

Abstract

A first insight into mercury distribution and speciation in soils from the Almadén mining district, Spain

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Abstract

Almost no environmental data on mercury distribution and speciation in soils have been published so far for the Almadén mining district (central Spain), despite its huge size and historic importance. The mercury distribution in soils of the district reveals the existence of high and extremely high mercury values (up to ~ 9000 ppm Hg). The Hg-thermodesorption curves for soils from a decommissioned metallurgical precinct (Almadenejos) and a phytoremediation site show that mercury occurs in the forms of cinnabar and as mercury bound to organic matter. The TEM-EDX study of the highly contaminated anthrosols from Almadenejos (samples with Hg >5000 ppm) shows the existence of cinnabar particles adsorbed to the surface of chlorite grains. Given the generally pyrite-poor character of the ores, and the presence of carbonates in the host rocks, cinnabar solubilization is limited, which in turn mitigates environmental hazards in the district. The only by-product of cinnabar leaching in the mineral dumps is schuetteite (Hg₃SO₄O₂). Preliminary results on local plants (*Asparagus acutifolius*, *Dittrichia graveolens*, *Marrubium vulgare*) show that mercury gets incorporated to roots, stems and leaves, with values of up to about 300 ppm Hg.

Keywords: Mercury; Almadén; Spain; Speciation; Soils; Hg-thermodesorption; TEM-EDX

1. Introduction

The Almadén mercury mining district in central Spain (e.g., [Hernández et al., 1999](#)) ([Fig. 1](#)) can be regarded as the largest known geochemical anomaly of mercury on Earth, having produced one-third of the

total world production of the element. The district includes a series of deposits comprising a variety of structural and textural styles, having in common a rather simple paragenesis including dominant cinnabar and minor pyrite. The best known deposit of the district is Almadén, which, together with El Entredicho, represent the classic type of mineralization for which the district is generally known, i.e., stratabound mineralizations hosted by the so-called Criadero quartzite (Lower Silurian) ([Fig. 1](#)). However, other deposits are truly discordant and cannot be associated

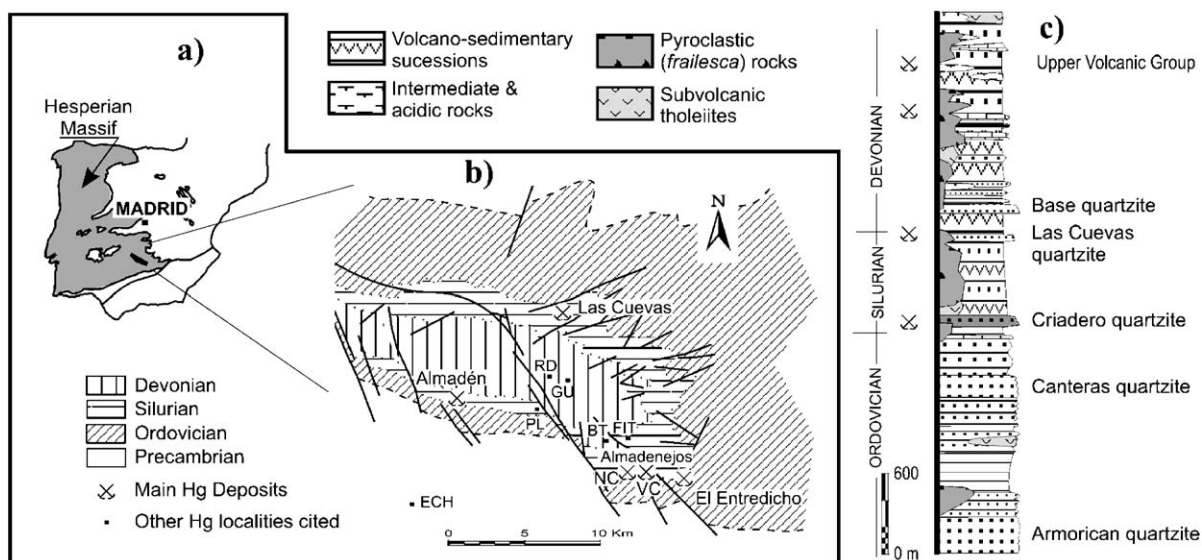


Fig. 1. (a) Location of the Almadén syncline. (b) Geological scheme of the Almadén syncline, with location of mining and sampling areas mentioned in the text. BT: Burcio–Tres Hermanas, ECH: Chillón sampling area, FIT: phytoremediation sampling area, GU: Guadalperal, NC: Nueva Concepción, PL: Pilar de la Legua, RD: Rodoviejo, VC: Vieja Concepción. (c) Stratigraphic column of the Almadén syncline, indicating position of mineralizations (after Higuera et al., 1999, 2000b).

with specific stratigraphic beds (e.g., Las Cuevas) (Higuera et al., 1999). The mineralizations have 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 the present day with almost no interruption except by mining disasters (floods, fires) or by external factors such as wars.

The least one would expect after 2000 years of mercury mining is district-wide contamination of the soils, 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. The results from four sampled areas in the district (Fig. 1) suggest that mercury has been introduced to the soils via three main mechanisms: (1) geologic dispersion from the deposits via erosion processes, (2) anthropogenic dispersion from abandoned mineral dumps and (3) as gaseous mercury deposited in the surrounding soils by the furnace emissions.

Although the emphasis on contaminants is usually put on the atmosphere, water or food, the study of soils may be even of higher importance. Soils affect human

health via direct and indirect links (Abrahams, 2002). The former include ingestion, inhalation and skin contact–dermal absorption. The indirect links include discharge of contaminants to the atmosphere and hydrosphere (gases, particulates, cations, salts, colloidal suspensions) and the incorporation of contaminants to the biosphere, e.g., intake of nutrients by the plants (and from there to the higher levels of the food chain). Given the high to extremely high levels of mercury in the soils of Almadén, and the health risks associated with the element, a first insight into this important issue follows.

2. Geology and mineralization

The Almadén district is located in central Spain, about 300 km to the south of Madrid (Fig. 1). The area is part of the so-called Meseta Sur, which has a Mediterranean climate with hot summers and cold winters, with average annual precipitations of ~ 400 mm. Average temperature ranges from 1–8 °C in January to 17–31 °C in July. The soils of the district are mainly entisols, with localized development of anthrosols. Entisols are soils of recent origin devel-

oped 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.

The Almadén mercury deposits are located in the southern area of the so-called Central Iberian Zone (CIZ) of the Hercynian Iberian massif in one of the characteristic tectonic 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 scarce in the Ordovician and very common in the Silurian and Lower Devonian sequence, forming the so-called Volcano-Sedimentary Group (Upper Devonian–Frasnian). The magmatic rocks are of varied lithologies, and can be grouped in four major groups (Higuera et al., 2000a). (1) Porphyritic rocks of variable composition, ranging from basanites/nephelinites through olivine basalts, trachybasalts, trachyandesites and trachytes, to rhyolites. These rocks are of alkaline affinity, typical of intracontinental tectonic settings. (2) Pyroclastic rocks formed by lapilli-size fragments of basaltic rocks with minor sedimentary rocks fragments in a volcanoclastic matrix. The basaltic fragments are always completely altered, which gives the rock a patchy aspect that causes its local name of *fraileasca*, after the robes of the early franciscan monks (*fraile* = monk). The *fraileasca* rocks constitute diatrema-shaped bodies in Ordovician, Silurian and Devonian host rocks, which indicates the recurrence of this type of activity. As the former type, they are of alkaline affinity. (3) Subvolcanic rocks of mafic composition and doleritic texture (diabases), which constitute dikes and sills, hosted in all the positions of the Palaeozoic stratigraphic record. The geochemical signature indicates a tholeiitic affinity for all the varieties. (4) Ultramafic rocks present as xenoliths in the porphyritic and pyroclastic lithotypes. An important fact is the close relationship between the volcanic rocks and mercury mineralizations: all the cinnabar deposits display at least a geometric relation with the *fraileasca* rock, and even the mercury contents seem to be controlled by the proximity to these rocks (Hernández et al., 1999). The alteration of these rocks is also an important point to consider. Different alteration facies can be distinguished. (1) A typical low-grade association formed

by prehnite–pumpellyite–actinolite–epidote, present in the tholeiitic subvolcanics, and showing no relationship with mineralization. (2) The so-called “regional” alteration, affecting the alkaline rocks (porphyritic and pyroclastic). The characteristic minerals are carbonates (calcite–dolomite–ankerite–magnesite–siderite), chlorite, illite (including Cr-illite/fuchsite) and Fe–Ti oxides (titanite–hematite). (3) The so-called “local alteration”, with quartz–pyrite–pyrophyllite–(kaolinite)–(illite), observed in discordant deposits such as Las Cuevas (e.g., Higuera et al., 1999).

The district hosts the huge Almadén mine, 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, is far away from this figure, with 350,000 flasks as original reserves (Fig. 1). The mercury deposits of the district display remarkable differences, for instance: (1) their host rock age: Ordovician, in Nueva Concepción; Silurian, in Almadén, El Entredicho, Las Cuevas, Vieja Concepción and Pilar de la Legua; Devonian in Corchuelo, Guadalperal and Burcio–Tres Hermanas; (2) the host rocks: quartzite in Almadén, El Entredicho, Vieja Concepción, Burcio–Tres Hermanas and Pilar de la Legua; pyroclastic rocks in Las Cuevas and Nueva Concepción; volcanic rocks in Corchuelo, Guadalperal, and in part at Nueva Concepción; and even in subvolcanic rocks (e.g., Corchuelo); (3) morphology: stratabound in Almadén, El Entredicho and Vieja Concepción; clearly discordant, vein-related, in the rest; (4) deposit size, from the 7.5 million flasks of the Almadén mine through the 350,000 flasks of El Entredicho, the 185,000 of Nueva Concepción, the 150,000 of Las Cuevas, and the 100,000 of Vieja Concepción, to the prospect/mineral showings category of the rest mentioned (Burcio–Tres Hermanas, Corchuelo and Guadalperal). The mineralogy is simple and consists of cinnabar and minor pyrite, the latter being relatively more important in deposits such as Las Cuevas (Hernández et al., 1999; Higuera et al., 1999, 2000b).

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),

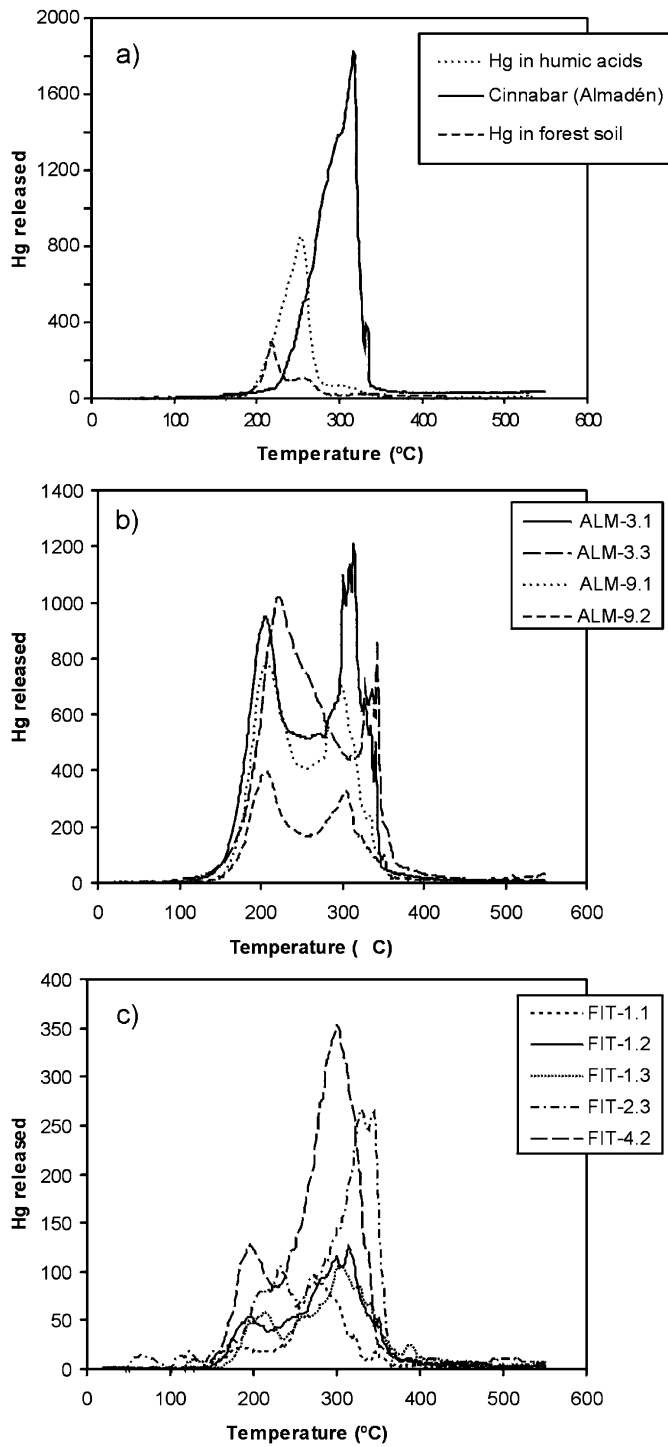


Fig. 2. Thermodesorption curves of mercury. (a) Cinnabar, forest soil and humic acid (after Biester et al., 1999). (b) Soil samples from the Almadenejos (ALM) site. (c) Soil samples from the phytoremediation (FIT) site.

to the modern Pacific furnaces of rotatory type, fuelled by propane gas.

3. Materials and methods

The environmental survey carried out in the Almadén mercury mining area comprised the study of several areas, which in turn represent different sources of mercury, e.g., mining and/or metallurgy, mercury transported by air from old metallurgical precincts, mercury from prospect areas with no mining activity (Fig. 1). (1) The Almadenejos metallurgical site (ALM samples), described later. (2) The Chillón railway station area (ECH samples). In this place, mercury was suspected to be accumulated by detrital processes in an alluvial plain in the 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 (RD samples); here, 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 showings 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 (FIT samples). In this locality, not far away from the Almadenejos metallurgical precinct, Hg contents in soil were also detected by means of soil geochemistry. In all these sites, the samples were taken at different depths, using an Eijkelkamp 04.15.SA undisturbed soil sampler device. The samples were dried at room temperature and sieved to <63 μm . We selected this fraction after several preliminary tests because it concentrated the highest contents of mercury. The pH of the soil samples was measured taking 10 mg of soil into 25 ml of distillate water using a CRISON GLP 21 pH meter.

Total Hg content in dried samples (50 mg) of soils and plants was analysed by means of cold vapour atomic absorption spectroscopy (CV-AAS) using an advanced mercury analyser (AMA 254 from LECO) at the Minas de Almadén y Arrayanes laboratories, with a detection limit of 2 ppb. Thermal speciation analysis of selected samples was 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, synthetic cinnabar, metacinnabar, HgO and HgSO₄ (among others; Biester et al., 1999). Fig. 2a displays the patterns (University of Heidelberg; Biester and Scholz, 1997; Biester et al. 1999) of these species of mercury. The TEM-EDX studies were carried out at the Centro de Apoyo Tecnológico (CAT) from the Universidad Rey Juan Carlos (Madrid) using a TEM-EDAX Philips Tecnai 20 at 200 kV. The instrument allows TEM imaging and EDX chemical analyses of the mineral phase, as well as the examination of individual mineral grains by electron diffraction.

4. Results and discussion

As expected, the anthrosols from the Almadenejos old metallurgical site display the most scattered set of values (6–8889 ppm) (Table 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 ppm Hg, respectively (Table 1). 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, Loredó et al. (1999) report values of mercury in soil samples near spoil heaps (Mieres, northern Spain) in the range of 1.7–2224 ppm Hg, whereas Viladevall et al. (1999) indicate contents of 6–1400 ppm Hg in soils and overburden from the mineralized area in Azogue Valley (SE Spain). Biester et al. (1999) report values from Idrija (Slovenia) of up to 1000 ppm Hg. However,

Table 1
Mercury concentrations and pH of soils in the different sampling sites

Site	N	Range	Hg (ppm)		pH	
			Average	S.D.	Average	S.D.
ALM	18	6–8889	2573	2979	6.87	0.81
ECH	8	12–132	57.8	33.1	6.76	1.54
RD	19	10–188	61.2	55.0	7.01	0.36
FIT	22	6–69	22.0	16.5	8.08	0.38

ALM: Almadenejos, ECH: Chillón, RD: Rodoviejo, FIT: phytoremediation site. S.D.: standard deviation. N: number of samples.

compared to normal soils (not subjected to contamination), the Almadén values are extremely high. Given that the usual contents of mercury in soils is in the range of 0.01–0.03 ppm Hg (Senesi et al., 1999), we may conclude that the studied soils from Almadén are enriched in mercury by a factor of 10^2 – 10^5 .

The thermal speciation analyses were carried out on samples from two areas of the district: the Almadenejos abandoned metallurgical precinct, and the phytoremediation site. The Almadenejos metallurgy was active between the 17th and 18th centuries, and finally decommissioned in 1860. The area is characterized by thin anthrosols, developed on top of Silurian shales and volcanic rocks, which in places have primary mercury contents. The research 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-thermodesorption curves (Hg-TDC) of the Almadenejos samples display a characteristic pattern

defined by peaks at 200–220 and 310 °C (Fig. 2b), 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. 2a). TEM-EDX studies carried out on soil samples from the Almadenejos metallurgical precinct (ALM samples) (Fig. 3) show that mercury is present in the form of detrital cinnabar particles, adsorbed to the surface of chlorite grains. Since chlorite is not associated with cinnabar in the deposits (Hernández et al., 1999; Higuera et al., 1999, 2000b), these minerals most probably arrived in the anthrosol via different ways. The source of chlorite can be traced to the widespread regional alteration (e.g., Higuera et al., 1999, 2000b) affecting the Silurian volcanic rocks, whereas, cinnabar was most probably introduced via careless transport, stockpiling, and loading of furnaces during the old days of the Almadenejos metallurgical site. These soils supported the activity of five furnaces, which may have processed some 300,000 flasks of mercury during its period of activity. On the other hand, we cannot rule 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

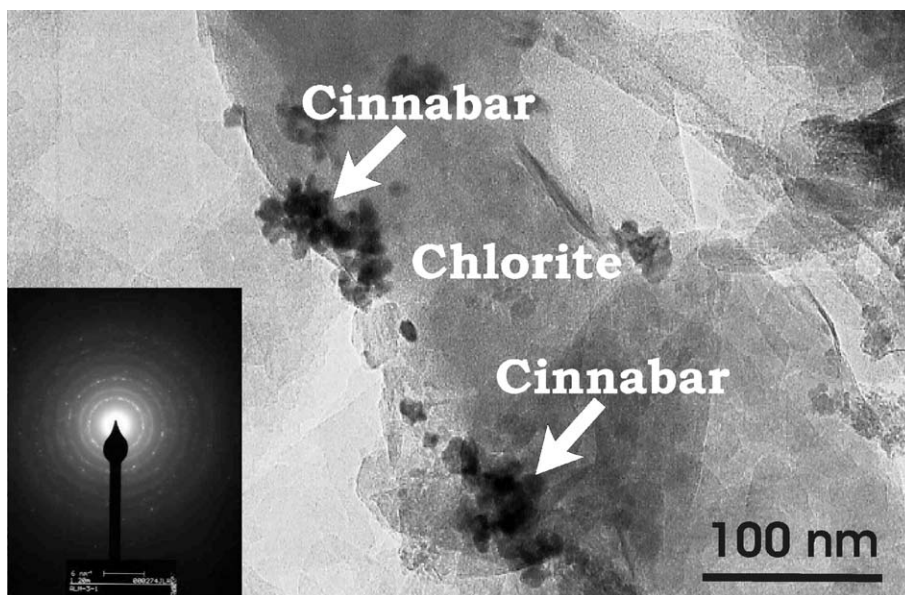
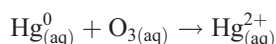
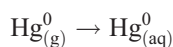


Fig. 3. TEM image of sample ALM 3.1 (5037 ppm Hg) showing the presence of cinnabar particulate on the surface of chlorite and electron diffraction pattern of cinnabar (see inset; main spacing: 0.33 nm). Detected spacings for chlorite (in nm) are: 0.44, 0.26, 0.23, 0.17, 0.15 and 0.13. Instrument: TEM-EDAX Philips Tecnai 20 at 200 kV. Technical Support Center, Rey Juan Carlos University (Madrid).

deposition of emitted Hg^{2+} , or from conversion of emitted Hg^0 to Hg^{2+} through ozone mediated processes (EPA, 1997) (g: gas phase; aq: aqueous phase; p: particulate phase):



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 (Fig. 2b–c).

The phytoremediation site was set up in 1999, and corresponds to a study carried out by the University of Castilla-La Mancha, the CIEMAT and the Almadén mining company (MAYASA). The goal of the project is the recovery of mercury via plant uptake. Since the phytoremediation area is relatively near to the Almadenejos highly polluted abandoned metallurgical precinct (some 1000 m to the northeast), the site is perfect to study the lateral zoning of mercury species. The other reason for selecting the site was the relatively low mercury values (as compared to Almadenejos). The site has been seeded with trees (*Eucalyptus*), and herbaceous agricultural plants (wheat, barley and lupine). The Hg-TDC for the FIT samples display a basically bimodal pattern, with peaks at about 200–

230 and 310 °C (Fig. 2c), thus, suggesting the existence of cinnabar and mercury bound to organic matter (forest soil, and humic acids) (Fig. 2a).

As shown by mechanical concentration tests and textural studies, the cinnabar present in the phytoremediation site has a detrital origin, and accumulates as in other sites, in the most superficial levels of the soils (Fig. 4). Since the oxidation and dissolution of mercury from cinnabar is minor because of cinnabar's low solubility and weak oxidation under ambient conditions (Rytuba and Klein, 1986; USGS, 1994), we may regard this phase as of primary origin. Thus, cinnabar was most probably eroded from source rocks, transported, and incorporated to these soils, either as individual grains, or included within small rock fragments. On the other hand, mercury bound to organic matter may have been incorporated to the entisols by processes equivalent to those described for the Almadenejos precinct. Note that the precinct and the phytoremediation site are in close proximity (~ 1 km). Since the superficial levels of the phytoremediation site are rich in organic matter, the possibility of mercury complexing by humic acids (e.g., Williams, 2001) must be also taken into account (see, for example, the Hg-thermodesorption curves for the FIT samples; Fig. 2c).

Although no important correlation is found between soil pH and mercury values (Fig. 5) (Table 1), the higher concentrations of the latter are essentially related to the higher pH values, which favours reten-

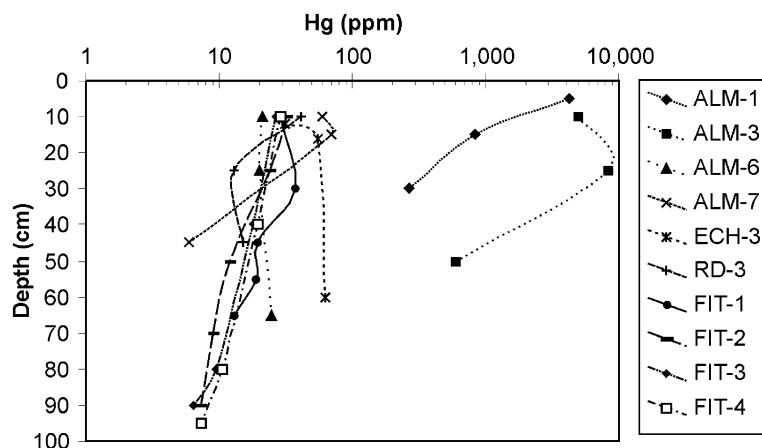


Fig. 4. Vertical distribution of mercury in soils from different sampling sites. ALM: Almadenejos, ECH: Chillón, FIT: phytoremediation site, RD: Rodoviejo.

Table 2
Mercury contents in three common plant species growing in the Almadén district

Plants (scientific and common names)	Location	Hg (ppm)	Description (Cullen, 1972; Ball, 1976; Valdes, 1980)
<i>Asparagus acutifolius</i> L. Wild asparagus, <i>Esparraguera</i>	Almadenejos, Nueva Concepción	Roots: 298.2 ^a , 2.6 ^b ; Stems: 7.7 ^a	Rhizomatous perennials with usually fusiform tubers. Stem up to 200 cm, woody, white or grey. Stem and branches longitudinally striate, papillose or almost smooth. Cladodes 2–8 × 0.3–0.5 mm, subequal, in fascicles of 10–30, patent, strongly spiny. Perianth segments 3–4 mm. Berry 4.5–7.5 mm, black, with one to two seeds.
<i>Dittrichia graveolens</i> W. Stinkwort, <i>Olivardilla</i>	Las Cuevas	Stems + leaves: 26.7	Plant erect, densely glandular, annual 20–50 cm, smelling of camphor. Lower leaves 20–75 cm × 2–13 mm, lanceolate to oblong-lanceolate, entire or remotely denticulate; upper leaves sessile, semiamplexicaul. Capitula small with ligules 4.7 cm. Achenes ca. 2 mm, hairy; pappus with ca. 20 setae.
<i>Marrubium vulgare</i> L. Horehound, <i>Marrubio</i>	Almadenejos	Stems: 52.5, 59.7; Leaves: 40, 155.6	Perennial herbs with stems up to 45 cm, white-lanate, at least below, with many short nonflowering branches. Leaves orbicular to broadly ovate, subcordate or rounded at the base, deeply and irregular crenate, sparsely tomentose to subglabrous above, more densely tomentose beneath; Verticillasters globose, many-flowered, distant. Corolla exceeding calyx teeth, white.

^a Almadenejos.

^b Nueva Concepción.

marrubio (Horehound; *Marrubium vulgare*) (Table 2), which yields high values of mercury in stems and leaves (up to 155.6 ppm Hg). In the same area, the roots of the wild asparagus *esparraguera* (*A. acutifolius*: a plant collected and eaten by the local population) (Table 2) yields alarming values of up to 298.2 ppm Hg (peeled roots), whereas concentration in the stem is only of 7.7 ppm Hg. This discrepancy is not surprising, because roots act as a barrier to mercury uptake, displaying values about 20 times larger than those observed in the shoots (Patra and Sharma, 2000). In the surroundings of the mineral dumps of Las Cuevas, the *olivardilla* (Stinkwort; *Dittrichia graveolens*) (Table 2) yields a value (stem + leaves) of 26.7 ppm Hg.

5. Conclusions

As expected in an area that has been subjected to mercury mining for about 2000 years, the soils of the

Almadén district are highly contaminated, with some zones displaying values well above 1000 ppm Hg. The combination of Hg-thermodesorption curves and TEM-EDX analyses indicate that mercury in the soils of Almadén is only in the forms of cinnabar particulate and as mercury bound to organic matter. Mercury has been 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) transport and stockpiling (mineral dumps) and (b) metallurgical activities. Due to the pyrite-poor character of the ores, cinnabar leaching in the mineral dumps has been restricted to in situ formation of thin films of schuetteite. Thus, we suggest that at least part of the mercury bound to organic matter must be related to deposition of atmospheric mercury, which in turn would have been generated by the metallurgical activity (e.g., see the Almadenejos case).

Finally, while the mere fact that the Almadén soils are highly contaminated is worrying by itself, the high mercury contents in plants has to be regarded as alarming, particularly if we take into account that plants such as the wild asparagus (*A. acutifolius*) are collected and consumed by the local people.

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