Holistic View of Water Affection in the Mercury Mining District of Asturias (Spain)

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Abstract In this paper, a summary of hydrogeochemical data for surface and groundwater of the Asturian mercury mining district (NW Spain) is presented and discussed. Low mobility and solubility of mercury, together with the presence of arsenopyrite and arsenical pyrite in the paragenesis of the deposits has led most of the samples to exceed US EPA limits for arsenic content.

Keywords mercury mining, arsenic, sediments, surface water

Introduction

Asturias (NW Spain) is a region with a prominent mining tradition: it is considered to be the most important mercury mining district of Spain behind Almadén, which was the most significant one worldwide (Loredo *et al.* 2010). An intense mining activity was carried out during the XIX and XX centuries; during the 1970s, related with the global mercury crisis, all the mines were closed with no restoration programs. Being that so, abandoned mine facilities and spoil heaps with mine wastes as well as tailings configure the current heritage of the past mercury mining activity.

The Asturian mercury mining district is constituted by small-size hydrothermal-type cinnabar mineralizations with a common mineralogical feature: the presence of arsenopyrite and arsenical pyrite in the paragenesis (Loredo *et al.* 2003a; Larios *et al.* 2012). At the disposal sites, mineral weathering is an inevitable phenomenon that led to the release and mobilization of mercury, arsenic and related metals to the surrounding environment (*e.g.* surface and groundwater, soils, sediments, air).In this paper, a review of the eight main mining sites that belong to the Asturian mercury mining district is undertaken, summarizing all the available hydrogeochemical data.

Area of study

From all the mercury mineralized areas existing in the region (about 18 evidences, according to Luque and Gutiérrez-Claverol 2006), only eight sites are considered here; those which are more significant from an environmental viewpoint (all of them were included in the "Inventory and Characterization of Contaminated Soils of Asturias", Gobierno del Principado de Asturias 2002). In the most important mining sites, metallurgical activity was also conducted (see Luque and Gutiérrez-Claverol (2006) for additional information).

Six mining sites (La Peña-El Terronal, Los Rueldos, La Campa del Trave, La Soterraña, Brañalamosa and Maramuñiz, see Fig. 1) are located, from a geological viewpoint, in the Cantabrian Zone (following the traditional Iberian Massif division of Lotze 1945), specifically in the domain kwon as "Central Coal Basin" (Julivert 1971). Mercury mineralization is supposed to be related to Permian-age hydrothermalism, being sandstones the host rocks and, in a lesser extent, thin limestone levels of Carboniferous age. A more detailed description of the geological features of the mercury occurrences is presented in Ordóñez *et al.* (2013).

The two remaining mining sites (Caunedo and Olicio, see Fig. 1), also related to Permian

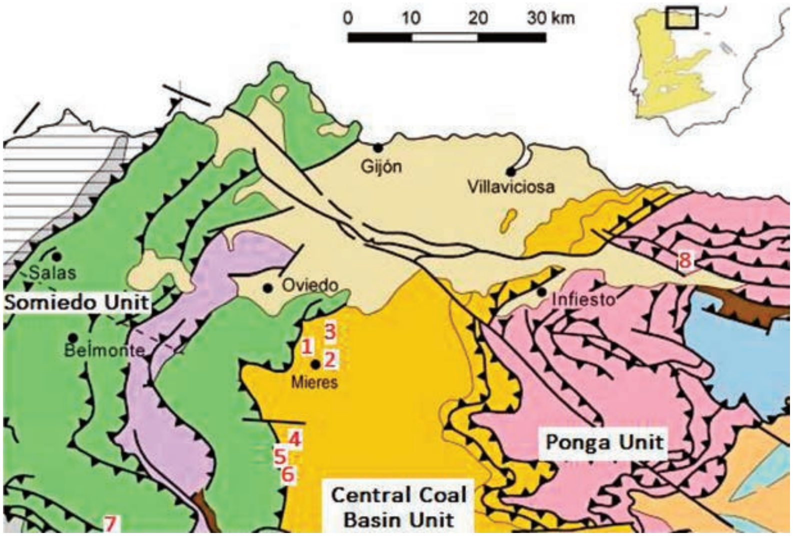

Fig. 1 *Location of the studied mine sites within the Cantabrian Zone (1: La Peña-El Terronal; 2: Los Rueldos; 3: La Campa del Trave; 4: La Soterraña; 5: Brañalamosa; 6: Maramuñiz; 7: Caunedo; 8:Olicio).Modified from Bastida (2004).*

hydrothermalism, are located in the Somiedo Unit (west part of the Cantabrian Zone) and Ponga Unit (East of the Cantabrian Zone) respectively. In the first case, the enclosing rocks are limestones and dolostones of Cambrian age, while the Olicio deposit is mainly embedded in thick Carboniferous organic-rich dark limestones.

Methods

Water

Downstream of each mine site, surface water (SW) samples from the nearest watercourse were collected. Groundwater flows across underground mining voids in a similar way to that occurring in karst aquifers: there are multiple flow paths with a wide range of hydraulic conductivity and unpredictability. For this study, groundwater was sampled at mine portals (mine drainage, MD), natural springs and man-made drills (here denominated as groundwater, GW).

Water samples were collected in plastic bottles and refrigerated until analysis. In order to preserve their physic-chemical characteristics (such as keeping metals in solution)each sample was acidified by adding two HNO_3 drops. Once filtered, both surface and groundwater samples were analyzed for Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, W and Tl by ICP-MSat ACME Analytical Laboratories in Vancouver (Canada). Minimum detection limit for Hg was established at 10^{-4} mg L^{-1}.The number of water samples analyzed at each mine site is presented in table 1.Surface water flow was determined when possible by means of a Hanna current meter.

Sediments

Sediment samples (here called stream sediments) were collected from the upper 20 cm in the streambed of the nearest watercourse to each mining site, within a distance of 1 km downstream from the considered mining site. About 1 kg of sediment was recovered per sample (by using a ceramic shovel). Samples were dried, sieved and analyzed by X-ray fluorescence (XRF) by means of a portable Niton XRF analyzer. The number of samples analyzed at mine each site is presented in table 2.

Results

Water

Analytical and physic-chemical results for mine drainage, surface and groundwater for each mine site are presented in table 1:

US EPA indicates that a concentration exceeding 10^{-8} mg L^{-1} Hg in stream waters may result in chronic effects to aquatic life (USGS 2005). In respect to As, the US EPA standard is set at 0.01 mg L^{-1} As (US EPA 2012).

	n	pH		EC (µS cm^{-1})		Flow (L s^{-1})		As (mg L^{-1})		Hg (µg L^{-1})	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
La Peña-El Terronal											
MD	1		3.0		4	<1	<1		1.6	<0.1	<0.1
SW	38	6.9-9.2	7.8	531-1,223	886	89-310	122	0.2-7.9	3.3		<0.1
GW	5					-	-	0.0-3.2	0.6	0.3-9.3	2.7
La Soterraña											
SW	27	6.9-9.1	7.7	289-2,027	1,366	0.01-0.8	0.2	0.3-171	39	<0.1	<0.1
GW	4					-	-	16-475	179	1.0-14	6.1
Brañalamosa											
MD	2	7.3-8.0	7.7	239-600	420	<1	<1	0.03-1.8	0.9	<0.1	<0.1
SW	6	7.1-8.6	8.0	186-380	277	<10	<10	<0.001-1.9	0.5	<0.1	<0.1
GW	6	7.3-8.0	7.6	183-617	357	-	-	<0.001-1.8	0.8	<0.1	<0.1
Maramuñiz											
MD	1		8.0		352	<1	<1		0.01		0.6
SW	3	8.5-8.7	8.6	130-200	173	<10	<10	<0.001-1.9	1.0	<0.1	<0.1
Los Rueldos											
MD	26	1.8-7.6	3.9	4,522-6,830	5248	<1	<1	2.4-18	7.3	<0.1	<0.1
SW	38	6.9-9.7	7.9	880-1310	1152	0.1-4.1	2.9	0.06-6.0	0.4	<0.1	<0.1
GW	4					-	-	<0.001-0.02	0.01	0.6-1	0.8
Olicio											
SW	3	8.0-8.6	8.2	300-540	443	<10	<10	<0.001-0.03	0.02	<0.1-3	1.3
GW	2					-	-	<0.001-0.04	0.01	0.7-0.9	0.8
Caunedo											
MD	1		8.3		210	<1	<1		0.02		0.3
SW	4	7.9-8.4	8.0	100-340	255	<10	<10	<0.001-0.002	0.001	0.4-1.0	0.7
GW	2	8.4-8.5	8.5	250-350	300	-	-	<0.001	<0.001	0.5-0.7	0.6
La Campa del Trave											
MD	8	2.2-3.3	2.8	290-940	645	0.1-0.2	0.1			0.3-10	2.1
SW	21	2.6-8.7	6.7	160-820	380	0.1-5.0	2.2			0.2-23	2.4

Table 1 *In situ measured parameters and mercury and arsenic contents in water samples (Gobierno del Principado de Asturias 2002; Loredo et al. 2003a; 2003b; 2005; 2006); MD=Mine drainage; SW=Surface water; GW=Groundwater.*

As it can be noted from data on table 1, the highest arsenic concentration (up to 475 mg L^{-1}) of the analyzed water samples was found at La Soterraña mine site. It should be pointed out that mine drainage at La Peña-El Terronal and Los Rueldos mine sites also contain high dissolved arsenic levels, and most of the sampled waters exceed the above-cited US EPA limit. With regards to mercury, and due to its low solubility, the 2.4×10^{-3} mg L^{-1} Hg maximum concentration recommended by the USEPA is not generally exceeded (excepting occasionally at La Soterraña, La Peña-El Terronal, La Campa del Trave and Olicio).

Taking into account the average flow of the sampled watercourses as well as their mean arsenic concentration, the average annual arsenic mass load carried to the Caudal River exceeds 12 t. Due to the high flow of this river, there is a great dilution, being arsenic undetectable in its water (Loredo *et al.* 2010). However, presumably, part of the arsenic load is retained in the river sediments, becoming a potential risk for the aquatic ecosystems.

Arsenic and mercury contents in groundwater are generally higher than those found for surface waters, probably due to infiltration of polluted leachates from wastes, both stored on surface (spoil heaps) and sub-superficially buried. On the other hand, Loredo *et al.* (2006) reported that the concentration of mercury organometallic species in mine drainage and spoil heap leachates is below 2 mg L^{-1}.

Sediments

It would be reasonable (as it was pointed out by previous studies: Gray *et al.* 2004; Gosar 2008; Gosar and Tersic 2012) to expect high

	As	Ba	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Sb	Zn
						La Peña-El Terronal (n=43)						
Min	9		8			31	2.0	1		9	36	18
Max	1,680		53			73	5.5	30		283	146	306
Mean	483		18			39	2.9	16		33	75	46
St. Dev.	320		7			9	0.7	6		41	21	46
						La Soterraña (n=41)						
Min	645	102	0.2	3	8	15	0.4	12	6	5	1.9	39
Max	62,184	573	0.3	19	22	125	17	3,267	38	2,060	8.9	3,620
Mean	11,310	338	0.3	11	15	49	4.1	627	22	106	5.4	475
St. Dev.	11,577	333	0.1	11	9	23	2.7	841	22	326	4.9	713
						Brañalamosa (n=4)						
Min	22	51	0.1	11	13	16	2.6	2.7	21	16	0.7	70
Max	35	88	0.2	14	14	21	3.1	107	27	20	1.6	82
Mean	26	75	0.2	13	13	18	2.8	51	25	19	1.0	78
St. Dev.	6	16	0.1	1.2	0.8	2.0	0.2	44	2.7	1.6	0.4	5.7
						Maramuñiz (n=3)						
Min	48	65	0.1	15	15	19	3.0	0.5	29	21	0.7	88
Max	796	79	0.2	16	16	25	3.8	62	32	23	2.1	110
Mean	456	74	0.1	15	15	21	3.4	23	31	22	1.3	97
St. Dev.	379	8	0.1	0.7	0.8	3.3	0.4	34	1.7	1.2	0.7	12
						Los Rueldos (n=31)						
Min	32	29	<0.2	<1	1	13	1.4	9	1	24	780	32
Max	46,931	42	<0.2	<1	12	195	38	1,260	9	4,032	1,254	383
Mean	18,229	38	<0.2	<1	8	41	13	132	5	1,101	1,076	80
St. Dev.	14,097	5			3	36	8.9	226	2	1,153	205	68
						Olicio (n=3)						
Min	30	23	<0.2	6.0	6.0	19	0.8	92	12	9.0	4.7	10
Max	98	39	0.2	17	9.0	47	1.4	250	35	61	11	22
Mean	74	33	0.1	13	7.7	36	1.2	172	25	27	8.2	16
St. Dev.	38	8.7	0.1	6.1	1.5	15	0.4	79	12	29	3.1	6.0

Table 2 *Elemental concentrations in sediment samples from six mine sites (Gobierno del Principado de Asturias 2002; Loredo et al. 2003a; 2003b; 2005; 2006). Contents in mg kg^{-1}, excepting Fe (%).*

mercury concentrations in stream sediments downstream of mine sites, usually in the form of cinnabar (USGS 2005). Results of the analyzed sediments (six mine sites: La Peña-El Terronal, Los Rueldos, La Soterraña, Brañalamosa, Maramuñiz and Olicio) are shown in table 2.

Very high arsenic concentrations have been detected at La Soterraña (up to 62,184 mg kg^{-1}) and Los Rueldos (up to 46,931 mg kg^{-1}), followed by La Peña-El Terronal (up to 1,680 mg kg^{-1}). Average arsenic contents are 5 (Brañalamosa) to 3,600 (Los Rueldos) times higher than normal arsenic concentrations in stream sediments for unpolluted areas (about 5 mg kg^{-1}, WHO 2001).Mercury contents are not so extreme, but very high at La Soterraña (up to 3,267 mg kg^{-1}), Los Rueldos (up to 1,260 mg kg^{-1}) and Olicio (up to 250 mg kg^{-1}). Average mercury contents are 16 (La Peña-El Terronal) to 600 (La Soterraña) times higher than the mean Hg content in world sediments (1 mg kg^{-1}, WHO 2001).

Conclusions

In the Asturian mercury mining district, as a consequence of past mining and metallurgical operations, there is a significant environmental impact, reflected in elevated concentrations of mercury and arsenic in mine drainage, surface and groundwater, as well as stream sediments. Although all the mines were closed about 40 years ago, this mining district has kept on releasing considerable quantities of these elements into the environment.

High metal and metalloid concentrations (especially arsenic) are found in mine drainage; spoil heap leachates in a humid environment severely affect surface and groundwater, as well as stream sediments and also aquatic ecosystems. Thus, fish consumption and water uses should be controlled, in spite of the decrease of arsenic concentrations when it is diluted in a major watercourse.

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