular annual precipitation reaches values between 1000 and 1200 mm per year and potential evaporation has been estimated at 600 mm per year, thereby implying an average effective rainfall of approx. 400 mm per year. In addition, heavy rain events are frequent (Méndez Pazos, 2013).

Industrial and mining activities associated with Hg ores have been going on in the valley since Roman times. However, peak production was recorded towards the end of the 19th century, particularly in the 1960s (Dory, 1984; Luque and Gutiérrez-Claverol, 2006). All the exploitations were closed in 1974 because of a crash in the Hg market. In particular, in addition to the mines, the site of El Terronal hosted a high-capacity pyrometallurgical plant, which was operating from the 1950s to 1974 (the main elements are detailed in Fig. 1b; see also Gallego et al., 2015). There is also a ruined duct (chimney) along the western hillside of the San Tirso valley that ends in a final stack (350 ma.s.l.), which once channelled a current of treated gas outside the complex.

Mining activities completely altered the hydrogeology of the area. In brief, a 200-m-deep well was drilled in El Terronal for ore extraction ("Pozo Esperanza", 235.21 ma.s.l.), whereas in the same area the Schultz crosscut (227.42 ma.s.l.) was used to exploit the cinnabar in siliceous breccias. Furthermore, there are a number of secondary drifts on the western side of the San Tirso valley connected to the Schultz crosscut. To the SW of El Terronal, there is an area named La Peña, where the shafts called Peña (202.15 ma.s.l., 150 m deep), Unión (201 ma.s.l., 420 m deep) and La Peña drift (202.07 ma.s.l.) were also used to extract cinnabar. It should also be taken into account that underground coal mining also occurred in the 20th century (some galleries still remain). Evidence of old coal mining works is also found in the study zone, mainly around 2 km NE of El Terronal, where an old gallery is drained through a pipeline, which finally discharges into the San Tirso River.

After >40 years of abandonment, currently El Terronal has only a few derelict buildings and stockpiles of waste—these having been irregularly disposed of (Gallego et al., 2015). Indeed, most of the mining waste was encapsulated in an area now covered by a highway constructed in the 2000s.

Finally, the older mining spoil heaps around La Peña (<2 km SW of El Terronal) are hidden below paved areas. This zone was also exploited for Hg in the 19th century and the first half of the 20th century.

3. Geology, hydrology and sampling locations

The study area is located in the NW limit of the Carboniferous Central basin, one of the main subdivisions of the Cantabrian Zone of the Iberian Massif (Lotze, 1945; Julivert, 1967). The area comprises siliceous breccias, sandstones, lutites and coal (Westphalien age), with an approx. NW-SE direction, in an anticlinal structure and limited to the N and S by the La Peña and La Carrera faults, respectively (Fig. 2). The Hg and As ores are associated mainly with breccias and less importantly with sandstones. Hg ores are formed by cinnabar and secondarily by metacinnabar, although native Hg has also been revealed. As is present mainly in realgar and As-rich pyrites. In the same paragenesis, minerals such as pyrite, melkinovite, sphalerite, guadalcazarite, galena, stibnite, marcasite and, exceptionally, native gold have been also described (Luque and Gutiérrez-Claverol, 2010). The deposits are epigenetic of hydrothermal origin and are strongly controlled by tectonics, as revealed by the presence of the main accumulations wherever two or more preferential fracturing directions are located, thus generating more permeable areas that facilitated the flow of the ore geofluids (Luque, 1985).

Regarding surficial hydrology, covering 7 km^2, the San Tirso River basin can be considered a small drainage basin. The average slope is 21.57° and the total height difference is 476.53 m. The river stretches a total of 4.5 km from the headwaters to the river mouth in the Caudal River, and the average slope of the channel is 9.17°. The characteristics of the rainy regime, including some episodes of heavy rain per year, and the presence of highly erodible materials imply that under certain circumstances this river becomes a torrential channel (Méndez Pazos, 2013). Remarkably, some of the abandoned facilities of the metallurgy industry (the derelict chimney, pipes, etc.) are currently preferential pathways for water runoff flow (Fig. SM1). Therefore, the rainwater passes through the chimney, where it picks up dust and soot; it then flows through the main area of the facilities and finally flows into the San Tirso River (Fig. SM1).

Regarding hydrogeological behaviour, breccias and sandstones are intergranular porosity aquifers, whereas lutites and coal can be considered aquicludes and aquitards respectively. It should be noted that the mining activity severely affected the initial hydrogeological conditions, promoting a notable increase in permeability and modifications of