The Almadén district (Spain): Anatomy of one of the world's largest Hg-contaminated sites

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Abstract

We present data from an early reconnaissance survey (stream sediments, soil, and water Hg chemistry; plants and water crustaceans Hg intake) of the Almadén district (central Spain), that was carried out to establish the potential environmental hazards derived from the anomalous mercury concentrations measured in this realm. The Almadén mercury district (~300 km^2) can be regarded as the largest geochemical anomaly of mercury on Earth. The district includes a series of mercury mineral deposits, having in common a simple mineralogy (dominant cinnabar: HgS, and minor pyrite: FeS_2). The ore deposits have been mined for more than 2000 years, and the main mine of the district (Almadén), has been active from Roman times to present day with almost no interruptions. The mercury distribution in soils of the district reveals the existence of high, and extremely high mercury values (up to 8889 $\mu g\ g^{-1}$), whereas concentrations in stream sediments and waters reach exceptional values of up to 16,000 $\mu g\ g^{-1}$ and 11,200 $ng\ l^{-1}$ respectively. On the other hand, very high concentrations of methylmercury (MeHg) have been detected in calcines (up to 3100 $ng\ g^{-1}$), sediments (0.32–82 $ng\ g^{-1}$), and waters (0.040–30 $ng\ l^{-1}$). Mercury gets incorporated to edible river crustaceans and plants. The red swamp crayfish *Procambarus clarkii*, has Hg concentrations of up to 9060 $ng\ g^{-1}$ (muscle) and 26,150 $ng\ g^{-1}$ (hepatopancreas). Regarding plants, the local wild asparagus (*Asparagus acutifolius*) yields values of up to 298 $\mu g\ g^{-1}$ Hg. Mercury also escapes to the atmosphere, and mineral deposits, together with metallurgical activities, generate strong anomalies of atmospheric Hg. The most important concentrations relate to the emissions from the Almadén metallurgical roaster, in the order of 14,000 ng Hg m^{-3}. Additionally, large open pit operations also contribute to the district atmospheric pool of mercury, with high concentrations above 1000 ng Hg m^{-3}. Thus, no system (rocks, soils, sediments, waters, atmosphere, biota) in the Almadén district is free from strong Hg contamination.

Keywords: Mercury; Contamination; Almadén; Soils; Sediments; Water; Atmosphere

1. Introduction

Mercury is well known as one of the most toxic metals in nature, and the Almadén mining district (Fig. 1) constitutes the world's largest natural concentration of this element (Saupé, 1990; Higueras et al., 2000a,b; Hylander and Meili, 2003). Because of this reason, the Almadén district can be regarded as one of the most Hg-contaminated places on Earth (natural and anthropogenic induced pollution), and as such supposes a clear hazard to human health and the environment, as shown by partial preliminary studies on the district, e.g., Ferrara et al. (1998), Berzas Nevado et al. (2003), Fernández Martínez and Rucandio (2003), Higueras et al. (2003), and Gray et al. (2004). The Almadén district extends throughout an area of about 300 km^2 in central Spain, and has produced one-third of the total world production of this chemical element. The district includes a series of mercury ore deposits having in common a rather simple mineral assemblage, including dominant cinnabar (HgS) and minor pyrite (FeS_2). The best known deposit of the district is Almadén, which together with El Entredicho represent the classic type of minerali-

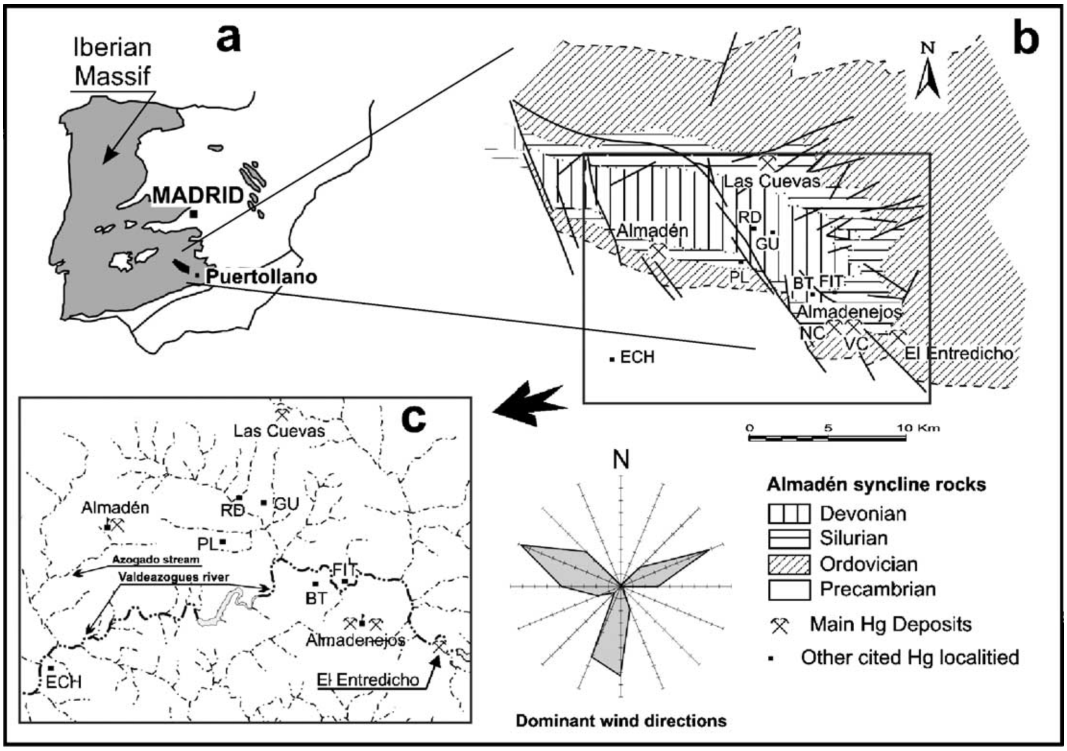

Fig. 1. a) The Iberian Massif and location of the Almadén district; b) simplified geologic map of the Almadén district, with location of mines, prospects, and other localities; BT: Burcio-Tres Hermanas, ECH: Chillón sampling area, FIT: phytoremediation sampling area, GU: Guadalperal, NC: Nueva Concepción, PL: Pilar de la Legua, RD: Rodoviejo, VC: Vieja Concepción; c) stream network (only the major streams have been plotted). After Higueras et al. (1999), Higueras et al. (2000b).

zation for which the district is generally known (Fig. 1). The mercury ore has been mined for more than 2000 years, and the oldest reference is from Pliny the Elder, who mentions the area as the site for the best vermilion for the dyes of the togas of the Roman principals. Almadén, the main mine of the district, has been active from Roman times to present day, with almost no interruptions, except by those caused by mining disasters (floods, fires), or external factors, e.g., wars. Thus, the least one would expect after 2000 years of mercury mining is district-wide contamination, which constitutes the main reason for this study: no other region in the world has been subjected to such an environmental impact for a longer time span. We show the results of combined stream sediments, waters, soils, and atmospheric geochemical surveys, as well as preliminary data on mercury concentrations on river crustaceans and plants.

2. Materials and methods

The surveys carried out in the Almadén mining district were aimed to cover different aspects of contamination pathways. The soil geochemical survey (67 samples) covered significant sites in the district (Fig. 1): the Almadenejos abandoned metallurgical site, the Chillón railway station area (detrital accumulations of cinnabar), the Rodoviejo area (Hg geochemical anomaly, mineral outcrops), and the phytoremediation testing area (Hg geochemical anomaly; detrital accumulations of cinnabar). In all these sites the samples were taken at different depths, using an Eijkelkamp 04.15.SA undisturbed soil sampler device. The stream sediment sampling corresponds to a reconnaissance survey ordered by MAYASA (Minas de Almadén y Arrayanes S.A.; the Almadén mining company) to allow detection of high-level Hg anomalies throughout the district. The survey was comprehensive, and more than 6000 samples were collected. Soil and stream sediment samples were dried at room temperature and sieved to <63 μm. Total Hg content in dried samples (50 mg) was analysed by means of Cold Vapor Atomic Absorption Spectroscopy (CV-AAS) at the MAYASA laboratories, with detection limits of 2 ng g^{-1} (soils) and 1 μg g^{-1} (sediments). These surveys were complemented with a stream water survey following the USEPA (1996) criteria for sampling ambient water for trace metals (method 1669). The survey concentrated in the heart of the district, with several sampling stations. Unfiltered water samples were collected in 100 ml plastic flasks, and preserved with ultrapure HNO_3 and 5 ml of $KMnO_4$. The Hg atmospheric surveys were carried out along the main roads of the district using a LUMEX RA-915+ (air) analyzer for continuous Hg measurements. The instrument allows determination of Hg in air directly with an ultra low detection limit in real time. This detection limit is governed by shot noise and equals CaDL = 2 ng m^{-3} (average measuring time = 5 s). The LUMEX RA-915+ analyzer is a highly versatile instrument, based on Zeeman atomic absorption spectrometry, with high frequency modulation of light polarization (ZAAS-HFM) (Sholupov and Ganeyev, 1995). Application of Zeeman background correction and a multipath analytical cell provide high selectivity and sensitivity of measurements. Addition of the RP-91 (cold vapor) and RP-91C (pyrolysis) attachments allows Hg measurements in liquid and solid samples. These attachments were used for the analyses of stream waters, soils, dried plants, and lyophilized tissues of crayfish, at the laboratories of the Almadén School of Mines. Detection limits for the different types of samples are: 0.5 ng l^{-1} (waters), 0.5 μg kg^{-1} (soils), 2 μg kg^{-1} (plants), and 5 μg kg^{-1} (tissues). Quality control at the laboratory was done by analyzing duplicate samples to check precision, whereas accuracy was obtained by using certified standards. Thermal speciation analyses of selected soil samples were carried out at the Institute of Environmental Geochemistry of the University of Heidelberg, by Hg pyrolysis (for details see: Biester and Scholz, 1997; Biester et al., 1999). This method has proved to be a useful technique to distinguish cinnabar (HgS) from mercury bound to organic matter, and other species such as native mercury, metacinnabar, HgO, and $HgSO_4$ (among others; Biester et al., 1999). Quality control at the laboratory was done by analyzing duplicate samples to check precision, whereas accuracy was obtained by using certified standards.

3. The Almadén district: main features

The Almadén district is located within the so-called Meseta Sur (the Spanish southern mesa), which has a

Mediterranean climate with hot summers and cold winters, with average annual precipitations in the order of 400 mm. Average temperatures range from 1 to 8 °C in January to 17 to 31 °C in July. The soils of the district are mainly entisols, with localized development of anthrosols. Entisols are soils of recent origin, developed in unconsolidated parent materials with usually no genetic horizons except an A horizon. Anthrosols are soils that form or are profoundly modified through human activities, such as the addition of wastes or organic materials.

From the geologic viewpoint, the Almadén mercury deposits are located in the southern area of the so-called Central Iberian Zone of the Iberian massif, in one of the characteristic geologic structures: the Almadén syncline (Fig. 1). The stratigraphic succession of the latter includes sedimentary rocks with volcanic interbeddings, which can account for the major part of the stratigraphic record. The magmatic rocks are very common in the Silurian and Lower Devonian sequence, forming the so-called Volcano Sedimentary Group (Upper Devonian–Frasnian). There are two types of rocks particularly relevant to mercury mineralization in the district: quartzites at different stratigraphic levels (e.g., the Criadero Quartzite, the Las Cuevas Quartzite), which usually host the ore, and the so-called *frailesca* rocks, explosion volcanic breccias, which are spatially related to the mercury deposits. The district includes the huge Almadén mine (underground), with original reserves of 7.5 million flasks (commercial unit for Hg sale: 34.5 kg of the metal), whereas the second in importance, El Entredicho (open pit), is far away from this figure, with 350,000 flasks as original reserves. Other deposits in the district include those of Las Cuevas, Burcio-Tres Hermanas, Corchuelo, Guadalperal, Nueva Concepción, Vieja Concepción, and Pilar de la Legua (Fig. 1). The metallurgy of cinnabar in Almadén is very simple, and involves the roasting of the ore, which decomposes at temperatures in the order of 300 °C. Mercury is subsequently recovered from the vapours by condensation. The technique evolved from primitive systems, using pottery (the so-called *xabecas* furnaces), through the use of pottery lines for condensing the vapours (the so-called *aludeles* furnaces), to the modern *Pacific* furnaces of rotatory type, fuelled by propane gas.

4. The geochemical surveys: results and discussion

4.1. Stream sediments and waters

The district has a well-developed drainage network. The local streams, mostly dried during the hot summer, become active during the autumn and spring months (winter is cold and rain deprived). Thus, the area is adequate for stream sediment sampling, and allowed collection of closely spaced 6061 samples. The survey covered an area (1500 km^2), which is much larger than that of the district s.s. (~300 km^2). To avoid statistical distortions induced by some extremely large mercury concentrations (of up to 16,000 $\mu g\ g^{-1}$), we eliminated data above the mean plus three times the standard deviation (i.e. $>1092.3\ \mu g\ g^{-1}$), which left nevertheless a large set of 6044 data (Table 1). The new variance is about two hundred times lower than the initial, and therefore, the corrected data set constitutes a more homogeneous and reliable population, better suited for geostatistical analysis. The latter is an important aspect of this work, because variogram modelization and subsequent kriging allows a better understanding of the regional distribution of a variable. Since stream sediment surveys are determined by the direction of the fluvial courses, one may argue that this technique generates a biased sampling, and therefore, a strong anisotropy on its own. For example, the drainage network in the Almadén region is defined by two main trends: NW–SE and NE–SW. However, in our case we must take into account three facts: 1) the high density sampling throughout the Almadén district and beyond (1500 km^2; >4 samples km^{-2}) minimizes this possible effect; 2) the Almadén drainage main directions reflect the regional geology, characterized by the existence of well-defined fracture trends at NE–SW (major) and NW–SE (minor); and 3) as a result of the latter, these trends mark the main pathways for Hg migration–contamination in the district.

Data were treated with the statistical package Surfer 8. The plot resulting from the experimental variogram adjust to a spherical model with strong nugget effect (Fig. 2). Given that the sample variance (sill) is at 800 $(\mu g\ g^{-1})^2$, and the curve interception with the $\gamma(h)$ axis occurs at 527 $(\mu g\ g^{-1})^2$, we can infer that about 66% ($527 \div 800$) of the variation in the sample

Table 1
Concentrations of Hg for Almadén, other mining districts, and baseline data

Locality	Number of samples	Range	Mean	Standard deviation	Reference
Hg in stream sediments (data in $\mu g\ g^{-1}$)					
Almadén district (all data)	6061	0.5–16,000	19.5	357.6	
Almadén district (filtered data)	6044	0.5–800	5.9	25.6	
West-Central Nevada Hg mines (USA)		0.008–170			Gray et al. (2002)
Punitaqui Cu–Au–Hg mining district (Chile)		0.3–5.3			Higueras et al. (2004)
Lake sediments		0.01–0.45			Fitzgerald and Lamborg (2004)
Baseline streams, SW Alaska		0.02–0.78			Gray et al. (2004)
Hg in soils (data in $\mu g\ g^{-1}$)					
Almadén district	67	6–8889	604.1	1798.5	Higueras et al. (2003)
Mieres mining sites (northern Spain)		1.7–2224			Loredo et al. (1999)
Azogue Valley mining sites (southeastern Spain)		6–1400			Viladevall et al. (1999)
Andacollo Cu–Au–Hg mining district (Chile)		2.5–47			Higueras et al. (2004)
Punitaqui Cu–Au–Hg mining district (Chile)			2.2		Oyarzún et al. (2001)
Punitaqui Cu–Au–Hg mining district (Chile)		3.2–16			Higueras et al. (2004)
Uncontaminated soils (baseline)		0.01–0.03			Senesi et al. (1999)
Hg in stream waters (data in $\mu g\ l^{-1}$)					
Almadén district	115	6–11,200	3518.9	1532.4	This work, Gray et al. (2004)
Hg mines (downstream) from Nevada (USA)		6–2000			Gray et al. (2002)
Baseline streams from SW Alaska (USA)		0.1–1.4			Gray et al. (2004)
Baseline for Almadén		9.1–43			Gray et al. (2004)
Health and environmental concerns: standard for aquatic life (USEPA, 1992): 12 ng l^{-1}; maximum contaminant level for drinking water (USEPA, 2004): 2000 ng l^{-1}					
Atmospheric Hg (data in ng Hg m^{-3})					
Almadén district (March)	15,337	2–9485	213.9	644.9	
Almadén district (June)	3760	2–6892	195.7	514.2	
El Entredicho mine (March)	932	2–605	27.7	45.5	
El Entredicho mine (June)	984	2–3111	291.3	567.6	
Mediterranean basin		2–3			Wängberg et al. (2001)
Northern Europe		~1.8–2			Wängberg et al. (2001)
Canada		1.3–1.8			Kellerhals et al. (2003)
Health and environmental concerns: maximum atmospheric Hg, revised air quality guidelines for Europe (WHO, 2000): 1000 ng Hg m^{-3}					

values is random (e.g., Clark, 1979), for which the range value (6900 m) should be taken with much caution (Fig. 2). Subsequent point linear kriging based on the previous variogram modelization, allowed recognition of two trends, one with major Hg anomalies (NE–SW) and a second one of relatively minor importance (NW–SE) (Fig. 3a). The first one includes mines or mineral prospects such as Almadén, Pilar de La Legua, or the highly polluted Azogado River, whereas the second one comprises the mineralized areas of El Entredicho and Almadenejos, among others. Given that both drainage trends are similar in importance and distribution, we must conclude that the potential Hg-derived environmental hazards in this realm have a strong NE–SW component (Fig. 3a). Apart from these considerations, the stream sediment samples from Almadén have Hg concentrations that strongly depart from the values measured in non-contaminated sediments. For example, the mean Hg concentration (after data filtering) for the Almadén samples is 5.9 $\mu g\ g^{-1}$ ($S=25.6$), a figure much higher than the average for sediments (range: 0.01–0.78 $\mu g\ g^{-1}$; Gray et al., 2004; Fitzgerald and Lamborg, 2004) (Table 1), and closer to polluted areas from elsewhere, e.g., 0.008–170 $\mu g\ g^{-1}$ (West-Central Nevada Hg mines, USA; Gray et al., 2002) or 0.3–5.3 $\mu g\ g^{-1}$ (the Punitaqui Cu–Au–Hg mining district, Chile; Higueras et al., 2004)

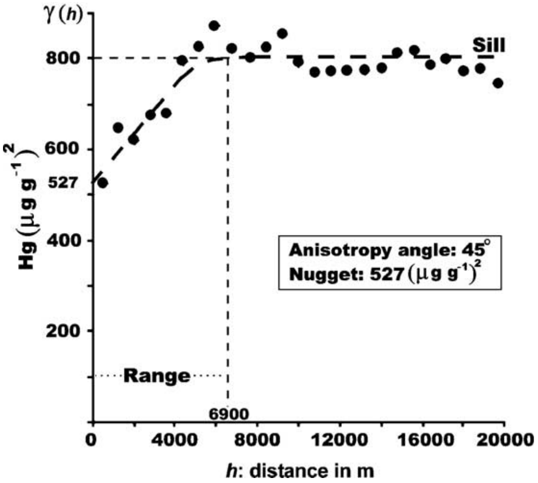

Fig. 2. Experimental variogram for the Almadén stream sediment data ($n = 6044$). The data adjust to a spherical model with a strong nugget effect Direction of the anisotropic trend: N 45° E (see also Fig. 3a).

(Table 1). Moreover, the truly high concentrations of Hg in Almadén (even after data filtering), reach exceptional values in the order of several hundreds microgram per gram. The latter figures concentrate near to the mines (e.g., Almadén, Las Cuevas), abandoned metallurgical installations (Almadenejos), or along the highly polluted Azogado stream (*azogado*, old Spanish for 'mercury bearer'), thus defining contamination 'hot spots' (Fig. 3a). The case for waters is similar, with a range of Hg concentrations from 6 to 11,200 ng l^{-1} (Table 1). As expected the highest figures follow a distribution pattern equivalent to that of the stream sediments, with maxima mean values near to the mines (e.g., Almadén), within the flooded El Entredicho open pit, and along the Azogado stream (Fig. 3b). However, even the lowest Hg concentrations in stream waters from the district are to be regarded as very high figures if compared to baseline concentrations, e.g., 0.1–1.4 ng l^{-1} (SW Alaska; Gray et al., 2004) (Table 1). Apart from this, some of the highest concentrations in the Almadén stream waters are far above the maximum contaminant level for drinking water (MCL, as defined by the USEPA, 2004) at 2000 ng l^{-1} Hg. Last but not least, most of the detected concentrations are also higher than USEPA (1992) standard for aquatic life at 12 ng l^{-1} (4-day average concentration), and as discussed later in this work, part of the mercury present in the Almadén stream waters is indeed introduced to aquatic life.

4.2. Soils

The soil geochemical survey for mercury (Table 1) was more restricted and comprised four zones within the district representing end members of different potential contamination sources (Higueras et al., 2003) (Fig. 1) (Table 1): 1) The Almadenejos metallurgical site, an abandoned metallurgical precinct, active between the 17th and 18th centuries, and finally decommissioned in 1860, characterized by the presence of thin anthrosols developed on top of Silurian shales and volcanic rocks, which in places have primary mercury contents. 2) The Chillón railway station area, where mercury was suspected to be accumulated by detrital processes in an alluvial plain (Valdeazogues river), downstream the mining areas. However, a careful inspection of the area showed pottery fragments, which may correspond to *xabecas* type furnaces. 3) The Rodoviejo area, where the presence of cinnabar was detected by means of a soil geochemistry survey for mercury. The area has never been subjected to mining activity, although some mineral outcrops were discovered in the context of the soil survey. Therefore, in this locality the mercury contents are natural, coming from the weathering of the mineralizations. 4) The phytoremediation area, near to the Almadenejos metallurgical precinct. Hg contents in soil were detected by means of soil geochemistry. As expected, the anthrosols from the Almadenejos old metallurgical site display the most scattered set of Hg concentrations (6–8889 μg g^{-1}). The other sampling areas, i.e., Chillón, Rodoviejo, and the phytoremediation site (entisols) are in the ranges 12–132, 10–188, and 6–69 μg g^{-1} Hg, respectively. These values should be considered as normal for a region so rich in mercury deposits and subjected to such an intense and prolonged mining activity. For example Loredo et al. (1999) report values of mercury in soil samples near spoil heaps (Mieres, northern Spain) in the range of 1.7–2224 μg g^{-1} Hg, whereas Viladevall et al. (1999) indicate contents of 6–1400 μg g^{-1} Hg in soils and overburden from a mineralized area in Azogue Valley (SE Spain). Biester et al. (1999) report concentrations from Idria (Slovenia) of up to 1000 μg g^{-1} Hg. However, compared to 'normal soils' (i.e., not subjected to

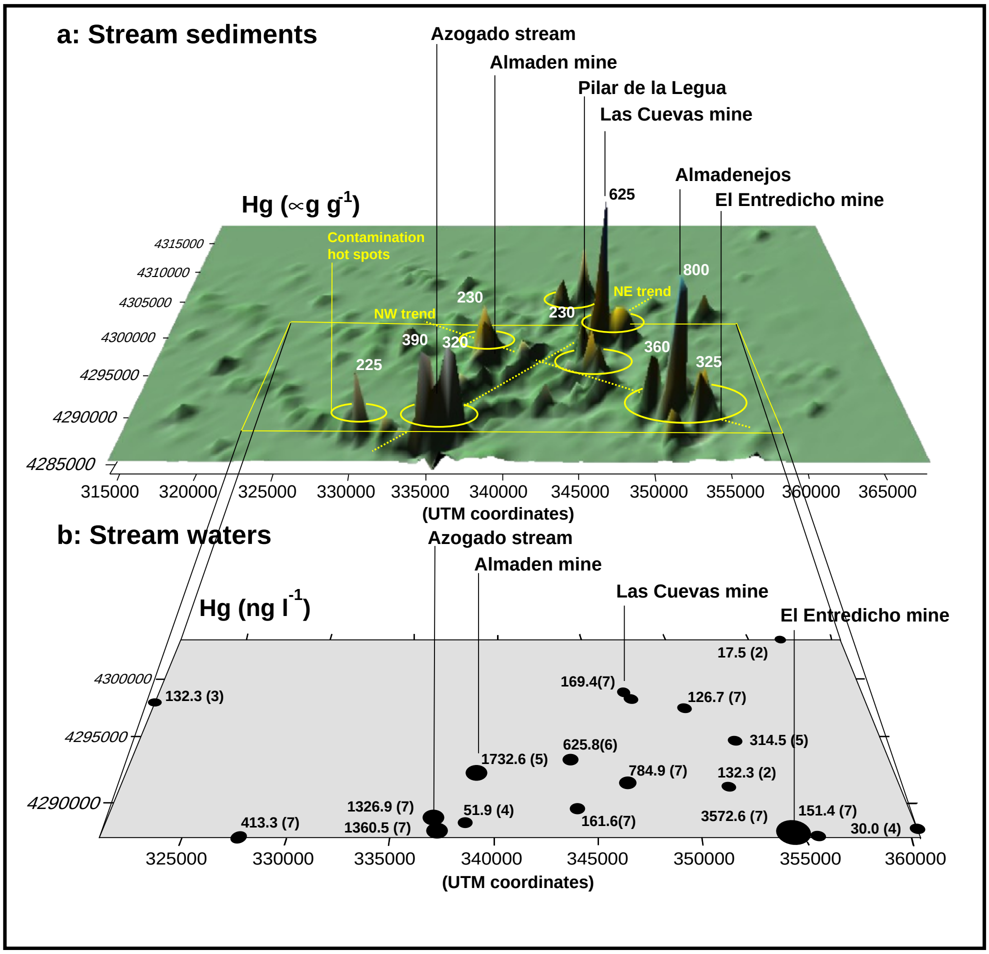

Fig. 3. a) 3D representation of stream sediment Hg data ($\mu g\ g^{-1}$) for the Almadén district after variogram modelization (see Fig. 2) and subsequent point linear kriging. b) Mean values and number of data for Hg concentrations ($ng\ l^{-1}$) in stream waters. The area is also depicted in (a): central rectangle. The solid circles indicate sampling sites and are proportional in size to the mean Hg value. Coordinates in UTM for (a) and (b).

active contamination), the Almadén concentrations are extremely high. Given that the usual contents of mercury in soils are in the range of 0.01–0.03 $\mu g\ g^{-1}$ Hg (Senesi et al., 1999) (Table 1), we may conclude that the studied soils from Almadén are enriched in mercury by a factor of 10^2–10^5. A major point regarding mercury in soils relates to the chemical and/or mineralogical species present in them. The thermal speciation analyses were carried out on samples from the Almadenejos abandoned metallurgical precinct (Fig. 1). This area is characterized by thin anthrosols, developed on top of slates and volcanic rocks, which in places have primary mercury contents. The samples were taken not only from the metallurgical site proper, but also from the areas hosting the old mineral dumps. The X-ray diffraction analyses of the clay size fraction reveal that these soils are smectite-poor (main minerals: illite–pyrophyllite–chlorite–kaolinite), which severely reduces the possibility of cation exchange. Thus mercury is not retained at interlayer sites but adsorbed to the surface of the other phyllosilicate minerals. The Hg-thermo-desorption curves (Hg-TDC) of the Almadenejos samples display a characteristic pattern defined by peaks at 200–220 °C, and 310 °C, which suggest the presence of mercury in the form of cinnabar (310 °C peak, Biester et al., 1999), and that of mercury bound to organic matter (forest soil, humic acids: 200–240 °C, Biester et al., 1999) (Fig. 4). These soils from Almadenejos supported the activity of five furnaces, which may have processed some 300,000 flasks of mercury during its period of activity (main period: 17th and 18th centuries). This would have involved intensive transport of cinnabar to the metallurgical plant, and therefore we would expect that part of the mineral went directly to the soils via careless handling. On the other hand, we do not rule out a source related to the gaseous mercury emitted by the furnaces, which may have been deposited in the surrounding soils as Hg^{2+}, either from direct deposition of emitted Hg^{2+}, or from conversion of emitted Hg^0 to Hg^{2+} through ozone mediated processes (USEPA, 1997) (g: gas phase; aq: aqueous phase; p: particulate phase):

$$Hg^0_{(g)} \rightarrow Hg^0_{(aq)}$$

$$Hg^0_{(aq)} + O_{3(aq)} \rightarrow Hg^{2+}_{(aq)}$$

$$Hg^{2+}_{(aq)} + \text{soot/possible evaporation} \rightarrow Hg^{2+}_{(p)}$$

Once deposited, the Hg^{2+} would have formed complexes with the Almadenejos soil organic matter (e.g., fulvic or humic acid), as shown by the Hg-thermodesorption curves. Whatever the case, the Almadén soils can be regarded as extremely contaminated with Hg, and some of them have the highest concentrations of MeHg (up to 3100 ng g^{-1}) ever reported from mining sites (Gray et al., 2004).

4.3. Atmospheric mercury

Atmospheric mercury concentrations in the Mediterranean basin (in the order of 2–3 ng Hg m^{-3}) relate to the existence of large and very large mercury mineral deposits and districts in this realm: Idria (Slovenia), Monte Amiata (Italy), and Almadén (Spain) (Wängberg et al., 2001). These Mediterranean concentrations are larger than those observed in northern Europe (~1.8–2 ng Hg m^{-3}) or Canada (1.3–1.8 ng Hg m^{-3}) (Wängberg et al., 2001; Kellerhals et al., 2003). Naturally enriched zones are long-lived sources of mercury to the global mercury atmospheric cycle (Gustin et al., 2000), and in this respect, the Almadén district may play an important role. An earlier, preliminary survey for atmospheric mercury in the Almadén district covered an area of 6 km^2, centered on the small mining town of Almadén (Ferrara et al., 1998). However, given the size of the district (~300 km^2) a larger survey was required to assess the potential hazards derived from both, the metallurgical operations carried out at Almadén, and other potential sources: ore deposits, mineral dumps, and contaminated soils. The latter is particularly relevant, because ore deposits are significant sources of gaseous mercury (Gustin, 2003). Thus, to study the district in its whole extent we carried out two surveys (March and June). The vast majority of the atmospheric Hg concentrations measured in the surveys can be regarded as anomalous, i.e., they are much higher than: 1) our local baseline measured in Puertollano (3.4 ng Hg m^{-3}), 70 km to the west of Almadén (Fig.

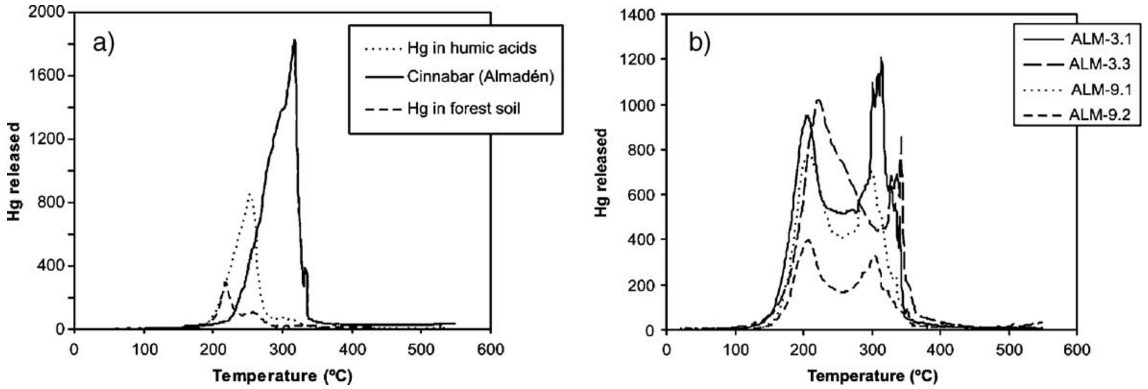

Fig. 4. Thermodesorption curves of mercury: a) standard thermodesorption patterns for Hg in the forms of cinnabar, forest soil, and humic acid (after Biester et al., 1999); b) thermodesorption curves for soil samples from the Almadenejos (ALM) abandoned metallurgical site, revealing the presence of cinnabar and Hg bound to humic acids and forest soil.

1); and 2) the few nanogram Hg per cubic meter observed in non-contaminated areas (e.g., Wängberg et al., 2001; Kellerhals et al., 2003).

A first approach toward the identification of the sources of atmospheric mercury in the Almadén district leads to the metallurgical (roaster) and mining complex of Almadén town, where Ferrara et al. (1998) measured up to 20,000 ng Hg m^{-3}. The main identified potential sources were the metallurgical plant, the mine ventilation system, the dumps of roasted cinnabar, droplets of native mercury covering the ground in the complex, and the particulate matter carried away by the wind and vehicular activity. However, given the size of the Almadén district we also expected other sources to contribute to the total budget of atmospheric mercury. The March survey showed a mean concentration of 213.7 ng Hg m^{-3}, whereas the June survey has a slightly lower mean concentration (195.7 ng Hg m^{-3}) (Table 1). This apparently odd result for June (warmer conditions—lower mean) can be explained in terms of the inactivity of the Almadén roaster: the furnaces had been shut down for several days when the survey was done. As shown by our measurements the roster generates extremely high Hg concentrations. For example, a static continuous measurement (67 min) at the entrance of the metallurgical site (250 m away from the chimney) showed a mean concentration of 14,236 ng Hg m^{-3}.

Both data sets (June and March) are characterized by a well-defined log-normal distribution. However, compared to the March data the June set shows the appearance of a second population with higher values, centered at about 1000 ng Hg m^{-3}, a case which is also observed in the area of El Entredicho mine (Fig. 5). Both data sets for June (district-wide and El Entredicho) present negative skewness, i.e., the lower values are fewer but farther from the mean than the higher ones.

Since concentration in the substrate is the dominant factor controlling the emission of mercury (Gustin et al., 2000), a naturally enriched realm such as the Almadén district (Table 1) is bound to be an important source of atmospheric mercury. Furthermore, natural-

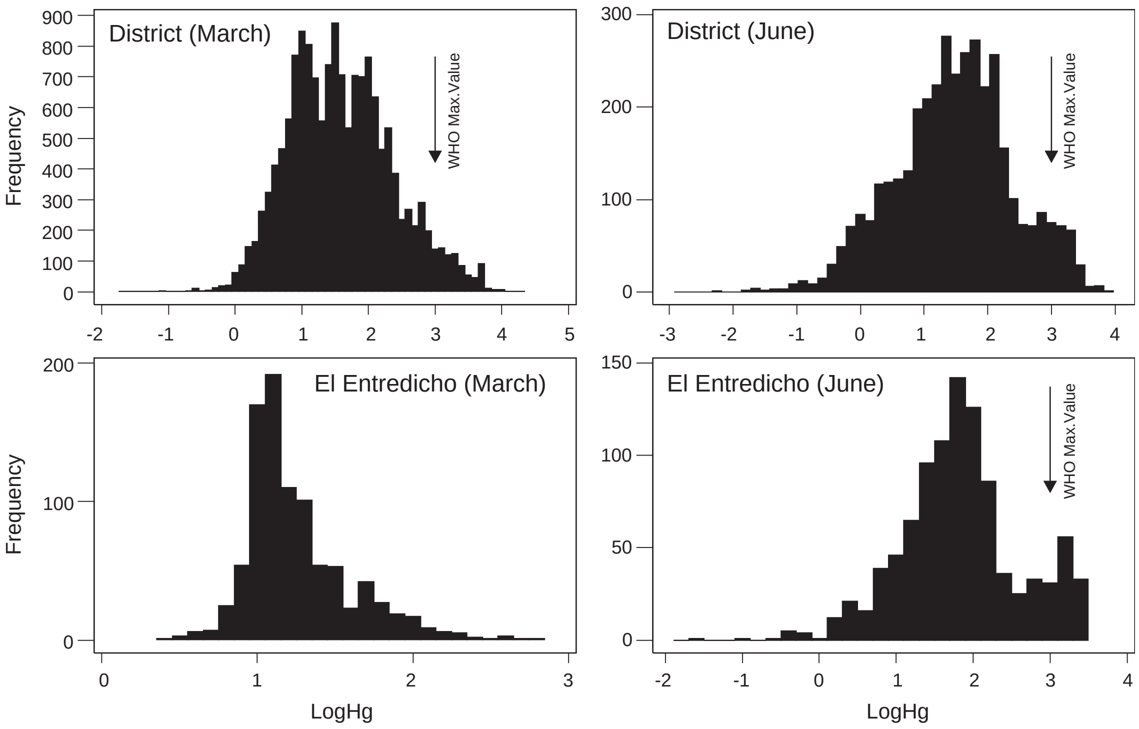

Fig. 5. Histograms for atmospheric Hg data (log ng Hg m^{-3}) from the Almadén district and the surroundings of the El Entredicho open pit mine.

ly enriched sources may contribute with more mercury than previously recognized to the atmospheric mercury pool, as shown by emission data from several sites from Nevada and California (USA), which are an order of magnitude higher than values applied in global models for natural sources (Engle and Gustin, 2000). Considering that an enriched substrate is that one containing >0.1 μg g^{-1} Hg (Gustin et al., 2000), we may regard the Almadén district as a highly enriched realm, with concentration (soils, sediments) largely exceeding 1 μg g^{-1} Hg (Table 1). On the other hand, large concentrations of Hg in ore deposits (>1000 μg g^{-1} Hg), are bound to generate important anomalies of atmospheric Hg (e.g. El Entredicho) (Fig. 5). However, a crucial aspect is provided by the chosen mining method. Underground mines offer little or no exposure of the ore. On the contrary, large open pit operations left the ore exposed to the air, and result in larger anomalies of atmospheric Hg. This is the case of El Entredicho (Fig. 1), where some concentrations of atmospheric Hg exceed the 1000 ng Hg m^{-3} (Fig. 5) (Table 1). According to Lamborg et al. (2002), and Hylander and Meili (2003) the present Hg global anthropogenic contribution is twice as large as natural emissions, a ratio that at Almadén could be much higher. Other European districts/mines where high concentrations of atmospheric mercury have been measured are those of Abbadia San Salvatore (Italy; up to ~1000 μg m^{-3} Hg) (Edner et al., 1993), and Idria (Slovenia; 1–4078 μg m^{-3} Hg) (Gosar et al., 1997).

5. Potential environmental hazards

The edible red swamp crayfish *Procambarus clarkii* is a common species in the biomonitoring programs of metal pollution (Alikhan et al., 1990), and can be found in some rivers and streams of the Almadén district, from where it is caught by the local population. Total Hg concentrations were measured in the tail muscle and the hepatopancreas of adult specimens of *P. clarkii* to assess wildlife Hg bioaccumulation in the Almadén district. Specimens were collected at El Entredicho (near the mine) and at the Pantano de Saceruela (a site located far away from the district). Total Hg concentrations were determined in lyophilized tissues. Concentrations of Hg were significantly higher in the muscle (2380–9060 ng g^{-1} dry weight) and hepatopancreas (2320–26,150 ng g^{-1} dry weight) in specimens from El Entredicho ($n=13$) than in those from Pantano de Saceruela ($n=17$) (muscle = 394–2050 ng g^{-1}; hepatopancreas = 144–1029 ng g^{-1}). It is well-known that the organic form of Hg has a higher tendency for bioaccumulation in aquatic organisms than inorganic mercury, which is explained by its high lipophilicity and stability. Fish uptake of MeHg is mainly from diet, whereas direct uptake from the water can be considered as negligible (Ullrich et al., 2001). In addition, the excretion of MeHg is slower than elimination of inorganic mercury (Trudel and Rasmussen, 1997). These phenomena account for a MeHg transfer along food webs (biomagnification), even in pristine environments (Bargagli et al., 1998). Mercury accumulation by aquatic invertebrates has been scarcely investigated (Boening, 2000). However, similar to the case of fish, MeHg appears to be the form of mercury more efficiently accumulated by aquatic crustaceans, and the soft tissues the primary accumulation sites. In a laboratory experiment, specimens of Norway lobsters (*Nephrops norvegicus*) were exposed for 30–50 days to organic and inorganic mercury in seawater and food. It was concluded that mercury was predominantly accumulated in the hepatopancreas, and the main route for accumulation in this soft tissue was from food (Canli and Furness, 1995). Similarly, uptake of mercury from seawater and food were the main routes for Hg accumulation in tail muscle. Based on this study and others involving fish, we conclude that the highest Hg concentrations found in the hepatopancreas of crayfish collected from the El Entredicho can be explained by an uptake process of MeHg from food. From a toxicological viewpoint, acute toxicity of inorganic mercury (as mercuric chloride) to freshwater invertebrates has been reviewed by Boening (2000). Values of 96h-LC50 of 20 mg l^{-1} and 50 mg l^{-1} have been reported by the crayfish species *Austropotamobius pallipes pallipes* and *Orconectes limosus*, respectively. In our study, total Hg concentrations of up to 11.2 mg l^{-1} have been measured in stream waters; a mercury level in the same order of magnitude of the lethal concentrations of inorganic mercury for crayfish. On the other hand, Hg concentrations found in soft tissue of *P. clarkii* from the

Almadén district should be considered as a high risk to human health. Maxima permissible concentrations of mercury of 0.5 and 1 mg g^{-1} have been suggested by the WHO (1989) and USFDA (1984), respectively. These safety levels are much lower than the total Hg concentrations found in the tail muscle (up to 9060 ng g^{-1}) of *P. clarkii* in our study.

Preliminary studies in the district have revealed high levels of mercury absorption by plants (Higueras et al., 2004). We investigated four areas in the district: Almadenejos, El Entredicho, Las Cuevas, and Nueva Concepción. The results show extreme concentrations of mercury in *Verbascum sinuatum* and *Polypogon monspeliensis*, the latter with Hg concentrations of up to 1500 µg g^{-1} in leaves and 850 µg g^{-1} in roots. Of particular significance are the concentrations of mercury in the roots of the wild asparagus (the so-called "esparraguera": *Asparagus acutifolius*), a plant collected and eaten by the local population, which yields values of up to 298 µg g^{-1} Hg in the roots.

On top of this we have to add the high concentrations of atmospheric mercury derived from natural sources, such as the ore deposit of El Entredicho, where many recorded values are well above 1000 ng Hg m^{-3}. This is particularly significant if we take into account that these concentrations largely exceed the revised air quality guidelines for Europe (maximum at 1000 ng Hg m^{-3}) (WHO, 2000).

6. Conclusions

We have completed the first comprehensive reconnaissance survey (stream sediments, soil, and water Hg chemistry; plant and water crustacean Hg intake) of the Almadén district (central Spain). The data analysis allows recognition of several potential environmental hazards derived from the anomalous mercury concentrations measured in this realm. As expected in an area that has been subjected to mining for about 2000 years, the sediments, soils, and waters of the Almadén district are highly contaminated. We have identified several contamination 'hot spots' (stream sediments and water contamination) in the district (Fig. 3). Among them, the most important are those of the Almadén mine—Azogado stream, Las Cuevas mine, and the El Entredicho mine—Almadenejos old metallurgical site. The Hg-thermo-desorption curves for soils show that mercury is in the forms of cinnabar particulate and as mercury bound to organic matter. Mercury has been transported and introduced to the soils of the Almadén district via: 1) geological dispersion, i.e., cinnabar particulate derived from the erosion of the mineral deposits; and 2) anthropogenic dispersion generated by the mining activity. The latter can in turn be subdivided into two categories: a) mining, transport, and stockpiling; and b) metallurgical activities. The case is equivalent for atmospheric mercury. The waters are also contaminated, with concentrations that largely exceed the standard for aquatic life (>12 ng l^{-1}), and mercury is being transferred to edible river crustacean such as the red swamp crayfish. As discussed above, most of the mercury being incorporated to the biota must be in the organic form (MeHg). In this respect, the concentrations of MeHg in the district are very high in calcines (up to 3100 ng g^{-1}), sediments (0.32–82 ng g^{-1}), and waters (0.040–30 ng l^{-1}).

Compared to other areas in the province (Puertollano: 3.4 ng Hg m^{-3}), or world concentrations (2–3 ng Hg m^{-3}), the Almadén district displays extremely high concentrations of atmospheric mercury, many of them in the order of several thousands nanogram Hg per cubic meter, i.e., above the revised air quality guidelines for Europe. Of particular relevance are those concentrations of Hg measured in the Almadén town, which are well above the WHO guidelines, and affect over 7000 inhabitants. A distressing fact arising from our data concerns the mining methods in the district. We have identified the El Entredicho open pit as one of the most important emission sources of atmospheric mercury in the district, being second only to the Almadén roaster.

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