Environmental Impact of Drainage from Abandoned Mercury Mines in Tributaries of Caudal River (Northern Spain)

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Abstract
In Asturias (Northern Spain) mercury mines have been operated from pre-roman times. As a consequence of the international mercury crisis in the 1970's, all mines were abandoned without remediation works. The potential environmental impact of the abandoned mine sites is enhanced by the presence of specific and non specific arsenic minerals in the ore deposits together with the targeted mercury minerals. With the humid climate of the area, the weathering of As-rich minerals produces the solubilisation of arsenic that impacts stream tributaries of the Caudal River. A systematic monitoring of physicochemical parameters of surface waters in selected sampling points (upstream and downstream from the main abandoned mine works) in the Caudal River catchment has been accomplished in order to characterize the pollution associated to abandoned mercury mine sites. Water flow, pH, electrical conductivity, dissolved oxygen, salinity, temperature and turbidity were controlled "in situ" by means of a portable multiparameter probe. Chemical analyses (Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Na, Mg, Mn, Mo, Ni, Pb, Se, Sr, Ti, V and Zn) were made by ICP-AES, FAES and an mercury direct analyser.

Key words: Hg mining, mine water, hydrogeochemical anomalies, arsenic.

Introduction
Asturias, in the north-west of Spain, has a long mining tradition and Hg mining was an important industry until the beginning of the 1970s. Asturias was at this time an important Hg producer on a world scale, and most productive mines were "La Peña - El Terronal" and "La Soterraña" both located in the Caudal River catchment. As consequence of the international Hg crisis ocurred on the 1970´s, all mercury mines in Asturias were abandoned between 1973 and 1974. The legacy of the Hg mining activities in Asturias remains in the form of abandoned mines and spoil heaps, and mine effluents and spoil heap leachates are polluting the surface watercourses (Loredo, 2000; Loredo et al., 1999, 2002, 2003, 2004a,b,c, 2006); the potential of these abandoned mine sites to pollute the environment is enhanced by the high content of arsenic in the ore and their proximity to watercourses.
Systematic monitoring of surface waters in the area of abandoned mine sites constitutes an essential step in the characterisation of pollution. The analytical data throughout a hydrologic period can be used for elaboration of a hydrological model and for selection of appropriate preventive and/or corrective technologies in order to avoid the pollution of the surface watercourses. Results of a systematic monitoring of physico-chemical parameters in samples taken in thirteen selected sampling points within the Caudal River catchment, at the main abandoned Hg mine sites in Central Asturias (Mieres and Pola de Lena districts), are presented in this paper. Three specific mine sites have been selected for study: La Soterraña, La Peña – El Terronal and Los Rueldos. The surface water characterization was made by determination of some physicochemical parameters "in situ" by means of a portable multiparameter probe and analyses of major and trace elements in laboratory.

Geology and hidrogeology
An extensive research has been done on the geological characteristics of Asturian mercury deposits (Luque, 1985; 1992). These deposits are hosted in Precambrian to Carboniferous sediments, and some of the most important deposits are located in conglomeratic horizons or siliceous breccias, and impregnating fractured lutitic carbonaceous sequences.
Mineralization, generally in relation to fractured zones, is irregularly distributed both in veinlets inside the conglomeratic-brecciated bodies which show a lenticular morphology or scattered inside the matrix of the conglomerate. It also appears either as irregular massive lenticular stocks in the

carboniferous limestones, either as irregularly distributed veinlets in fracture planes, and occasionally constituting disseminations in the enclosing limestones and sandstones. Although mercury is present in the form of cinnabar, metacinnabar and native mercury are also occasionally found. The presence of arsenic is frequent in the form of orpiment, realgar and As-rich pyrite. Other primary metallic minerals, which are present in the paragenesis of the ore deposits, are pyrite, melnikovite, sphalerite, marcasite, chalcopyrite, arsenopyrite, galena, and stibnite. Smithsonite, hemimorphite, cerusite, goethite, malachite, jarosite, melanterite and gypsum are present as secondary minerals. The gangue constituents are quartz, carbonates (calcite, dolomite and ankerite) and argillaceous minerals (kaolinite and dickite). The ore deposits, from their geological, geochemical, mineralogical and metallogenetic characteristics can be considered a mineralization of epigenetic type formed by the circulation of low temperature hydrothermal solutions along distensional fractures (Loredo et al., 1988). Generally, these mineralizations show important litologic and tectonic controls; and there is a clear spatial relationship between mercury deposits and late-hercynian fractures.

From a hydrogeological point of view, the substrate of the mineralised areas is mainly constituted by alternation of limestones, sandstones, shales and some coal beds, which can be considered as impermeable with the exception of the limestones and sandstones bars which constitute small local aquifers. The springs in the areas are scarce and most of them are associated to the limestone bars; springs associated to sandstones have a very poor flow.

Methodology

In thirteen selected sampling points located in the three areas of study (La Soterraña, Los Rueldos and La Peña-El Terronal), electrical conductivity, pH, Eh, salinity, dissolved oxygen, turbidity and temperature of water were measured in situ. Water samples were filtered "in situ" before being stored in plastic bottles. Samples of surface water, taken both upstream and downstream from the abandoned mine sites (including shafts and spoil heaps), were collected for analysis. They were stored refrigerated until analysis; in order to conserve their chemical characteristics and to keep metals in solution, special precautions were used including the previous acidification of samples with HNO_3. Major and minor elements (Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Se, Sr, Ti, V and Zn) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using two Jobin Ivon spectrometers (simultaneous JY38+48 and sequential JY38 PLUS), Na and K by flame atomic emission spectro-photometry (FAES) using a Perkin Elmer 2280 and Hg by a Milestone direct mercury analyzer (DMA-80). Ultrapure water from a Milli-Q system (Millipore Bedford, MA) was used throughout. The chemicals used were of analytical-reagent grade. Nitric acid (65%) and stock standard solutions for each element were obtained from Merck (Darmstadt, Germany). Working standard solutions were prepared freshly from individual 1000 $mg.L^{-1}$ stock standard solutions by sequential dilution with 0.5 N HNO_3. All glassware and bottles used were cleaned in 0.5 M HNO_3 for 2 days and rinsed three times with water before use. Several certified reference materials (Fresh water CRM 398 and CRM 399 from BCR, Simulated Fresh Water IAEA/W-4, and Waste Water SPS-WW-1 from Spectrapure Standards AS) were selected for this study in order to assess the accuracy of the results. Found errors in the analysis of these reference materials were always less than 3%.

Results and Discussion

La Soterraña is located in the valley of the Lena River, a tributary of Caudal river. A small stream with average flow ranging from 0.15 to 0.80 $L.s^{-1}$ circulates by a side of the mine site, on the valley, collecting mine water and spoil heap leachates. At Los Rueldos mine site runs the Morgao stream, which is underground canalized in the mine site. Mine drainage and spoil heap leachates reach the Morgao stream when it reappears on surface. Average flow of Morgao stream when it receives mine drainage and leachates ranges from 1 and 5 $L.s^{-1}$, depending of the period of the hydrological cycle. In the area of La Peña – El Terronal, flows San Tirso River, which is a tributary of the Caudal River. For the monitoring period, average water flow this river ranged from 3 to 140 $L.s^{-1}$. A summary of the average values of different parameters obtained for the samples colected upstream and downstream for the three mine sites included in the study are presented in Table1.

Table 1 *Average physicochemical parameters in monitoring points at the three mine sites*

Mine	**La Soterraña**		**El Terronal**		**Los Rueldos**	
Location	upstream	downstream	upstream	downstream	upstream	downstream
Flow ($L.s^{-1}$)	0.33±0.81	0.16±0.20	53±45	53±42	112±203	55±144
Cond. ($\mu S.cm^{-1}$)	407±50	1028±380	942±184	844±150	600±533	3670±2356
Salinity (ppt)	0.20±0.03	0.55±0.16	0.45±0.09	0.42±0.07	0.29±0.26	2.0±1.3
pH	7.2±0.8	7.8±0.4	8.3±0.2	8.3±0.4	6.7±1.5	4.9±2.8
E_{Redox} (mV)	251±49	277±52	268±49	265±49	625±266	777±230
Diss. O_2 ($mg.L^{-1}$)	5.0±3.3	4.2±2.7	3.5±2.2	3.9±2.4	3.3±1.3	12±9
Turbidity (NTU)	14±8	34±38	18±9	19±10	87±129	146±188
T^a (ºC)	16±3	13±2	15±2	16±2	15±4	15±3
Al ($mg.L^{-1}$)	0.07±0.03	0.12±0.06	0.06±0.01	0.08±0.05	0.55±1.02	91±81
As ($mg.L^{-1}$)	0.19±0.04	35±15	0.18±0.05	4.6±1.1	0.19±0.04	4.9±4.2
B ($mg.L^{-1}$)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.45±0.37
Ca ($mg.L^{-1}$)	65±9	198±61	123±22	111±13	81±67	124±13
Cd ($mg.L^{-1}$)	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.06±0.03
Co ($mg.L^{-1}$)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.23±0.17
Cr ($mg.L^{-1}$)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.06±0.01
Cu ($mg.L^{-1}$)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.25±0.19
Fe ($mg.L^{-1}$)	0.09±0.11	0.32±1.06	< 0.05	0.15±0.26	0.30±0.44	440±389
K ($mg.L^{-1}$)	0.61±0.26	12±11	6.9±1.4	6.2±1.1	3.3±3.4	3.6±1.2
Mg ($mg.L^{-1}$)	16±1	39±17	79±17	67±14	34±31	67±7
Mn ($mg.L^{-1}$)	< 0.03	< 0.03	< 0.03	< 0.03	0.23±0.35	1.21±0.67
Na ($mg.L^{-1}$)	5.5±1.4	19±6	14±4	12±3	41±66	34±36
Ni ($mg.L^{-1}$)	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.54±0.45
V ($mg.L^{-1}$)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.14±0.09
Zn ($mg.L^{-1}$)	< 0.05	< 0.05	< 0.05	< 0.05	0.06±0.01	3.7±3.9

At the site of La Peña – El Terronal,only minor differences between waters collected upstream and downstream were detected in comparison with the other sites, excepting As concentration that increases from <0.20 $mg.l^{-1}$ to 4.58 $mg.l^{-1}$ downstream from the site. The study revealed significant differences between samples taken upstream and downstream from La Soterraña site, mainly as a consequence of their enrichment in As, leached from the mine area. The environment of Los Rueldos is affected mainly for an important decrease of pH values in their waters and consequently dissolution of metals and metalloids (including arsenic, iron, etc) present in the sediments and soils. The impact is limited and it only affects the closest area to the mine, being the drainages quickly diluted in the Morgao stream and, in a higher extension, in the San Juan River where the pollution was not detected.

Conclusions

The systematic monitoring accomplished in streams of the area of abandoned three mine works (La Soterraña, Los Rueldos and La Peña-El Terronal) makes evident the presence of hydrogeochemical anomalies, reflected mainly by the high concentrations of arsenic. Waste materials spread on the land are considered as a pollution generator system that releases arsenic and heavy metals from the mined areas to surface watercourses. Mine drainage and spoil heap leachates show occasionally very acidic

conditions, although these conditions are easily neutralised when they reach streams or rivers with enough flow to produce a dilution.

At the scale of the mining district, total As concentration increases from average values lower than 0.2 $mg.L^{-1}$, upstream of the mine works, to values up to 57 $mg.L^{-1}$ at the bottom of La Soterraña spoil heap. They are particularly disquieting if it is considered that arsenic-enriched waters are eventually discharged to streams that are incorporated to important rivers at regional level. Mercury concentrations in surface waters upstream and downstream of the mining operations were always lower than 1 $\mu g.L^{-1}$ (detection limit of the equipment used for analysis), in agreement with its reduced solubility.

In order to achieve the water quality standard demanded on the Water Framework Directive, it is necessary a progressive reduction of pollution from anthropogenic sources, including also abandoned mines and spoil heaps. Then, for an effective water pollution control in abandoned mine sites, an adequate monitoring network and water quality control program is necessary. This dense monitoring network must be designed at the scale of the local subcatchment of the mine site, where the pollution source is located, and before dilution of mine waters into the surface watercourses are produced.

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