Surface water monitoring in abandoned mercury mine sites in Asturias (Spain): Comparative Studies

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ABSTRACT
Systematic monitoring of surface waters in the area of abandoned mine sites constitutes an essential step in the characterisation of pollution from historic mine sites. 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. This paper overviews a systematical monitoring of physico-chemical data in thirteen selected sampling points of the Caudal River catchment, at the sites of the main abandoned Hg mines in Central Asturias (Mieres and Pola de Lena districts), in north-western Spain. In these Hg deposits arsenic is present in the form of As-rich pyrite, realgar and occasionally arsenopyrite. Some mining drainage and leachates from spoil heaps show acidic conditions and high arsenic contents, and they are incorporated to streams tributaries of important rivers. Multivariate statistical studies reveal important differences between the physico-chemical data of the samples taken upstream and downstream mines, mainly in La Soterraña mine site.

INTRODUCTION
The presence of Hg in the environment has been widely recognised as a growing problem for both humans and ecosystems, therefore abandoned mercury mining possesses a particular interest in relation to environment pollution. Environmental regulation about mercury releases began in the U.S. and Canada about 1970, partly as a general consequence of the environmental activism which began in the late 1960s but also as a very specific consequence of scientific revelations which showed that inorganic mercury could be methylated in the environment and lead to levels in fish and other high-level predators which posed a human health risk (Turner and Southworth, 1999).
As consequence of the decline in mercury prices from about U.S.$600 per flask in 1965 to U.S.$120 per flask in 1975 (Ferrara, 1999), on the 1970´s have had a crisis leading to a total interruption of the extractive activity in many mining districts in the world. In Asturias (north-western Spain) this crisis gave rise to not only the paralysation of some important mining projects, but the successive closure of all up till then active mines, between 1973 and 1974. The decade comprised between 1962 and 1972 represents the most active period for the mercury mining in Asturias, with average annual productions of 15,000 flasks (SADEI, 1968-1991); Asturias was at this time an important mercury producer on a world scale. The main exploited Hg mines correspond to Mieres and Pola de Lena districts, which are located in Central Asturias. “La Peña - El Terronal” and “La Soterraña” were the most productive mines. Other minor mines have been intermittently exploited in these areas (Los Rueldos, El Rucio, La Campa del Trave, La Vallina, Brañalamosa, La Maramuñiz, etc.). The legacy of the historical mercury mining activities remains in the form of abandoned mines and spoil heaps, where polluted water flows to reach the surface watercourses (Loredo, 2000; Loredo et al., 1999, 2002, 2003, 2004a,b,c). In Asturias Hg mining district, the potential of abandoned mine sites to pollute the environment is enhanced by the high content of arsenic in the ore, and their proximity to streams.

GEOLOGY AND HYDROGEOLOGY
An extensive research has been done on the geological and metallogenetical characteristics of Asturian mercury deposits (Luque, 1985; Luque, 1992; Loredo et al., 1988; Luque et al., 1989; Luque et al., 1991). They 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. A schematic geological map of the Cantabrian Zone and localisation of main mercury mineralizations is represented in figure 1. In particular, the most important ore deposits are located in the north-western margin of the Asturian Central Coal Basin, in a zone of intense tectonic deformation, in the proximity and inside the influence domain of important fractures.

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 (Luque, 1985). 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 (Luque, 1985; Luque et al., 1989). 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 an hydrogeological point of view, the substrate of the mineralised areas is mainly constituted by alternation of limestones, sandstones and shales, which can be considered impermeable with the exception of the limestones and sandstones bars which constitute small aquifers. The springs in the areas are slight and most of them are associated to the limestone bars. Springs associated to sandstones have a very poor flow. In some cases, as Los Rueldos site the hydraulic characteristics of the different materials constituting the substrate of the catchment (alternance of sandstones, shales and some coal beds) can be considered as an impermeable substrate from an hydrogeological point of view. In these conditions the water does not evaporate nor flows superficially is infiltrated on the more permeable colluvial materials and weathered shales, giving rise to a number of small springs.

SURFACE WATER MONITORING

In contrast to other regions of Spain, Asturias has a humid temperate climate characterised by abundant precipitation during a great part of the year. In Mieres and Pola de Lena districts, the average relative humidity is about 78% and the average annual effective precipitation is about of 275 mm/year. In order to know the evolution on the time of the surface water quality in the area of main abandoned mercury mine sites, a surface water monitoring campaign has been accomplished.

Sampling

Samples of superficial water, upstream and downstream of the mining-metallurgical works and spoil heaps, were collected for analysis. At the abandoned mine sites, the circulation of surface water in oxidic conditions through the underground mining works and spoil heaps promotes in some cases the formation of acidic mine drainage with its typical reddish precipitates and spoil heap acidic leachates. Both, mine drainage and spoil heap leachates have been sampled in different periods of the hydrologic year. Water samples were filtered “in situ” before to be placed in plastic bottles. They have been stored refrigerated until analysis, and 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.

Monitoring point	Abandoned mine site	Description
P-1	La Soterraña	Runoff upstream La Soterraña Mine.
P-2		Channel downstream La Soterraña Mine, receiving spoil heap leachates.
P-3		Downstream La Soterraña Mine at the bottom of the spoil heap
P-4A		Stream receiving leachates from La Soterraña Mine spoil heap
P-5	La Peña – El Terronal	San Tirso River upstream mine operations
P-6		San Tirso River downstream mine operations
P-7A	Los Rueldos	Upstream Los Rueldos mine operations
P-7		Los Rueldos Mine leachates
P-8		Los Rueldos mine drainage (in a water pond at the end of the gallery)
P-9		Los Rueldos mine drainage (inside the gallery)
P-10		Downstream Los Rueldos mine operations, in Morgao stream
P-11		San Juan River upstream Los Rueldos mine operations.
P-12		San Juan River downstream Los Rueldos mine operations.

Table 1. Description of the sampling points in three abandoned mine sites.

Monitoring has been made fortnightly from mid April 2005 to the end of July 2005, in thirteen selected sampling points, located upstream and downstream the mine operations developed in the areas of study. Abandoned mine sites monitored correspond to the most important mine operations developed in Mieres and Pola de Lena districts. Table 1 summarizes the characteristics and description of sampling points.

Physico-chemical and statistical Analyses

At each point station water flow was measured, anyway pH, electrical conductivity, dissolved oxygen, salinity, temperature and turbidity were controlled “in situ” by means of a portable multiparametric probe.

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), Na and K by flame atomic emission spectro-photometry (FAES) and Hg by a direct mercury analyser.

A statistical processing of the data was carried out by using the SPSS program, version 11.5 for Windows®. Correlation and multivariate statistical analyses were performed with the physico-chemical results classified by their sampling points (upstream and downstream mine sites).

RESULTS AND DISCUSSION

La Soterraña mine site

At the site of the Soterraña mine do not exist important streams flow through the area of the mine operations. As they are located in a scenic valley, at the top of the southern slope of the Campusas Mountain, between 650 and 341 m above sea level, into the valley of the Lena River, 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 the spoil heap leachates, rainwater, and effluents from a local industry devoted to the manufacture of ceramics. Conductivity is generally high with values comprised between 882 and 1753 with tendency to increase in dry periods. The hydrogeochemical study shows high As concentrations reaching 57 mg.l^{-1}. Hg concentration is always lower than 1 µg.l^{-1}. Table 2 describes the physico-chemical and analytical data corresponding to two sampling points in the area for a period of the hydrological year.

Sample	Date DD-M	Conduct. µS.cm^{-1})	pH	Diss. Ox. (mg.l^{-1})	Al (mg.l^{-1})	As (mg.l^{-1})	Ca (mg.l^{-1})	Fe (mg.l^{-1})	K (mg.l^{-1})	Mg (mg.l^{-1})
P-1	27-4	415	7.88	8.5	0.06	<0.20	71	0.05	0.72	15
P-1	10-5	422	7.13	10.3	0.07	<0.20	68	0.36	0.51	16
P-1	26-5	397	7.99	2.2	< 0.05	<0.20	56	< 0.03	0.40	15
P-1	8-6	421	6.25	2.2	< 0.05	<0.20	59	0.07	0.43	15
P-1	23-6	432	6.63	4.9	< 0.05	<0.20	59	< 0.03	0.52	16
P-1	4-7	441	6.55	1.5	< 0.05	<0.20	61	< 0.03	0.54	16
P-1	28-7	289	6.72	3.2	0.06	<0.20	63	< 0.03	0.55	17
P-2	12-4	832	7.31	-	0.07	26	170	0.09	14	29
P-2	27-4	698	7.85	4.1	0.07	26	130	< 0.03	6.5	23
P-2	10-5	955	7.50	7.3	0.09	6.5	152	4.7	55	17
P-2	26-5	705	8.41	2.5	0.05	25	117	0.04	3.9	22
P-2	8-6	865	7.81	1.7	0.06	29	142	0.07	5.2	27
P-3	12-4	1029	7.31	-	0.16	26	220	0.10	6.4	46
P-3	27-4	809	8.2	8.2	0.06	0.54	85	0.05	1.1	13
P-3	10-5	1052	8.02	10.4	0.23	24	176	0.11	7.0	39
P-3	26-5	882	8.16	2.2	0.22	29	149	0.2	7.9	36
P-3	8-6	1484	6.47	2.1	0.14	39	219	< 0.03	9.6	47
P-3	23-6	1397	7.70	5.7	0.18	41	252	0.13	13	60
P-3	4-7	1486	7.72	1.5	0.15	48	234	< 0.03	14	68
P-3	28-7	1753	7.75	4.3	0.22	44	341	0.18	16	80
P-4A	10-5	1029	8.17	7.0	0.10	48	228	0.07	11	39
P-4A	26-5	951	8.26	2.7	0.09	43	183	0.04	9.1	32
P-4A	8-6	1115	7.96	2.0	0.07	57	215	0.04	10	38
P-4A	23-6	1185	8.03	5.4	0.10	52	232	0.05	11	42
P-4A	4-7	1299	7.94	1.2	0.14	46	254	0.04	12	47
P-4A	28-7	1.278	7.98	4.0	0.12	46	256	< 0.03	11	46

Table 2. Physico-chemical data for monitoring points at La Soterraña mine site.

La Peña – El Terronal mine site.

At the site of La Peña – El Terronal mines, on the area of the abandoned mine and metallurgical operations flows the San Tirso River, which is a tributary of the Caudal River (important to a regional level). Average flow of San Tirso River for the monitored period ranges from 3 to 140 $l.s^{-1}$. This river drains the valley where the mine operations are located. Excepted As concentration, not big differences are in water quality for samples collected upstream and downstream mine operations. Hg concentration is always lower than 1 $\mu g.l^{-1}$. Table 3 describe the physico-chemical and analytical data corresponding to two sampling points in the area for a period of the hydrological year.

Sample	Date DD-M	Conduct. (µS.cm^{-1})	pH	Diss. Ox. (mg.l^{-1})	Al (mg.l^{-1})	As (mg.l^{-1})	Ca (mg.l^{-1})	Fe (mg.l^{-1})	K (mg.l^{-1})	Mg (mg.l^{-1})
P-5	10-5	837	8.46	7.6	0.08	<0.20	119	0.07	6.1	69
P-5	26-5	775	8.45	2.0	0.07	<0.20	94	0.10	5.8	63
P-5	8-6	984	8.19	1.9	< 0.05	<0.20	127	0.05	6.8	80
P-5	23-6	1093	8.20	4.8	< 0.05	<0.20	141	< 0.03	7.7	94
P-5	4-7	1019	8.20	1.2	0.07	<0.20	134	< 0.03	7.7	91
P-5	28-7	1200	8.09	3.4	< 0.05	<0.20	153	< 0.03	9.3	99
P-6	12-4	731	7.33	-	0.06	4.0	107	0.08	5.3	61
P-6	10-5	760	8.60	8.1	0.10	4.0	107	0.06	5.7	58
P-6	26-5	716	8.45	1.9	0.06	3.3	95	0.06	5.3	55
P-6	8-6	898	8.49	1.9	0.05	4.6	109	0.07	6.2	70
P-6	23-6	974	8.62	5.6	< 0.05	5.7	126	0.05	7.1	77
P-6	28-7	1085	8.46	3.8	0.08	6.7	125	0.04	8.2	88

Table 3. Physico-chemical data for monitoring points at La Peña – El Terronal mine site.

Los Rueldos mine site

At the site of Los Rueldos mine runs the Morgao stream, which is underground canalised in the area of the mine operations, which have been of small importance. Mine drainage and spoil heap leachates reach the Morgao stream when it reappears on surface. Average flow of Morgao stream at the end of the canalisation, when mine drainage and leachates are incorporated is comprised between 1 and 5 $l.s^{-1}$ depending of the period of the hydrological cycle. Conductivity is low upstream mine operation, in the order of 200 $\mu S.cm^{-1}$ but high downstream mine operation, with average values in the order of 1200 $\mu S.cm^{-1}$. pH although shows very acidic at the site of the mine and spoil heap, in the order of 2.5 units, reaches neutral values when polluted waters from abandoned mine operations are incorporated to Morgao stream, when they experiment a big dilution. With respect to hydrogeochemistry, aluminium increases significantly in mine drainage and spoil heap leachates, when pH has acidic values, but it decreases after polluted waters reach the Morgao stream. As, and Fe increase too significantly on mine drainage and spoil heap leachates and the concentrations of these elements remain high enough in Morgao stream downstream mine operations, with values comprised between 0.34 and 0.61 $mg.l^{-1}$, and 4.3 and 7.1 $mg.l^{-1}$ respectively. Hg concentration is always lower than 1 $\mu g.l^{-1}$. Table 4 describes the physico-chemical and analytical data corresponding to sampling points in the area for a period of the hydrological year.

In comparison with the mean of total arsenic typical concentrations in stream waters at a world scale, which is estimated in 4 $\mu g.l^{-1}$ (Reimann and Caritat, 1998), concentration measured downstream mine operation are very high and pollution is incorporated to San Juan River, which is a tributary of Caudal river. The Spanish legislation about mining/industrial effluents limits the total arsenic content to 0.50 $mg.l^{-1}$, and 0.05 $mg.l^{-1}$ for superficial waters destined to production of drinking water. Mercury concentrations measured in samples of surface waters are always lower than 1 $\mu g.l^{-1}$, according to the low solubility of this metal.

Sample	Date DD-M	Conduct. µS.cm^{-1})	pH	Diss. Ox. (mg.l^{-1})	Al (mg.l^{-1})	As (mg.l^{-1})	Ca (mg.l^{-1})	Fe (mg.l^{-1})	K (mg.l^{-1})	Mg (mg.l^{-1})
P-7	27-4	129	4.46	5.6	0.44	<0.20	12	< 0.03	1.0	4.5
P-7	10-5	134	5.09	3.5	0.45	0.07	10	< 0.03	1.0	4.4
P-7	26-5	135	4.90	2.2	0.38	<0.20	11	< 0.03	0.9	4.2
P-7	8-6	408	6.74	1.8	< 0.05	<0.20	54	0.11	1.0	14
P-8	12-4	5320	2.28	-	175	11	135	879	2.5	69
P-8	27-4	6100	2.53	20	144	6.5	112	725	2.1	52
P-8	10-5	5459	2.52	17.8	153	8.0	115	770	2.5	60
P-8	26-5	5450	2.50	20	144	8.5	98	725	2.0	59
P-8	8-6	5736	2.28	20	167	9.2	120	827	2.3	68
P-8	23-6	5560	2.40	20	155	8.3	124	744	2.2	70
P-8	4-7	5505	2.48	20	168	8.9	127	718	3.0	73
P-8	28-7	5865	2.50	20	164	5.9	154	736	3.4	67
P-9	12-4	-	-	-	186	12	141	927	5.0	74
P-9	27-4	4543	2.49	20.0	183	8.5	131	927	3.1	63
P-9	10-5	5862	2.55	6.4	152	6.3	119	757	2.8	59
P-9	26-5	6355	2.55	20.0	140	9.1	118	705	2.4	61
P-9	8-6	6455	2.45	20.0	149	7.9	104	728	2.9	63
P-9	23-6	6115	2.50	20.0	143	8.4	110	695	2.6	70
P-9	4-7	6260	2.54	20.0	165	8.5	135	684	2.6	73
P-9	28-7	5065	2.28	20.0	160	6.0	121	718	2.1	67
P-10	12-4	1149	7.34	-	1.3	0.43	153	5.4	4.6	85
P-10	27-4	1008	8.60	4.2	1.6	0.34	126	4.3	4.1	66
P-10	10-5	1116	7.77	4.2	1.3	0.37	130	4.3	4.6	68
P-10	26-5	1080	7.41	2.9	1.6	0.44	121	5.1	4.4	64
P-10	8-6	1190	8.03	2.4	1.3	0.43	121	5.8	4.7	73
P-10	23-6	1256	6.45	6.4	0.94	0.52	117	7.1	5.5	78
P-10	4-7	1250	7.80	2.2	0.84	0.43	129	5.0	5.4	81
P-10	28-7	1200	7.50	4.9	0.83	0.61	102	6.7	5.7	72
P-11	27-4	933	8.72	3.6	< 0.05	<0.20	131	0.07	4.2	63
P-11	26-5	1030	8.26	2.4	0.07	<0.20	123	0.19	4.6	61
P-11	8-6	1169	8.12	2.1	0.11	<0.20	126	0.29	5.4	66
P-11	23-6	1684	8.16	5.3	1.1	<0.20	147	0.35	12	83
P-11	4-7	-	-	-	3.8	<0.20	185	1.5	6.0	62
P-11	28-7	989	7.96	4.4	0.46	<0.20	170	0.97	5.8	62
P-12	27-4	954	8.72	3.2	0.10	<0.20	131	0.23	4.2	61
P-12	10-5	1015	8.66	4.8	0.08	<0.20	134	< 0.03	4.9	58
P-12	26-5	1036	8.46	2.3	0.09	<0.20	126	0.18	4.5	61
P-12	8-6	1196	8.36	2.2	0.17	<0.20	127	0.34	5.4	69

Table 4. Physico-chemical data for monitoring points at Los Rueldos mine site.

Statistical analyses

The results of bivariable correlations showed an association of several chemical elements such as Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, V and Zn with a very high correlation coefficients among them as a consequence of the nature of the waters. Besides these elements are highly related to some of the parameters measured “in situ”: electrical conductivity, salinity, dissolved oxygen and, in a lower extent, turbidity. pH values showed a high correlation with those elements, but in a negative form, since a lower pH provides an increase in those parameters level, and a higher leaching and weathering effects.

A Supervised Pattern Recognition study was applied to the physico-chemical results. Linear Discriminant Analysis was designed to develop a set of canonical discriminant functions which can help to extract significant differences in their composition (García Giménez et al., 2005a&b). The samples were previously classified in six groups: samples taken upstream and downstream for each three mine sites. This study revealed significant differences between samples taken upstream and downstream La Soterraña mine site, mainly as a consequence of their high enrichment in As leached from the mine area. On the other hand, samples of Los Rueldos mine site showed a remarkable decrease of pH from 7 to 4 due to this source, together with an increase of the level of the Al, Fe and their associated elements. In this case, an enrichment in As was also noticed, but in a lower proportion. As it has been mentioned, at the site of La Peña – El Terronal mines only minor differences between waters collected upstream and downstream were detected in comparison with the other sites.

CONCLUSIONS

The systematic monitoring accomplished in streams of the area of abandoned mine works makes evident the presence of anthropogenic hydrogeochemical anomalies in the area, which represent an important environmental impact, reflected mainly by the high concentrations of total arsenic. Although in some particular areas, the local geochemical background of Hg and As is naturally high by weathering of mineralised rocks, this enrichment is clearly exacerbated by the presence of abandoned mines and spoil heaps, where the increase in secondary porosity favours the capability of sulphide minerals in ore and/or mineralised rocks to be unstabilised. The weathering of arsenic-bearing minerals in mines and spoil heaps results in the transport of dissolved arsenic to superficial watercourses. Mercury as consequence of its low solubility do not reach high concentrations in water.

Waste materials from mining and metallurgical operations spread in the areas, are considered as a generator system of polluting leaching that carries out 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 of pollutant, in particular arsenic.

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 filtered superficial 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 carry out the objective of water quality demanded on the Water Framework Directive, it is necessary a progressive reduction of pollution from anthropogenic sources, including among them 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 superficial watercourses will be produced.

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