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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 = $3.6 \times 10^4 \text{ m}^2$); and 2) a less detailed sampling grid planned to determine the extension of contamination beyond the metallurgical site ($n=35$ samples; area = $1.2 \times 10^6 \text{ m}^2$). 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 $4220 \mu\text{g Hg g}^{-1}$ (4.2×10^5 times baseline concentration). In turn, these highly polluted soils induce strong emissions of $\text{Hg}_{(g)}$, 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 ($0.6\text{--}443 \mu\text{g g}^{-1}$) and stems ($0.3\text{--}140 \mu\text{g g}^{-1}$). 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 $\sim 36,000 \text{ m}^2$ 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 (Higuera et al., 2003, 2005; Gray et al., 2005). However, although pilot sampling had been done at the CDA (Higuera 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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