Sampling high to extremely high Hg concentrations at the Cerco de Almadenejos, Almadén mining district (Spain): The old metallurgical precinct (1794 to 1861 AD) and surrounding areas

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ABSTRACT

The Cerco de Almadenejos (CDA) is an old metallurgical site located in the province of Ciudad Real (Spain) that operated between 1794 and 1861. The metallurgical precinct was built for the roasting of the Almadén and Almadenejos cinnabar ore to extract Hg metal. A previous pilot geochemical study of soils at the CDA had already shown extremely high concentrations of Hg. To analyze the extent and intensity of contamination, we planned and executed a geochemical survey to cover the CDA and the surrounding areas. The survey covered soils, air, and plants. The planning involved the design of two sampling grids in order to obtain a comprehensive picture of potential environmental hazards in the area: 1) a detailed sampling grid centred on the metallurgical precinct ($n = 16$ samples; area $= 3.6 \times 10^4\,\mathrm{m}^2$); and 2) a less detailed sampling grid planned to determine the extension of contamination beyond the metallurgical site ($n = 35$ samples; area $= 1.2 \times 10^6\,\mathrm{m}^2$). After variogram modelization of geochemical data, the kriging plots showed that contamination, even if centred at the precinct, extends beyond the site, with Hg concentrations of up to 2200 times those of uncontaminated soils (world baseline). The detailed study of the soils from the precinct shows an extremely high mean concentration of 4220 µg Hg g^{-1} (4.2×10^5 times baseline concentration). In turn, these highly polluted soils induce strong emissions of Hg$_{(g)}$, with concentrations of up to 970 ng Hg m^{-3}. The study of the edible wild asparagus Asparagus acutifolius shows extremely high concentrations of mercury in roots (0.6–443 µg g^{-1}) and stems (0.3–140 µg g^{-1}). The data indicate that the study area constitute a hot spot of contamination and is a potential health/environmental hazard for the inhabitants of Almadenejos, livestock, and wild life, that requires immediate action via remediation procedures.

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1. Introduction

The Almadén mercury mining district (Spain) (Fig. 1) comprises a number of now inactive (and some abandoned) mines as well as other areas acting as sources of mercury pollution, such as decommissioned metallurgical sites. Almadenejos is a small village (490 inhabitants in 2008) located some 12 km to the ESE of Almadén, and in its vicinity there are three mercury mines (Fig. 1): 1) La Vieja Concepción (active from 1699 to 1800, located just beneath the village); 2) La Nueva Concepción (active from 1795 to 1861, located some 750 m to the WSW); and 3) El Entredicho (active from 1981 to 1997, located 3 km to the ESE). Besides, Almadenejos is also the site of a historical metallurgical precinct, the so-called Cerco de Almadenejos (CDA) (Fig. 1, 2A). The CDA is located immediately to the north of the village, has an area of ~36,000 m^2 and is completely surrounded by a deteriorated stone wall. The metallurgical operation was active from 1794 to 1861. It is not clear whether this inner wall was built to prevent robbery of mercury metal or to impede prisoners from escaping: forced labour operations were common in the old days. In fact, the Spanish word *cerco* means siege, blockade, only that in this case, the blockade was not enforced by an army but by a stone wall. Besides, the whole village and the local northern pastures are surrounded by a second wall (Fig. 1). The metallurgical precinct originally had six red-brick furnaces for cinnabar roasting (Fig. 2B), which are currently in ruinous conditions (Fig. 2C). At present the precinct is used by the locals to raise pigs and other livestock (Fig. 2D). From the viewpoint of Hg pollution, the CDA can be regarded as one of the most contaminated sites in the whole Almadén district (Higueras et al., 2003, 2005; Gray et al., 2005). However, although pilot sampling had been done at the CDA (Higueras et al., 2003), the area lacked a comprehensive geochemical survey. Thus, in November 2008 we carried out a detailed survey of the area including soils, plants, and air. The results from this study follow.

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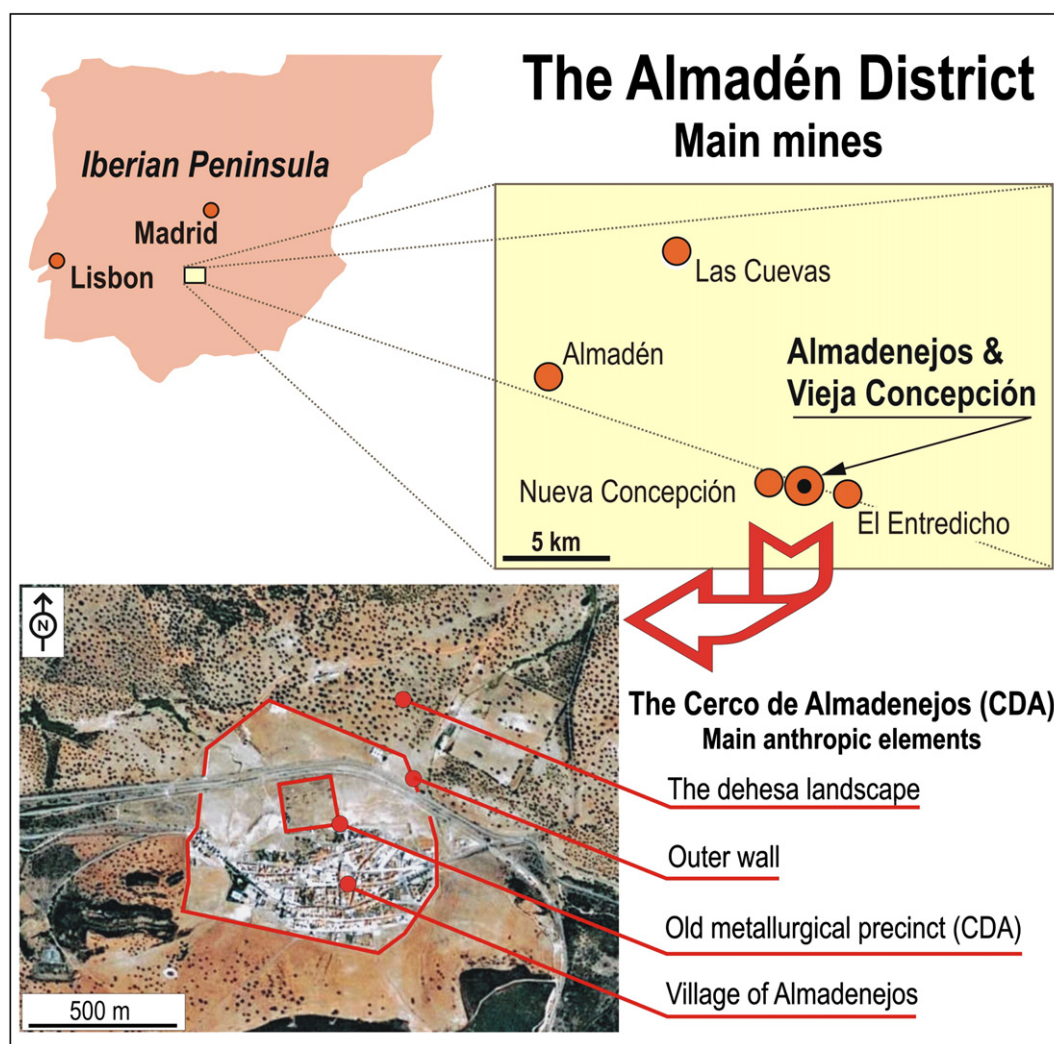E-mail address: pablo.higueras@uclm.es (P. Higueras).

Fig. 1. Location of the Almadén district, Almadenejos, and environmental features.

2. A brief introduction to the Almadén district: environmental and geologic setting

The Almadén district (Fig. 1) is located within the so-called Meseta Sur (Spanish southern mesa), which has a continental Mediterranean climate with contrasted seasonal variations in mean temperatures: 6–8 °C (winter) and 26–28 °C (summer). The rain concentrates in late autumn and early spring, with an annual total of 500–700 mm. The district is located within a region morphologically characterized by WNW trending valleys and sierras, within a landscape ranging in altitude between 200 and 1000 masl. The soils of the district are mainly entisols, with localized development of anthrosols derived from centuries of mining and metallurgical operations. The natural potential vegetation of the Almadén district (Molina et al., 2006) corresponds to *Quercus rotundifolia* forest. The understory includes Mediterranean shrubs such as: *Pistacia lentiscus*, *Asparagus acutifolius* (here studied), *Cistus ladanifer*, *Cistus monspeliensis*, among others (Molina et al., 2006). The whole system constitutes the so-called *dehesa*, the typical man-modified landscape from central Spain (Figs. 1, 2A), in which the initial evergreen oak forest (e.g. *Q. rotundifolia* or *Quercus suber*) is reduced to isolated groups of trees in a landscape dominated by perennial grasses of *Poa bulbosa*.

From the geologic viewpoint, the Almadén district (Higueras et al., 2000a,b) is located in the southern sector of the so-called Central Iberian Zone of the Iberian massif, in one of the characteristic Hercynian geologic structures: the Almadén syncline. The stratigraphic succession includes sedimentary rocks with volcanic interbeddings, which can account for most of the stratigraphic record. The magmatic rocks are very common in the Silurian and Lower Devonian sequence, forming the so-called Volcano Sedimentary Group. There are two types of rocks particularly relevant to mercury mineralization in the district: quartzites from 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 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. These deposits have in common a simple mineralogy dominated by cinnabar (HgS) and minor pyrite (FeS_2). The Almadén district 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 (Higueras et al., 2003, 2005). Almadén, the main mine of the district was active from Roman time to 2002, with almost no interruptions, except by those caused by mining disasters (floods and fires), or by external factors such as wars. Having said all this, it is easy to understand the pervasive character of mercury pollution in the district, either because of natural (geologic) or anthropic
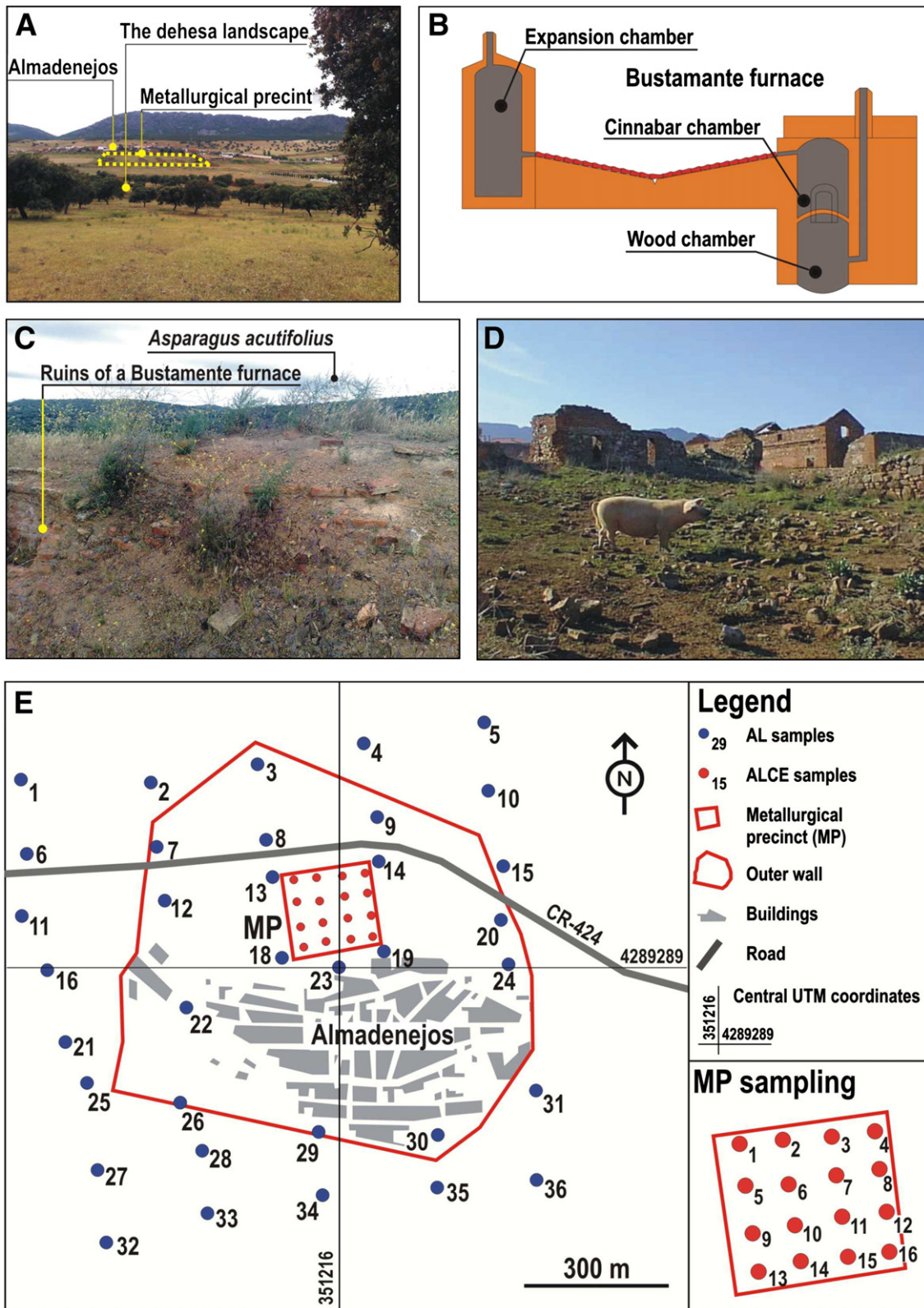
Fig. 2. Almadenejos. A: the Cerco de Almadenejos (looking south). B: schematics of a Bustamante furnace. C: ruinous state of Bustamante furnaces and edible vegetation growing on top of them. D: livestock within the Cerco de Almadenejos. E: the AL and ALCE sampling grids. MP: metallurgical precinct.

(mining and metallurgy) causes (Higueras et al., 2005). The mercury distribution in soils of the district reveals the existence of high to extremely high mercury concentrations (up to 8889 μg g^{-1}) (Higueras et al., 2003), whereas concentrations in stream sediments and waters reach exceptional values of up to 16,000 μg g^{-1} and 11,200 ng l^{-1}

respectively (Higueras et al., 2005). Besides, high concentrations of methylmercury have been detected in calcines from the Almadén metallurgical plant and the CDA old metallurgical installations (up to 3100 ng g^{-1}), sediments (0.32–82 ng g^{-1}), and waters (0.040–30 ng l^{-1}) (Gray et al., 2004).

3. Materials and methods

3.1. Sampling

Different from a typical environmental study spatially focused on a highly polluted industrial site, we chose a comprehensive approach, aiming to cover not only the highly contaminated sector (old metallurgical precinct) but also the surrounding areas. Thus two sampling grids for soil and air were planned (Fig. 2E): one inside the walled metallurgical precinct (ALCE samples; $n = 16$; area $= 3.6 \times 10^4$ m^2), and a second one (AL samples; $n = 35$; area $= 1.2 \times 10^6$ m^2) extending beyond the precinct. Given that our field study had to cover both urbanized areas and agricultural/livestock raising lands, the sampling was based on common sense and two basic principles (Conklin, 2004): 1) when sampling, local rules apply; and 2) general sampling principles will need to be adapted for each field and sampling situation. Thus, based on field operating restrictions, each sampling station was spatially readjusted if necessary to new coordinates (as near as possible to the planned sampling sites) and GPS marked. We additionally collected 13 samples of the wild asparagus *A. acutifolius*; 10 samples were taken inside the walled metallurgical precinct and 3 in the surrounding areas. Special consideration was given to the criteria used for the selection of soil horizons. Given that the topsoil is the most important part of the soil profile for degradation control (Spaargaren and Nachtergaele, 1998), we concentrated our efforts on this superior horizon (5 to 30 cm in this sampling). We previously tried and improved this sampling procedure in another highly polluted mining and metallurgical site: the Rodalquilar mining district in SE Spain (Oyarzun et al., 2009). The soil samples (~1.5 kg) were stored in plastic bags, and sieved at the Almadén School of Mines (ASM) laboratory.

3.2. Analytical techniques and instrumentation for Hg

We used the portable LUMEX RA-915+ analyzer for mercury determination. This 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 the Zeeman background correction and a multipath analytical cell provide high selectivity and sensitivity of measurements. Addition of the RP-91C (pyrolysis) attachments allows Hg measurements in solid samples. This attachment was used for the analyses of soils and dried plants at the Almadén School of Mines (ASM) laboratories. Mercury in the samples is converted from a bound state to the atomic state by thermal decomposition in a two-section atomizer. As a first step the sample is vaporized and the mercury compounds are partly decomposed. This is followed by heating to 800 °C, when the mercury compounds become fully decomposed, whereas organic compounds and carbon particles are catalytically transformed to carbon dioxide and water. The analysis takes 1–2 min. The detection limits for total Hg are 0.5 µg kg^{-1} (soils) and 2 µg kg^{-1} (plants). The detection of Hg by direct atomic absorption is complicated in samples with a complex matrix (e.g., plants and soils) because of the presence of organic compounds. However, the use of the background correction in the Zeeman atomic absorption mercury spectrometer RA-915+ overcomes the problem. In order to check the validity of the procedure, we have run analytical tests (Standard Addition Method, using the NIST 2710, NIST 2711, and BCR 146R standards; see below) on single (leaves) and composite (leaves plus a known amount of a standard) samples (e.g., Molina et al., 2006). Quality control at the ASM laboratory is accomplished by analyzing replicate samples to check precision, whereas accuracy was obtained by using certified standards: (SRM) NIST 2710, (SRM) NIST 2711, and BCR 146R. An aliquot of each soil sample was kept at the ASM for the determination of pH following the International Soil Reference and Information Centre (ISRIC) standard procedures (Van Reeuwijk, 2002). Regarding atmospheric mercury, the LUMEX RA-915 allows determination of Hg in air directly with an ultra low detection limit in real time. The dynamic range covers 4 orders of magnitude (2–20,000 ng m^{-3}). The real time measurements are made with visualization of the process on a digital display (Sholupov and Ganeyev, 1995). The whole process was completed in the field with geographic location of single data using a GPS. Specific meteorological parameters (temperature, wind speed, and solar radiation) were obtained from a DAVIS Vantage Pro2™ field station, located at UTM coordinates 4289428 N and 348345E. Measurements for Hg$_{(g)}$ were done at ~1.5 m above the ground.

3.3. Analytical procedures for Cu, Pb, and Zn

Apart from mercury we checked other heavy metal contents of soils (Cu, Pb, and Zn) using an OXFORD X-MET 3000TX a lightweight XRF analyzer for metals. Our instrument is presently certified by OXFORD Instruments to analyze heavy metals in soils following the USEPA method 6200. The dynamic range for the studied metals is (data in µg g^{-1}): Cu $= 0$–3584, Pb $= 0$–2342, and Zn $= 4$–6791. The OXFORD X-MET is a fully portable instrument and can be operated in the hand-held mode at a sampling site with a good overall performance (United States Environmental Protection Agency; USEPA, 2006), allowing metal identification and quantitative measurement of concentration. Modern field-portable X-ray fluorescence element analyzers enable researchers to determine metal concentrations both rapidly and easily, which provides an ideal approach for the assessment of metal-contaminated soil (Kalnicky and Singhvi 2001; Carr et al., 2008). In this regard, despite the Hg focused character of this work (after all Almadén is a single-metal district), the study of other elements such as Cu, Pb and Zn proved to be extremely useful, because as shown below (see Results and discussion), the ultimate fate of Hg in the soil matrix is also controlled by the presence of other metals that compete for sorption sites.

3.4. Statistical analysis of data

In order to study metal spatial distribution from a geostatistical point of view, we did variogram modelization and used the best fit model to do point linear kriging with Surfer 8® (Golden Software Inc.). The variogram model mathematically specifies the spatial variability of the data set and the resulting grid file. The interpolation weights are direct functions of the variogram model. Kriging with Surfer 8 is a flexible gridding method that can be custom-fit to a data set by specifying the selected variogram model. Thus, the kriging gridding method uses the variogram model to estimate the Z values (in this case metal concentration and pH at any given point) throughout the sampled area. For a detailed description of the method see Bresnahan and Dickenson (2009). Basic statistics were performed with Statgraph plus.

4. Results and discussion

4.1. Main results for Hg in soils

The results for Hg in soils, plants and air are shown in Table 1. The TRA local (Almadén) baseline data were obtained during the course of a previous survey of soils and plants throughout the Almadén district and beyond (Molina et al., 2006). The TRA sampling area was chosen because it is distant from either natural sources of Hg (mineral deposits) or mining–metallurgical sites. However, as shown in Table 1 these Hg concentrations are up to 2200 times those of uncontaminated soils (global baseline; Senesi et al., 1999) (Table 1). This reveals the true nature of the Almadén district, which as a whole represent what might be termed as the largest Hg anomaly on Earth. Given that the district has been subjected to almost continuous mining since Roman time, it is more than understandable that a combination of

Table 1

Concentrations of Hg for Almadenejos, Almadén district, and baselines.

	Hg soils ($\mu g\ g^{-1}$)	Hg air ($ng\ m^{-3}$)	Reference
Almadenejos			
Metallurgical precinct (MP)			
n = 16			
Mean	4220	137	
Maximum	15,900	972	
Minimum	25	7	
Standard deviation	4926	230	
Surrounding areas (SA)			
n = 35			
Mean	43	21	
Maximum	174	80	
Minimum	4	2	
Standard deviation	40	21	
Total (MP and SA)	1296 (4–15,900)	58 (2–972)	
Almadén district			
El Entredicho mine (March)		28 (2–605)	Higueras et al. (2005)
El Entredicho mine (June)		291 (2–3,111)	Higueras et al. (2005)
Baselines			
TRA Almadén baseline data	20–22		Molina et al. (2006)
Uncontaminated soil	0.01–0.03		Senesi et al. (1999)
Mediterranean basin		2–3	Wängberg et al. (2001)

natural and anthropic factors have resulted in high to extremely high Hg concentrations in soils, air, plants, and even animals (Higueras et al., 2005). In this regard, the Cerco de Almadenejos (CDA) has all the prerequisites to be regarded as 'the anomaly among the Almadén anomalies': 1) the CDA is near or even above Hg mines (Vieja Concepción); and 2) the CDA was the site of primitive metallurgical procedures, at a time when concepts such as *safety* were beyond the historical technical lexicon. Pilot sampling at the CDA (Higueras et al., 2003; Gray et al., 2004) had already shown that the old furnaces had left behind a legacy of contamination. What was unknown at the time

was the extent and overall magnitude of such contamination. In this regard, our sampling allowed a much better definition of mercury distribution at the CDA and surrounding areas. Given the extreme range of variation in Hg concentrations (Table 1) we decided to test the type of statistical distribution to avoid ulterior distortions. The Gaussian or normal distribution is assumed to describe the random variation that occurs in a data set. However, many distributions show important skewness, which disappears if we deal with the logarithm of the values (log x). If this is the case, we say that log x has a normal distribution, or simpler, that the distribution is log-normal (e.g., Limpert et al. 2001). The results for Hg (soils) indicate that the distribution is log-normal, of the bimodal type, with well defined background and anomalous populations (Fig. 3).

4.2. Some clues for the understanding of the dispersion of Hg in soils and air

The kriging plots for Hg show a remarkable anomaly centred at the CDA, which nonetheless extends beyond the precinct (Fig. 4A,B). After variogram modelization and point linear kriging we observed a strong WNW–ESE anisotropy component, which in principle does not match any remarkable physiographic feature of the area. However, if the old road (the current CR-424 linking Almadén and Ciudad Real) and the area defined by the outer wall are taken into account (Figs. 1, 2E), a clearer picture may unfold. As shown by Higueras et al. (2003), the anthrosoils from the CDA may even contain fragments of the ancient pottery used recover mercury. In this respect, the metallurgical technique evolved from primitive systems, using pottery (the so-called *xabecas* furnaces) to the use of pottery lines within red-brick structures for condensing the vapours (the so-called *Bustamante* furnaces) (Fig. 2B). Cinnabar and other species of mercury were most probably introduced to the Almadenejos soils via careless transport, stockpiling, and loading of furnaces during the old days of the metallurgical precinct. In this regard, we can envisage an old scenario in which the mined Hg ore was brought to Almadenejos by road (either by mule- or oxen-drawn wagon trains), stockpiled within the area defined by the outer wall (Fig. 1, 2E, 4A), and periodically transferred to the CDA to feed the Bustamante furnaces. The CDA soils
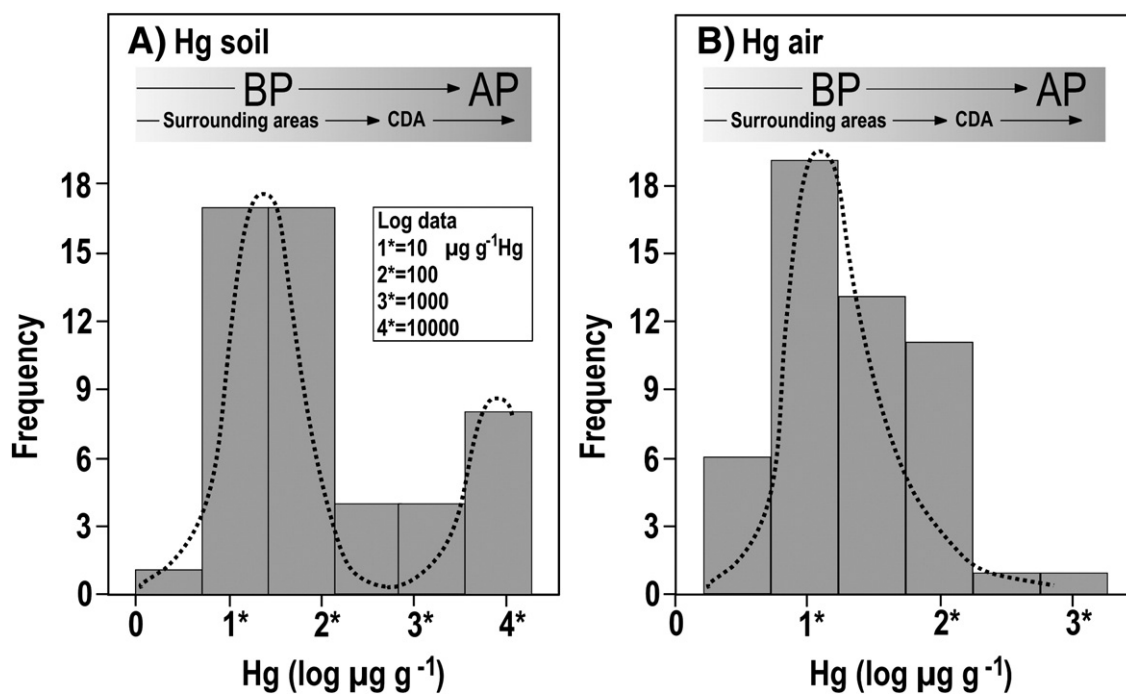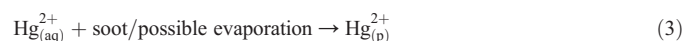

Fig. 3. Histogram showing the bimodal log-normal distribution of Hg concentration in soils from Almadenejos, and the idealized passage from the surrounding areas (local background population: BP) to the Cerco de Almadenejos (CDA) truly anomalous population (AP).
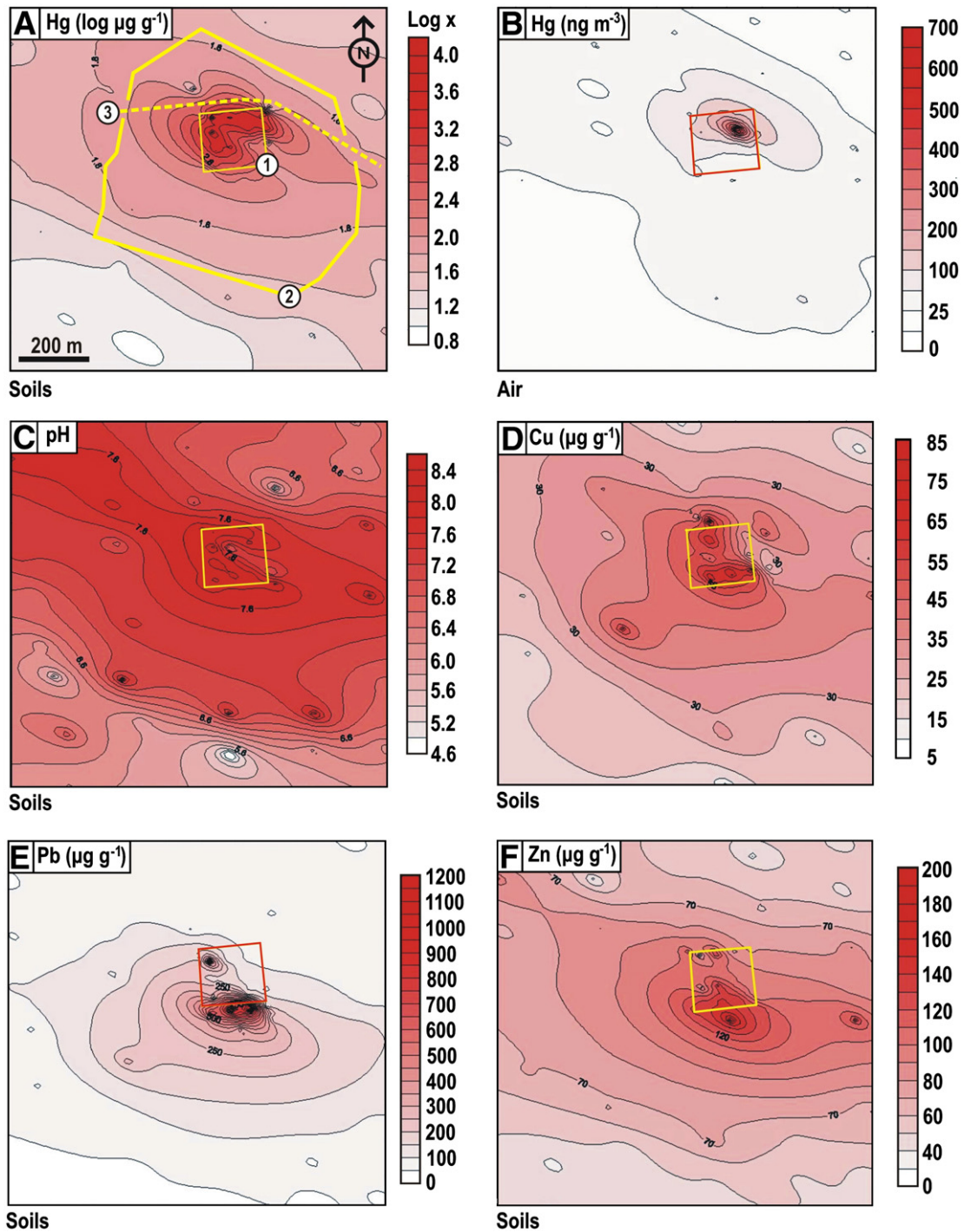
Fig. 4. Almadenejos: point linear kriging plots for: A: $Hg_{(soil)}$; B: $Hg_{(g)}$; B: pH: D: Cu: E: Pb; and F: Zn. 1: Cerco de Almadenejos. 2: Outer wall. 3: A segment of the CR-424 road. Best variogram fit model for kriging (A–F): logarithmic. See also Fig. 1 and 2E for location.

supported the activity of six Bustamante furnaces, which may have processed some 300,000 flasks of mercury during their period of activity; a flask carried 34.5 kg (= 76 lb) of mercury and had a volume of 2.5 L. On the other hand, part of the gaseous mercury emitted by the furnaces 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; and p: particulate phase):

$$Hg_{(g)}^0 \rightarrow Hg_{(aq)}^0 \tag{1}$$

$$Hg_{(aq)}^0 + O_{3(aq)} \rightarrow Hg_{(aq)}^{2+} \tag{2}$$

$$Hg_{(aq)}^{2+} + soot/possible\ evaporation \rightarrow Hg_{(p)}^{2+} \tag{3}$$

Besides, the Almadén soils are smectite-poor, which severely reduces cation exchange (Higueras et al., 2003). This increases the availability of metals from the inorganic matrix, leaving the organic matter as the sole agent for metal retention (e.g., Alloway, 2004). On the other hand, photolysis of inorganic Hg^{2+} to Hg^0 at the soil surface may in turn contribute significantly to the emission of gaseous mercury to the atmosphere (Scholtz et al., 2003). In fact, even if part of

the mercury in the soil becomes bound to an organic or inorganic matrix, the element would be eventually released by photo-reduction (Gustin et al., 2002), thus further contributing to the atmospheric pool. In this respect, desorption of Hg^{2+} from the organic matrix in soil decreases with a pH from ~3.0 to 5.0, levels off at ~5.0–7.0, and increases again with a pH of 7–9 (Jing et al., 2007). This may explain the distribution patterns of Hg and pH in the studied area (Fig. 4A–C), with the highest Hg concentrations in or near to the metallurgical precinct, where the highest pH values were measured. Besides, Cu, Pb and Zn concentration data gathered with the OXFORD X-MET portable XRF analyzer also added valuable information regarding Hg availability (Fig. 4D–F) (Table 2). Man continuously introduces metals to the environment, thus it did not come as a surprise to find important concentrations of other metals within the CDA and surrounding sectors, because abandoned industrial areas may easily become illegal trash dumping sites. Given that Cu^{2+} or Zn^{2+} successfully compete with mercury for adsorbing sites, desorption of Hg^{2+} increases with increasing concentrations of copper and zinc (Jing et al., 2007). Conspicuously, anthropic addition of metals to the CDA sector by the locals (mostly trash left to rust in open air conditions) has resulted in Cu–Pb–Zn anomalies (Fig. 4D–F) that may have further contributed to increase Hg^{2+} availability. Whatever the case, all the studied metals in their cationic form (Hg^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}) compete for sorption sites (e.g., McLean and Bledsoe, 1992), thus the largest the cationic pool of metals, the more difficult for Hg^{+2} to be bound to the soil matrix.

Since concentration in the substrate is the dominant factor controlling the emission of mercury (Gustin et al., 2000), an overwhelmingly Hg enriched realm such as the CDA is bound to become an important source of atmospheric mercury. Reduced adsorption of mercury by the organic matrix of soils results in increasing availability of Hg^{2+}. As explained above, this Hg^{2+} may in turn convert to Hg^0 by photolysis, which significantly contributes to the emission of gaseous mercury to the atmosphere (Scholtz et al., 2003). However, given that this process can be reversible (Eqs. (1–3)), it is likely that part of the mercury emitted as $Hg_{(g)}$ may in fact return to the soils. If this is correct, then we may be facing a long lasting process of partial mercury cycling, from soils to air and then part of the emitted Hg being returned to the soils. In this respect, the CDA $Hg_{(g)}$ anomaly is by no means anecdotic (Fig. 4B). The survey was carried out in November, thus meaning colder temperatures (8–13 °C during the survey), less light, therefore lower $Hg_{(g)}$ concentrations (e.g., Gustin et al., 2002; Scholtz et al., 2003). However, we recorded concentrations of up to 970 ng Hg m^{-3}, that is, close to the World Health Organization (WHO, 2000) recommendation regarding chronic exposure to Hg air: 1000 ng m^{-3}. Given that seasonal variations in mean $Hg_{(g)}$ concentrations in the Almadén district (e.g., El Entredicho

Table 2
Concentrations of Cu, Pb, and Zn for Almadenejos and baseline.

	Cu ($\mu g\,g^{-1}$)	Pb ($\mu g\,g^{-1}$)	Zn ($\mu g\,g^{-1}$)	Reference
Almadenejos				
Metallurgical precinct (MP)				
$n = 16$				
Mean	52	372	105	
Maximum	94	1,683	165	
Minimum	9	30	43	
Standard deviation	27	526	40	
Surrounding areas (SA)				
$n = 35$				
Mean	19	64	74	
Maximum	72	346	213	
Minimum	2	8	16	
Standard deviation	18	81	45	
Total (MP and SA)	29	164	80	
Baseline				
World soils	22	30	66	Callender (2004)

Table 3
Range of Hg concentration in the wild edible plant *Asparagus acutifolius*.

	Hg roots ($\mu g\,g^{-1}$)	Hg stems ($\mu g\,g^{-1}$)	Reference
Almadenejos			
Metallurgical precinct (MP)			
$n = 10$			
Mean	96	30	
Maximum	443	140	
Minimum	0.9	5	
Standard deviation	151	49	
Surrounding areas (SA)			
$n = 3$			
Mean	0.7	0.7	
Maximum	0.7	1.2	
Minimum	0.6	0.3	
Standard deviation	0.05	0.5	
Total (MP and SA)	0.6–443	0.3–140	
Almadén district			
Almadén	0.1–4.9	0.04–12.2	Molina et al. (2006)

mine; Table 1) can be as high as 10 times (summer/winter), our measured concentrations of $Hg_{(g)}$ could dramatically increase during summer.

4.3. Hg in A. acutifolius

We sampled an Almadén Type 2 Hg accumulator (*sensu* Molina et al., 2006): *A. acutifolius* (Fig. 2C), a plant characterized by a woody stem, branches longitudinally striatae, papillosae or almost smooth. The cladodes (modified stems) are short (2–10 mm × 0.3–0.5 mm), strongly spiny, subequal and grouped in fascicles. This wild plant grows in the Mediterranean region where is widely eaten as a vegetable (Valdés, 1980). Almadén Type 2 plants have a complex behaviour characterized by an initial positive linear relationship between Hg_{soil} and Hg_{plant} ($Hg_{plant} = f(Hg_{soil})$). After a high concentration is reached, no increases in Hg_{plant} are observed (saturation level; slope = 0). Our results for the CDA indicate extremely high concentrations of mercury in *A. acutifolius* (Table 3). The roots have higher concentrations than stems (Table 3), which reflects an exclusion strategy for metal tolerance, with the former acting as a semi barrier to mercury intake (e.g., Patra and Sharma, 2000; Boening, 2000; Molina et al., 2006). The high concentration of Hg in edible plants such as the wild asparagus *A. acutifolius* raises concerns regarding potential environmental hazards at the CDA. The case is particularly sensitive because the abandoned metallurgical has been used for decades to keep livestock (particularly pigs) that breathe and eat on a highly polluted site (Fig. 2D). If these animals are slaughtered for meat consumption, then there could be a health risk involved. Whatever the case, this would be a matter of an entirely different study, much more in the field of the ecotoxicology.

5. Conclusions

The CDA is a highly polluted site with high to extremely high Hg concentrations in soils, air and plants. Different from other sectors of the Almadén district, pollution in the CDA can be regarded as essentially anthropic. Hundreds of years of primitive Hg metallurgical practices have left a legacy of highly contaminated soils. The environmental hazards induced by such contamination do not end at the walls of the CDA, because as shown above, high concentrations of Hg are persistent and extend well beyond the precinct. But it is not only the soils, the $Hg_{(g)}$ anomaly also extend beyond the precinct. In this respect, Hg concentrations are currently being monitored to assess the real environmental danger posed by these emissions. The CDA is the last place in which livestock should be allowed to live in. In fact, pigs are not particularly selective regarding what they eat, and if

plants are also contaminated (as shown above), Hg must be passing to the animals (or even people) via voluntary and involuntary ingestion of contaminated plants and soils respectively. Taking all this into consideration, we conclude that the CDA requires immediate action regarding soil remediation. This could involve the removal of soils or the permanent capping of them to create an impermeable barrier. The latter procedure has many advantages (Evanko and Dzombak, 1997): 1) prevents water infiltration and therefore underground water contamination; 2) prevents gas emissions from the site; and last but not least, 3) eliminates risks associated with dermal contact and/or involuntary ingestion of contaminated soils.

Acknowledgements

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