Mercury Contents in Waters from the Valdeazogues Watershed (Almadén, Spain)

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Keywords: mercury, surface waters, Almadén, Spain.

ABSTRACT
The survey was carried out in Almadén mercury mining district, the first producer of mercury in historic times. During the last 18 months, we have been controlling monthly mercury contents and other physical-chemical parameters in the waters of the main streams of the Valdeazogues watershed. Sampling network is distributed in 16 points in the Valdeazogues River and other streams close to mining areas, finding the higher values in the artificial lake of El Entredicho (3.573 μg/l) and in the streams that drain the city of Almadén: Azogado (1.733 μg/l) and La Pila (0.626 μg/l) streams. Monthly, contents of total mercury in the waters of the mining district are lower in the dry months than in rainy ones. Most of the sites have values of total mercury higher than USEPA standard for aquatic life (0.2 μg/l) and in a few cases higher than the WHO limits for drinking water (1 μg/l). The transport of this mercury is mainly in particulate form and come from well located sources: El Entredicho open pit, Las Cuevas mine and the Almadén town and mine area.

INTRODUCTION
The Almadén mercury district ceased completely the mining activity in September 2004, after more than 2000 years of almost continuous activity. During this period the mines from the district produced almost 250.000 t of the liquid metal, with 88% of this total production coming from the Almadén mine. These figures represent one third of total world mercury production in historic times.
During these more than 2000 years, mercury production from the ore, cinnabar (HgS) based exclusively on roasting, has suffered important changes, from primitive procedures with very significant looses of mercury vapours to the atmosphere, to the last technologies implanted in the 50's, which still caused considerable Hg presence in the atmosphere (Higueras et al., 2005).
In the same way, the extraction of cinnabar and related minerals from the mines and it's exposure to the meteorological agents has favoured the lixiviation of sulphides and the presence of the corresponding soluble compounds in the local waters. On the other hand, the scarcity of pyrite (FeS_2) and the abundance of carbonates in the deposits have prevented the formation of Acid Mine Drainage (Higueras et al., 2004).
Local sources of this pollution process include the main mines and metallurgical plants of the district, summarised in *Table* 1, and which geographic location is shown in *Figure* 1. The Figure also displays a scheme of the Valdeazogues watershed network, and the location of the sampling points described later on.

Source description	Activity period	Hg production (t)
Almadén mine	~ aD – 2003	220.000
Almadén metallurgical precinct	*? – 2004*	*~ 235.000*
El Entredicho	(Romans and Arabs times) 1984 – 1997	10.000
Las Cuevas	(Romans times) 1987 – 2000	6.500
Nueva Concepción	1795 – 1861	5.400
Vieja Concepción	1702 – 1800	4.000
Almadenejos metallurgical precinct	*1725 – 1865*	*~ 9.000*
Other minor mines	Diverse	~ 3.000
Other minor metallurgic sites	*Diverse*	*~ 3.000*

Table 1. Main sources of mercury in the District. In italics, metallurgical production.

In the last years the mining company has been doing important efforts to minimize the dispersion of the mining lixiviates, through the reclamation of mine dumps, and the flooding of El Entredicho open pit. The results of these actions probably will be patent in the next future.

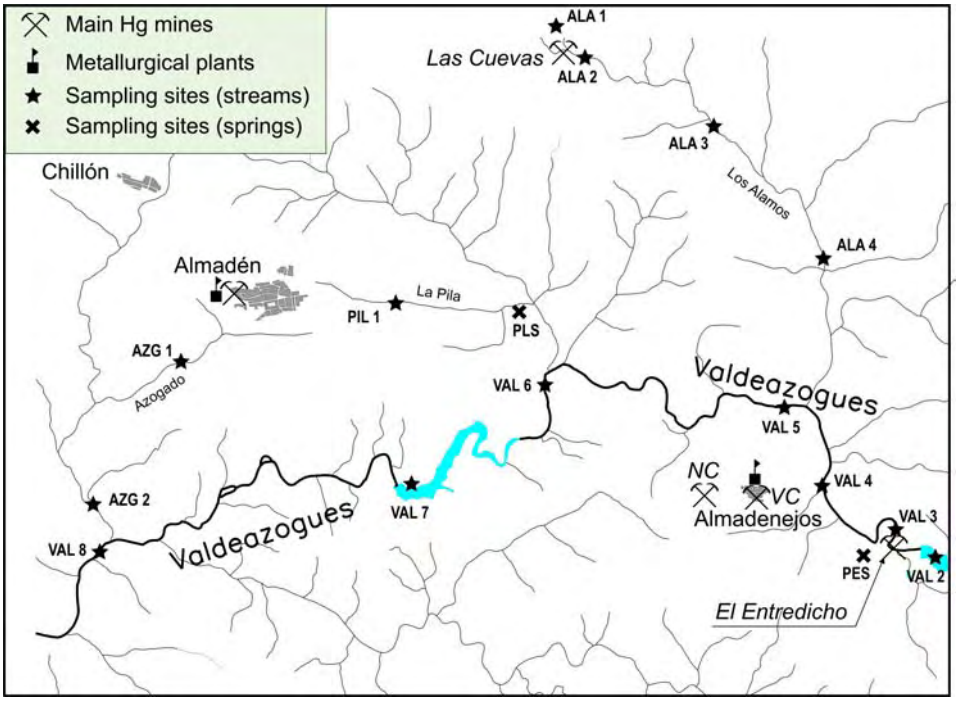

Figure 1. Location of sampling sites and main punctual sources for Hg pollution in the Almadén district. NC: Nueva Concepción mine; VC: Vieja Concepción mine. PLS: Pilar de la Legua spring; PES: Peñarroya spring. The area does not include the reference areas, located to the East (VAL 1) and to the NE (RIB 1), neither the La Serena reservoir sampling site (VAL 9), located some 9 km to the west of VAL 8.

In this work we summarize the results of a survey on water Hg contents and quality, in relation to all this mining and metallurgic activity. The study includes monthly variations in the parameters and metal contents during 18 months, and includes the characterization of reference areas, located next to the district.

MATERIALS AND METHODS

During the period of March 2004 - August 2005 we have performed a semicontinuous (monthly) monitoring of mercury contents on unfiltered and filtered waters in the streams waters of the Almadén mercury mining district. The sampling network includes 16 stations in the main streams of Valdeazogues watershed, not only in the neighbourhood of the mining and metallurgical plants, but also in reference areas of the same river and its tributaries (Los Alamos River, La Pila and Azogado streams) and several stations occasionally sampled of springs or drinking water reservoirs. Figure 1 displays sampling sites locations.

The sampling method was based upon the USEPA (1996) criteria for sampling ambient water for trace metals (method 1669). The samples were collected in 100 ml plastic flasks, preserved with 0.5 ml of ultrapure HNO_3 and the same quantity of $KMnO_4$ and fridged below 4ºC until the analysis (Parker et al., 2004). Samples for soluble mercury analysis were filtered in situ with syringe filters of 0.45 µm (Horowitz et al., 1996). Simultaneously, physical-chemical parameters including pH, Eh, conductivity, dissolved oxygen, turbidity and temperature were measured in each sampling site.

The analyses were carried out with a LUMEX RA-915+ analyser, based on Zeeman atomic absorption spectrometry, with high frequency modulation of light polarization (ZAAS-HFM) (Sholupov and Ganeyev, 1995), using the RP-91 Cold Vapour accessory and $ClSn_2$ as reducer agent . Dissolutions with know concentrations were prepared every day for calibration, from certified standards.

RESULTS AND DISCUSSION

As we explained in the introduction, the area has a well developed drainage network, and its general climatic conditions include dry summers and winters, that's the reason why the Valdeazogues River flows preferably in springs and autumns. A typical profile of the mercury contents in the Valdeazogues River and its tributaries from upstream to downstream is shown in *Figure* 2 and corresponds to January 2005. The background levels (0.006 – 0.041 µg/l) are located 10 Km to the East of El Entredicho open pit, the first mining activity along the Valdeazogues river. From this site to the mouth of the river in La Serena reservoir, located some 10 Km to the west of the main mining area, there are several punctual sources of mercury to the waters, as indicated by the mercury contents variations throughout the river course.

In the Valdeazogues River course, the old mine of El Entredicho produces a strong contrast between contents upstream (0.150 µg/l) and downstream this point (0.780 µg/l in average). The second main source of mercury is Los Alamos river, the site of Las Cuevas mine (0.368 µg/l). After that, the next location with high mercury

contents is the town of Almadén, with La Pila (0.626 μg/l) and Azogado (1.327 – 1.733 μg/l) streams draining the area. The rest of the drainage network has Hg contents lower in average (0.006 – 0.413 μg/l). At La Serena reservoir, values of total mercury (0.156 μg/l are higher than in the reference site upstream from the mining area (0.033 μg/l).

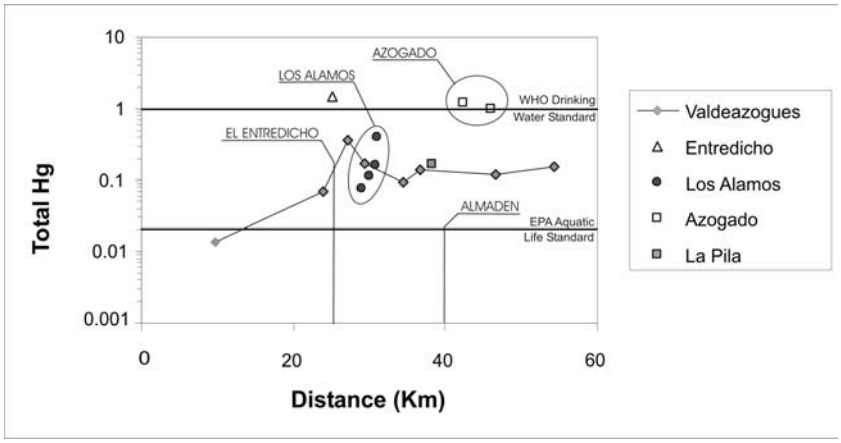

Figure 2. Contents of total mercury (in μgr/l) along Valdeazogues River and its tributaries in January 2005.

Mercury contents, as shown in *Figures* 3 and 4, reach maximum values during the dry months, and decrease during the rainy ones. This effect is more evident in Valdeazogues River, with higher water flow than tributaries and with more dilution too.

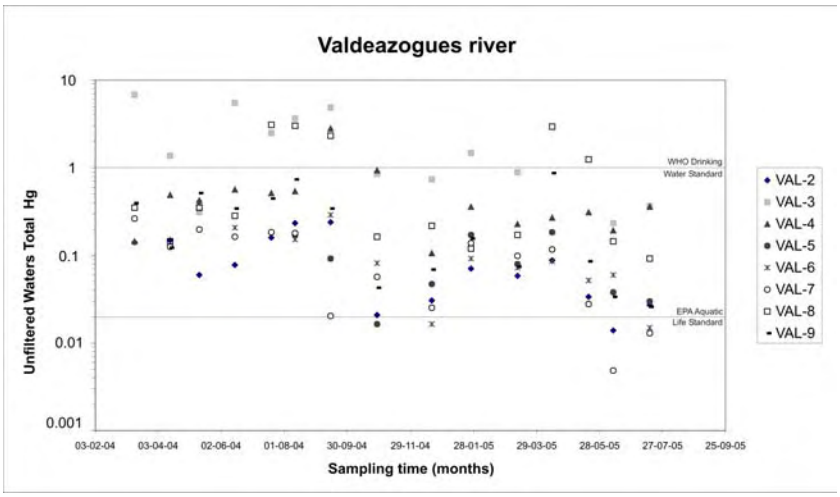

Figure 3. Total mercury contents (in μg/l) of Valdeazogues River between March 2004 and July 2005.

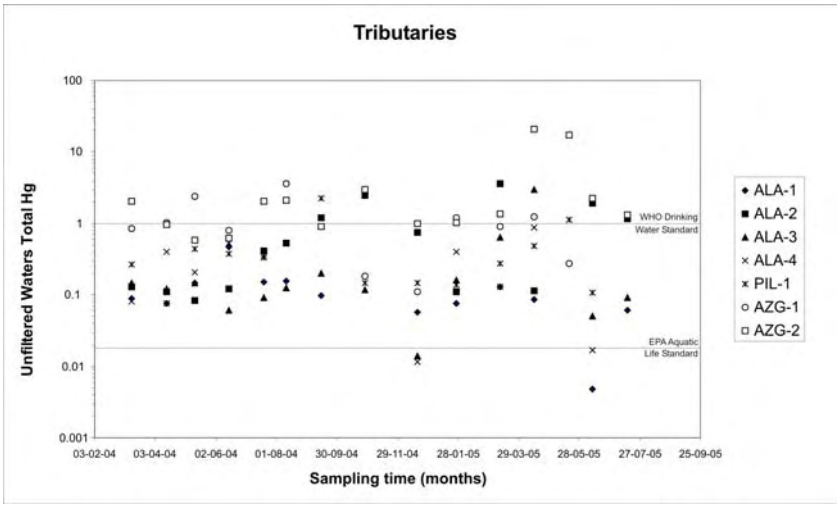

Figure 4. Total mercury (in µg/l) contents of tributaries of Valdeazogues River between March 2004 and July 2005.

This monitoring of Almadén waters has included random sampling of springs and reservoirs, which has put forward very low values of total mercury in the springs (0.008 – 0.062 µg/l), and even lower Hg contents in Ribera de Gargantiel reservoir (0.001 – 0.003 µg/l), that stores the drinking waters for Almadén population.

The maximum values for total mercury in the studied area have been found in El Entredicho pit lake (3.573 µg/l) and in the streams that drain the city of Almadén: Azogado stream (1.733 µg/l) and La Pila stream (0.626 µg/l). These results are similar to other measured in recent years (Gray et al., 2004). In that study, the amounts of MeHg measured in Azogado stream were the highest observed in waters samples collected near other Hg mines worldwide. In this sites the maximum content of soluble Hg is low (2%-37%) compared with the rest of the sites (3%-90%).

As consequence of the intentional flooding of El Entredicho Hg mine pit during the spring of 2004, contents of mercury increased (0.143 µg/l – 0.488 µg/l) downstream and decreased (6.805 µg/l – 1.365 µg/l) in the pit itself.

Most of the mercury transported by the fluvial course is in particulate form, as it can see in *Figure* 5. The lower proportion of soluble mercury belongs to sites with also higher total mercury contents. For example, El Entredicho pit lake have 3.573 µg/l of total mercury in average and 19%–34% of dissolved mercury. In the other hand we have the reference site of El Quintillo, with the lowest total mercury content (0.033 µg/l) and a high proportion of dissolved mercury (77%-90%).

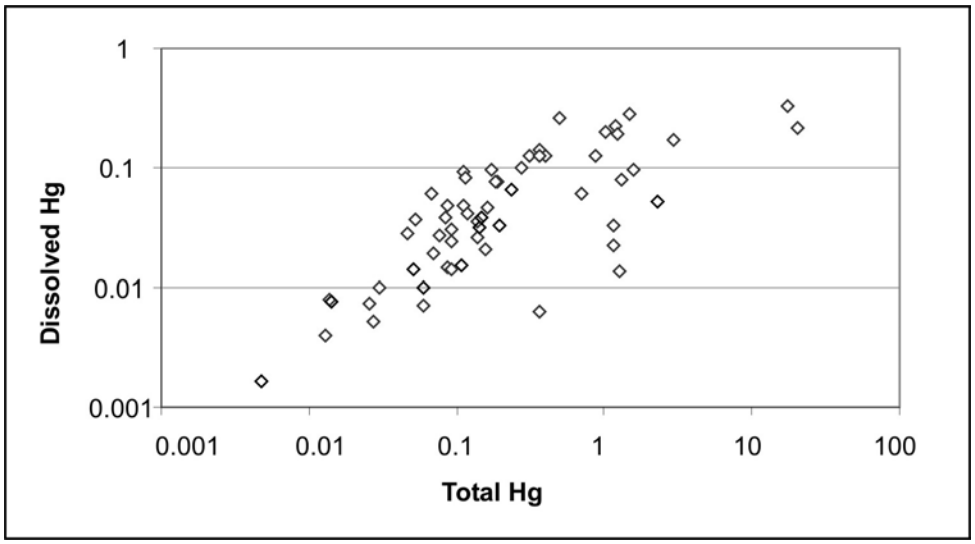

Figure 5. Relationship between total mercury and dissolved mercury (in µg/l).

CONCLUSIONS

As expected in an area that has been subjected to mining for about 2,000 years, the waters of the Almadén mining district have high mercury contents. There is a significant amount of mercury that has been discharged to La Serena reservoir, as we could see in the difference between Hg content of reference site (0.033 µg/l) and La

Serena reservoir (0.156 μg/l). Most of this transported mercury is in particulate form and come from well located sources: El Entredicho pit lake, Las Cuevas mine, and the town of Almadén.
Most of the sites have mercury contents higher than standard for aquatic life (> 0.012 μg/l), and this Hg is being transferred to the food web as demonstrated in bivalves (Berzas et al., 2003) and fish and crayfish (Higueras et al, 2005).
In sites like Azogado stream and Entredicho pit lake, total mercury concentrations exceeds international drinking water standard (WHO, 1971), but these sites are not a source of drinking water to the people of Almadén. In the town drinking water comes from Ribera de Gargantiel reservoir, which values of total mercury were in a low range of 0.001 – 0.003 μg/l during 2005.
Springs waters have mercury contents lower than WHO standards too, even near old mines, like Peñarroya spring (0.022 – 0.062 μg/l), close to El Entredicho open pit.

ACKNOWLEDGEMENTS
This research was founded by Spanish *Ministerio de Ciencia y Tecnología* (Grant PPQ2003-01902).

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