Water arsenic pollution related to historic mercury mining in Asturias (Spain)

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Abstract

In Asturias, abandoned Hg mines constitute a significant part of the industrial heritage. A great volume of waste materials related to ore extraction and processing operations remains in spoil heaps of different age and size; they represent potential pollution sources. In these abandoned mines, As is usually associated with Hg ore in the form of As-rich minerals. Wastes are exposed to oxidative weathering, and the instability of As-rich minerals leads to the production of acid and As-rich leachates. Polluted waters (mine drainage and spoil heap leachates) reach the surface watercourses and/or are infiltrated through the land. At the mine sites, elevated concentrations of As in surface and groundwater have been detected. Surface water downstream of some spoil heaps reaches up to 7.9 mg l^{-1} of As. Groundwater in supply wells used for irrigation and as drinking supply for animals, shows As contents ranging from 1.2 to 15 $\mu g.l^{-1}$.

Key Words: Arsenic, Water pollution, Mine wastes, Mercury mining, Spain.

1. Introduction

Asturias, in northwestern Spain, is a region with a long mining tradition (coal mining has been the economical motor of the region for centuries). Mercury mining goes back to centuries I and II, but it was in the 19th century when it began to be an important industry in the region. The decade 1962-1972 represented its most active period, with average annual productions of 15,000 flasks of mercury. The falling demand of mercury, as a consequence of emerging toxicological problems during its use and production, gave rise to the decline of prices from about U.S.$600 per flask in 1965 to U.S.$120 per flask in 1975 (Ferrara 1999). This factor resulted in a general crisis in the sector, leading to the total interruption of the extractive activity in many areas that up until then had been important Hg mining districts in the world. In Asturias, this crisis initiated the abandonment, between 1973 and 1974, of all active mines.

The most important abandoned Hg mines are located in the districts of Mieres and Pola de Lena, at distances of less than 30 km from Oviedo, the capital. The potential of these mine sites to pollute the environment is enhanced by the presence of As-rich minerals in the mined ore. During the period of Hg production, the environmental controls on mining and metallurgical operations were limited, in accordance with the absence of environmental legislation. This absence of environmental control continued after the abandonment of the extractive activities. The magnitude of the impacts is considerable at some sites, and environmental problems related to these abandoned mine sites have been the subject of much research (Loredo 2000; Loredo et al. 1999; Loredo et al. 2002).

2. Historical Hg mining and characteristics of the sites

2.1. Mining heritage

Mercury mining in the area dates back to antiquity (vestiges of tools and objects attributed to the Roman occupation have been found in some old mining works). However, the largest mine workings and mine waste piles are a consequence of extractive activities in the sixties and seventies, in the XX century, when the Hg deposits were intensively mined and rotary furnaces were used for mercury production. Consequently, wastes from smelting operations were stored in the spoil heaps together with the rejected material from the underground mining works. Asturias was at this time an important mercury producer on a world scale, and the most important mines were located at the sites of La Peña – El Terronal (Mieres district) and Muñón Cimero (Pola de Lena district), within the Caudal River catchment.

2.2. Climatological characteristics

At abandoned mine sites, climate is an important regulator of the flux of elements to the hydrosphere, and is consequently a decisive factor in the mobilisation of As from As-rich wastes. Sulphide oxidation rates increase with temperature and humidity. In contrast to other regions of Spain, Asturias has a humid and temperate oceanic climate characterised by abundant rainfall during a great part of the year. Annual average maximum and minimum temperatures are 17ºC and 8ºC respectively, with an annual average of 13ºC over the last twenty years. The annual relative average humidity is about 78% (between 74 and 84%). Average yearly rainfall is 971 mm and potential evapotranspiration, calculated by the Thorntwaite expression, is 691 mm/year. Consequently, the average annual effective precipitation is about 275 mm/year.

2.3. Geological characteristics

The Hg deposits are located in Precambrian to Carboniferous formations, associated with important faults. In general, Carboniferous limestones host the deposits, but some important deposits, such as La Peña – El Terronal, are associated with conglomeratic horizons or siliceous breccias in sandstones. They are epigenetic mineralizations, formed by the circulation of low temperature hydrothermal solutions along distension fractures (Loredo et al. 1988). Ore deposits show a tectonic control and there is a clear spatial relationship between them and late-hercynian fractures. The mineralization appears either as irregular massive lenticular stocks in the carboniferous limestones, or as irregularly distributed veinlets in relation to high porosity fracture zones (Gutierrez Claverol and Luque 1993).

Although Hg is always present in the form of cinnabar, metacinnabar and native mercury are also occasionally found. The presence of As in the form of As-rich pyrite, arsenopyrite, orpiment, realgar and scorodite has also been recorded (Luque 1985; Loredo et al. 2003). Other primary metallic minerals present in the paragenesis of the ore deposits are pyrite, melnikovite, sphalerite, marcasite, chalcopyrite, galena, and stibnite.

Smithsonite, hemimorphite, cerusite, goethite, malachite, jarosite, melanterite and gypsum are present as secondary minerals.

2.4. Hydrogeological characteristics

Hg mines are located in the Asturian Central Coal Basin, which is characterised by marked relief, small basins and humid climate. In general, groundwater systems within carboniferous series consist of a multi-bed hydrogeological system. At the base, these systems comprise alternating layers of lutites and limestones, followed by hundreds of para-sequences of lutites, limolites, sandstones and coal beds. Limolites, lutites and sandstones have very low permeability, and water circulation is only important in thicker sequences of fractured sandstones, giving rise to a large multi-bed system.

At depth, the groundwater travels long distances, but in the upper zones, it circulates over short distances, discharging to local surface watercourses. These aquifer levels are greatly affected by 200 years of underground coal mining and mined areas are characterised by slower-moving diffuse flow through the intergranular pore spaces and/or fractures in the rock. This gives rise to a complex system of double porosity, similar to karstic systems. In these cases, groundwater flow is essentially characterised by multiple flow paths, extreme ranges of hydraulic conductivity, and a high degree of unpredictability. The spoil heaps are comprised of unconsolidated sediments, and weathered highly fractured rocks, and they are located over low permeability materials of the carboniferous basement. They behave as a low transmissivity zone, and represent low permeability free aquifers that discharge into the local surface watercourses, transporting heavy metals and metalloids.

In some cases, as at Los Rueldos mine, the hydrogeological characteristics are strongly affected by the presence of very low permeability materials in the substrate (alternating sandstones, shales and some coal beds). In these conditions, the water that is not lost to evaporation or surface runoff infiltrates through the more permeable colluvial materials and weathered shales, giving rise to small springs. In other cases, as at La Soterraña mine site, the substrate is mainly comprised of alternating limestones, sandstones and shales, which have very low permeability, with the exception of the limestone bars that constitute small aquifers. The springs in this area are scarce and most of them are associated with these limestone bars.

3. Water pollution related to Hg mining: Hydrochemistry

Abandoned historic Hg mines and spoil heaps are important sources of water pollution in some areas of Asturias, and their situation is continuing to deteriorate. A high correlation between Hg and As concentrations in wastes and surrounding soils has been observed. Nevertheless, the ratio Hg/As is higher in wastes and soils of Pola de Lena Hg mining district ($[Hg] = 42.051[As]^{1.0323}$ in “La Soterraña” mine) than in wastes and soils of the Mieres Hg mining district ($[Hg] = 0.1254\ [As]^{0.9988}$ in “La Peña – El Terronal” mine and $[Hg] = 0.0002\ [As]^{1.349}$ in “Los Rueldos” mine), where [Hg] and [As] represent the Hg and As contents in mg.kg^{-1}, respectively. Wastes and soils from Mieres district contain the highest As presence. The concentration of total As in wastes and soils versus distance downhill from the source for four mine sites, is represented in Fig. 1.

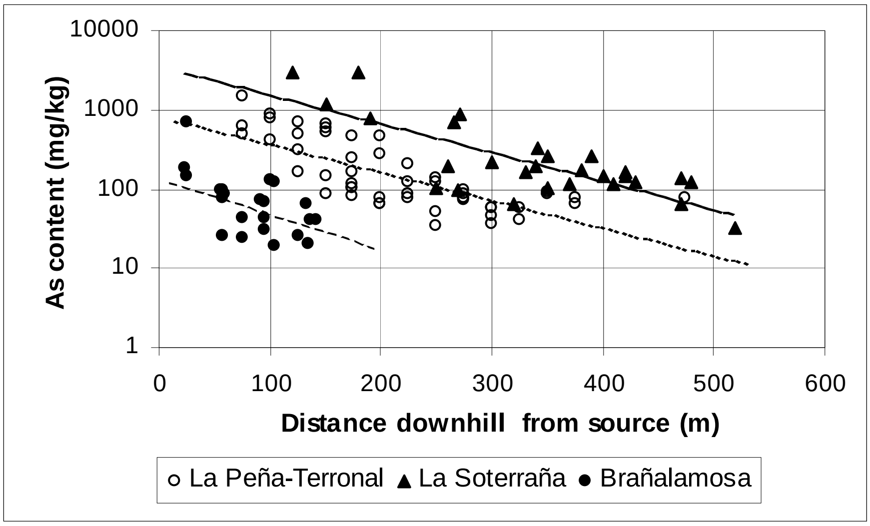

Fig. 1. Total As in wastes and soils versus distance downhill from the source at four mine sites in Central Asturias

Wastes typically have a pH ranging from 3.3 to 7.59 units, and they are stored on the surface and subjected to the erosion and washing effects of rainfall. In these conditions, quite intense chemical and mechanical dispersion occurs, and leachate production is profuse. Mineralogy of wastes has a decisive influence on spoil heap leachate composition. As is quite abundant in the form of As-rich pyrite, arsenopyrite, realgar, orpiment, and scorodite. In order to understand the As pollution mechanism and its association to non specific As minerals such as pyrites, quantitative microprobe analyses of pyrite and goethite have been undertaken. Data from 62 analyses of representative pyrite samples show As concentrations up to 10.11 %, and 31 analyses of goethite show As contents ranging between 0.56 % and 9.38 %, which provides evidence for the effect of iron oxides in the As immobilisation process. Chemical analyses of clays collected in trenches made at the bottom of some of the spoil heaps show high As contents (up to 7,848 mg.kg^{-1} at La Soterraña mine spoil heap).

Water samples were collected in rivers and streams (upstream and downstream of the mining works), mine drainage, spoil heap leachates, springs (upstream and downstream of the mining works), drills and trenches made at the bottom of the spoil heaps. Samples were filtered through 0.45 µm pore size membrane filters, acidified to a final concentration of 1% nitric acid, stored in a polyethylene recipient, and refrigerated until analysis. Non-acidified samples were measured in situ for pH and electrical conductivity (µS.cm^{-1}). Acidified samples were analysed for major cations and trace elements by inductively coupled plasma – atomic emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS) at ACME Analytical Laboratories Ltd. (Vancouver, Canada). Internal reference samples and duplicates of samples assured data quality. Portable HANNA meters, calibrated with standard buffers, have been used for in-situ measurements of pH and electrical conductivity.

Although in the Caudal River catchment the local hydrochemical background of As is naturally high (9 µg.l^{-1}), As enrichment in superficial waters and groundwater is exacerbated by the presence of abandoned Hg mines and associated spoil heaps. Surface waters upstream of mine works show As concentrations lower than 1 µg.l^{-1}. The concentration of total As in San Tirso River, collected immediately downstream of La Peña-El Terronal mining works, ranged from 0.9 to 7.9 mg.l^{-1}. Samples collected 300m downstream of the mine works showed average As concentrations of 2.7 mg.l^{-1}. These waters are discharged from a tributary to the Caudal River; where, 20m downstream of the confluence with San Tirso River, it shows an average As concentration of 1.6 mg.l^{-1}. This content decreases to about 0.01 mg l^{-1} at a distance of 150m from that confluence. The spoil heap at the site of La Peña – El Terronal was isolated in a security landfill in 2002, and at the time of the remediation works, total As contents increased notably in surface waters, reaching up to 13.9 mg.l^{-1}, caused by the movement of the materials. These concentrations tend to decrease with time, reaching maximum values of 5.1 mg.l^{-1} in 2003 (Fig. 2).

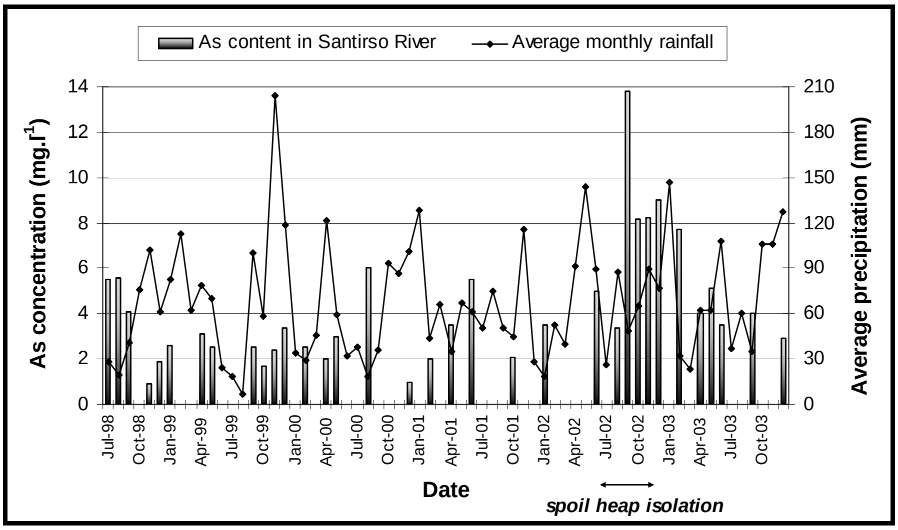

Fig. 2. Relation between rainfall and As concentration in samples of San Tirso river immediately downstream of La Peña-El Terronal mining works

In general, mine drainage is very acidic. Analysis of mine water flowing intermittently through the portal located between Union and Peña shafts (Mieres district) shows an average pH of 3, conductivity of 4 mS.cm^{-1}, and As concentration of 1.6 mg l^{-1}. At Los Rueldos mine, pH ranges from 1.60 to 2.45 units and average electrical conductivity shows values in the order of 5,527 µS.cm^{-1}. Average sulphate concentrations are approximately 5,000 mg.l^{-1}, and As concentrations range from 9.1 to 17.7 mg.l^{-1}. The chemical characteristics of leachates from the mine spoil heap are very similar to the mine drainage, with pH between 2.15 and 2.63 units, sulphate concentrations between 2,900 and 4,600 mg.l^{-1}, As concentrations between 1.4 and 9.2 mg.l^{-1}, and Hg concentrations between 2 and 5 µg.l^{-1}. Mine drainage and leachates are incorporated into a tributary of the Caudal River, where they are significantly diluted and the As contents are reduced to 5 - 8 µg.l^{-1} (Loredo et al. 2002). This dilution is due to the difference between the flow of the stream receiving the mine drainage and leachates (aprox. 5 to 20 l.s^{-1}), and the flow of the receiving river where they are discharged (490 l.s^{-1}).

Bibliographic data show that average As content in world groundwater is about 1-2 µg·l^{-1}, apart from in areas with volcanic rocks and sulphide mineral deposits (Robertson 1989). In some mining areas, As concentrations of up to 48 mg·l^{-1} have been reported (Welch *et al.* 1988). At El Terronal, upstream of the mine and spoil heap, the As content in groundwater, collected in private wells used for irrigation and as drinking supply for animals, showed total As concentrations ranging from 1.2 to 15 µg.l^{-1}. Downstream of the mining works, concentration of total As ranges from 0.9 to 5.6 mg l^{-1}. At Los Rueldos, in situ measurements of pH in groundwater collected in springs shows values around 7.1 - 7.3 units. At the same site, the total As concentration in groundwater ranges from less than 1 to 23 µg.l^{-1} (average 10 µg.l^{-1}). Downstream of the mining works at Los Rueldos, As concentrations in groundwater ranged from less than 1 µg·l^{-1} to 6.05 mg·l$^{-1.}$ At La Soterraña, water sampled in the superficial aquifer represented by mine voids and in materials stored in spoil heaps ranged from 14.8 to 57.5 mg·l^{-1} As. Concentrations of total As in samples of surface water and groundwater in the Caudal River catchment are summarised in Table 1.

Table 1. Total As in surface and groundwater sampled within the Caudal River catchment for the period 1998-2003

	pH	**As (mg.l^{-1})**	**Hg (µg.l^{-1})**	**Fe (mg.l^{-1})**
Surface water upstream mines (n = 23)	6.78–7.15	< 0.001	0.001–0.11	0.10–0.19
Surface water downstream mines (n = 34)	6.0–6.8	0.9–13.9	0.001–2.5	0.19–0.53
Mine drainage (n = 12)	1.60–2.11	9.1–17.7	1.2–3.7	679-829
Spoil heap leachates (n = 11)	2.15–3.0	1.41–9.2	0.6-14	619-748
Groundwater downstream mines (n = 11)	7.1–7.3	0.001–0.023	0.1–0.9	0.23–2.58

5. Conclusions

Historic Hg mining activity in Central Asturias has spread on land with abundant waste materials from mining and smelting operations in spoil heaps of different size and characteristics. Geochemical and mineralogical data from waste materials suggest that arsenopyrite, As-rich pyrite, realgar and scorodite are the main contributors to the high As contents found in waters downstream of the mine works. Weathering processes increase the instability of these minerals, abandoned in a humid environment and affected by surface waters. These geochemical processes produce metal rich leachates, which have an obvious impact on the environment and promote elevated concentrations of As in surface waters of the Caudal River catchment. The circulation of surface water through the underground mining works and spoils heaps, under oxidizing conditions, promotes the formation of acidic water with its typical reddish precipitates. These waters, very polluted at the source, are rapidly diluted when entering major watercourses, since the flow of acid mine waters is generally low in relation to the receptor watercourses. During dry periods, the polluting effect of these waters is higher, due to both the elevated As concentrations that the mine water can reach and the reduction of flow in watercourses.

Surface water quality degradation at the mine sites occurs only in a limited area directly affected by polluted discharges and spoil heap leachates. Arsenic contamination of surface water in the vicinity of the mines is regulated by the river or stream hydrological conditions, its buffering capacity and the relative size of the mined area within the catchment. Once the polluted water leaves the mine area, it enters the natural superficial watercourses (rivers and streams). Dilution, by mixing with tributaries, and adsorption reactions are the main cause of further observed decreases in As concentrations.

The co-precipitation of As and Fe, and the adsorption of As onto the Fe oxides, is enhanced in oxidising environments, within neutral to slightly acidic conditions, such as the case reported here. As is also linked to clays. Both Fe oxides and clays are major components in the spoil heaps and they turn out to be limiters of As mobility.

In recent years, the mining heritage aspects of abandoned mines have become more recognized and are now a significant factor in any consideration of rehabilitation of polluted areas. Apart from environmental aspects, the rehabilitation of abandoned mine sites involves important socio-economic aspects. In the case of abandoned Hg mine sites in Central Asturias, if proper corrective measures are not applied, polluted mine drainage and leachates from spoil heaps will occur, incorporating As into tributaries of Caudal River, which has traditionally been a salmon river, before pollution by coal mining. Due to the highly toxic nature of As, the management of As-rich wastes must be planned in such a way that the environment of the surrounding area is least affected. Disposal of wastes and its handling is one major aspect in mining from an environmental viewpoint. Due emphasis must be given for waste handling in the case of small mines.

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