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Mercury distribution in an abandoned metallurgical plant

R. Millán[1], M. J. Sierra, T. Schmid**,** S. Carrasco Gil, D. M. Sánchez Ledesma and F. J. Díaz Puent

[1] CIEMAT- Environmental Department. Avenida Complutense 40, 28040 Madrid, SPAIN, rocio.millan@ciemat.es; mj.sierra@ciemat.es

Abstract. The aim of the work is to evaluate the spatial distribution of Hg in the soil-plant system within an area where intense activity of Hg was dominant over a long period. An abandoned metallurgical plant from the 17th-18th centuries was chosen as the study area. It is situated in Almadenejos within the Almadén mining district (Spain) that constitutes the largest and most unusual concentration of mercury in the world and has provided a third of the entire world production of mercury (Hg). Nowadays, this study area is covered with cinnabar mine tailings and village habitants use it for livestock. The area has elevated Hg concentrations of natural origin and from human activities. Soil parameters are similar throughout the study area; however, data reveal high variability in total and available Hg concentrations in soils, making it difficult to establish a tendency. *Marrubium vulgare L.* has been studied due to its high presence in the field plot, and there is no evidence of phenological toxicity. Furthermore, in spite of elevated Hg concentrations, a good biological activity is tested in the soil samples. All these characteristics, spatial variation, high Hg concentration, good biological activity, enhance the peculiarity of the study area for studies involving Hg.

Key words: Mercury, soil, *Marrubium vulgare L.*, physical-chemical soil parameters, microbial biomass carbon, soil microbiological activity.

Introduction

The Almadén area in Central Spain was the mining area with the largest exploitation of Hg, until mining activities ceased at the beginning of this decade. The Almadén Hg mining district included cinnabar extraction sites (open pits and underground mines), storage areas and metallurgical plants, including mineral furnaces. In two millenniums of activity, this area produced one third of the Hg used in the human history (Hernández *et al.* 1999).

The study area for this work is located on the abandoned metallurgical site in Almadenejos. The site dates from the 18th century and is located 12 km from Almadén. The studied area is approximately 30,000 m^2 surrounded by a wall built between 1756 and 1759, and where six pairs of abandoned roasting furnaces are found in ruins. These furnaces were used to obtain primary Hg from cinnabar.

Higueras *et al.* (2003) found Hg concentration in village of Almadenejos that range from 6 to 8889 mg kg^{-1}. For their part, Millán *et al.* (2006) found values of up to 550 mg kg^{-1} within the abandoned metallurgical plant.
Nowadays, the abandoned site is covered with cinnabar mine tailings and the habitants of the village use it as pasture land for livestock. The dominant vegetation includes *Marrubium vulgare* among other species (Millán *et al.*, 2006).

The main aim of this study is to evaluate the spatial distribution of Hg in the soil-plant system within an area where human activity was dominant over a long period. Furthermore, a physico-chemical analysis of soil and study of biological soil parameters were carried out.

Materials and Methods

Soil and plant samples were obtained in three field campaigns between 2006 and 2008 during the autumn time. After each campaign, laboratory analyses were carried out to determine physical, chemical and biological soil properties as well as total and available Hg concentrations for both plant and soil samples.

Soil samples were taken from seven points at regular 10 m spacing. This points were organized in transect that was constituted of three areas: A1, A2 and A3 (Figure 1). At each sampling point, *Marrubium vulgare* L. plants were also collected.

Plant samples were washed using an ultrasonic bath treatment to remove external contamination and divided into two fractions: the shoot (stem and leaves) and the

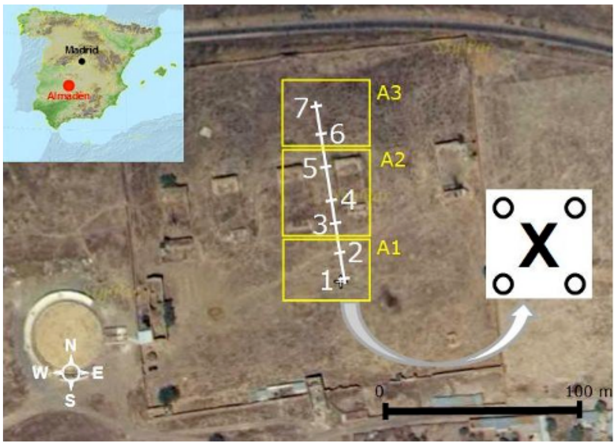

Fig. 1. Experimental field plot and location of the samples areas (O=soil and X = soil+plant)

root system. Soil and plant samples were dried at room temperature, homogenized and ground. Afterwards, mercury concentration was determined in them using an Advanced Mercury Analyzer (AMA-254).

Microbial analyses were performed with fresh sample after 2 mm mesh.

Furthermore, a specific six-step sequential extraction procedure developed by Sánchez *et al*. (2005), was applied to study the distribution of Hg in soil samples.

Results and Discussion

Regarding pedological properties of soil, standard soil parameters indicate slight variations along the studied transect. The obtained values for them imply a good condition for pasture land, which is the actual land use at this site.

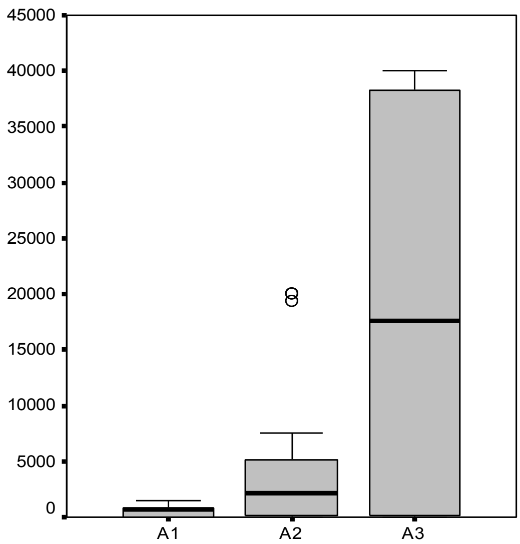

Fig. 2. Total Hg concentration in soil for the three study areas (A1, A2 and A3)

Figure 2 and 3 show total and available mercury concentration in the three areas (A1, A2 and A3). In all cases, maximum values were obtained in samples collected downslope from the furnaces area (A3) where, cinnabar was stockpiled and, in some cases, slag and waste produced in the roasting processes was deposited. Moreover, the lower part of the transect acts as the reception and accumulation area for the sediments that come from the upper part of the site (A1 and A2).

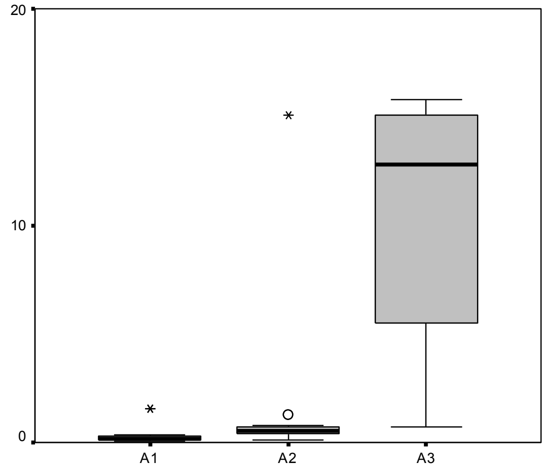

Fig. 3. Available Hg concentration in soil for the three study areas (A1, A2 and A3).

Regarding the ratio of the percentage of available Hg concentration in soil with respect to total Hg concentration in soil, it remains below 3% in the three areas. It has to be taken into account that in these samples, Hg is mainly in cinnabar form, which is very stable.

As regards mercury concentration in *Marrubium vulgare* plant samples, mercury in leaves varied from 6 to 323 mg kg^{-1}, whereas Hg concentration measured in stems gave lower values, from 1.5 to 77 mg kg^{-1}. Mercury concentration in root varied from 8 to 651 mg kg^{-1}. Our results are within the ranges presented by Millán *et al.* (2006) and Higueras *et al.* (2003).

In the three studied areas, Hg concentration in the stems were similar and in all cases lower than in leaves and roots. The area located upslope from the roasting furnaces (A1), gave similar values in all plant fractions and lower than the other sampling sites. The area along the furnaces (A2), Hg in plant increased in roots and leaves. In the downslope area (A3), a maximum Hg concentration was reached and this coincides with the maximum total and available Hg content in soil.

There is a significant correlation between root Hg concentration and available Hg concentration in soil ($r=0.450$, $\alpha=0.05$), but no correlation between root Hg concentration and total Hg concentration in soil was observed.

With regard to the distribution of Hg between the different soil fractions, the results indicate that Hg distribution among them in the three areas is similar. Mercury is mainly found in the fraction assigned to the final insoluble residues (31-70%) that correspond to resistant mercury sulphides. The next major amount is released with 6 M HCl, that indicated the Hg associated to crystalline Fe-Mn oxyhydroxides and/or presented as 6 M HCl-soluble compounds (22-59%). After, the Hg associated to oxidizable fraction that can be assigned to the association with organic matter and traces of elemental Hg is in the range of 5 to 20%. Finally, Hg associated to water-soluble phases, exchangeable fraction, carbonates and amorphous oxyhydroxides is less than 0.2 %.

The experimental area was an historical cinnabar roasting site. The mineral roasting process in the 17^{th} and 18^{th} centuries was incomplete and, accordingly, less efficient than modern systems. This fact justifies the fact that most Hg was associated to resistant mercury sulphides and to metacinnabar soluble in 6 M HCl due to the roasting process. Furthermore, a high amount of Hg was found in the oxidizable fraction that could be associated to high organic matter values and traces of elemental Hg. In the case of the abandoned metallurgy site in Almadenejos, lower cinnabar roasting temperatures were used at the time of activity. This led to lower mercury recovery (Bernaus *et al*., 2006) and as a consequence higher soil Hg concentrations are found at the site.

Regarding biological parameters, microbial activity and biomass may indicate the incidence of environmental changes and reveal situations of stress and disruption in soil systems. To avoid the seasonal influence in the magnitude of these parameters, they were analysed for samples obtained in autumn and spring of 2006 and 2007, respectively. This is when the biological activity has reached a maximum in this area. The study of biological parameters took into account several plots within Almadén mining district with different land uses in addition to Almadenejos in order to obtained reference values.

Soil microbial biomass obtained by substrate induced respirometry (SIR) (Anderson and Domsch, 1978) has a value of 919± 341 mg C_{mic} Kg $soil^{-1}$ (n=6) while values obtained for the whole area of Almadén (n=42) range from 117.5 to 2104.47 with a mean value of 656.26 mg C_{mic} Kg $soil^{-1}$. Estimating soil microbial biomass by fumigation extraction (FE) (Vance *et al.* 1987) value obtained in Almadenejos is 989±278 mg C_{mic} Kg $soil^{-1}$ (n=3) the highest obtained in the whole area of Almadén (n=15) mean = 500 mg C_{mic} Kg $soil^{-1}$.

High values of metabolic quotient (qCO_2) should be expected in the Almadenejos furnace, according with the heavy metal concentration in these samples, but values obtained in this plot range (n=6) from 0.64 to 1.43 mgC-CO_2 g C_{mic}^{-1} h^{-1}. Values obtained for Almadén (n=42) range from 0.57 to 8.11 mgC-CO_2 g C_{mic}^{-1} h^{-1} with a median value of 2.58 mgC-CO_2 g C_{mic}^{-1} h^{-1}. Therefore, the samples from Almadenejos site shown low metabolic quotient values, suggesting that the high mercury concentration is not a disrupting factor in these soils.

Maximum respiratory is proposed as OECD test (Dott, 1995) for assesing if soil contamination has any effect on soil microbial activity. For this estimation is suggested that soils with CO_2 production rates under 0.5 mg CO_2 100 g^{-1} h^{-1} may be exposed to chemical pollutants. All samples from Almadén (n=42) show maximum respiratory rates from 1 to 16 mg CO_2 100 g^{-1} h^{-1}, so the reference value is not of utility for assessing soils from Almadén, but we can compare the maximum respiratory rate of Almadenejos, ranging from 3.51 to 7.11 mg CO_2 100 g^{-1} h^{-1} with the values obtained for Almadén with a median value of 3.33 mg CO_2 100 g^{-1} h^{-1}. C_{mic} to C_{org} ratio should show high values in metal polluted soil (Dhalin *et al. 2010)* due to the loss of soil microbial biomass (Brookes and McGrath, 1984) and the slow rate of soil organic matter mineralization (Baath, 1989). C_{mic}/C_{org} values obtained from Almadenejos range from 1.39% to 4.14% while Almadén values (n=42) range from 0.67 to 5.04% with a median value of 2.1%, only the lesser value of Almadenejos is under the median value of Almadén.

No one of the analysed soil microbial activity parameters indicate any type of stress/disruption over soil superficial samples of Almadenejos either when comparing when the values obtained for all the analysed soil samples in Almadén or when possible when comparing to external standards, this may be explained by a low microbial availability of mercury and to some extent to physical, chemical and physico-chemical characteristics of the soils in the Almadenejos plot (Millán *et al.* 2011), with high organic matter content in comparison with the rest of the samples from Almadén and with pH close to neutrality vs acidic pH in the rest of the samples.

Conclusion

Soil parameters are similar in all the samples taken in the study area.

There is correlation between total and available Hg in soil samples. However, it is important to point out the low percentage of available Hg despite the significant high amounts of Hg in soil.

Mercury is mainly found in a form associated to resistant Hg sulphides and metacinnabar as 6 M HCl-soluble compounds and to organic matter and traces of elemental Hg. The lowest Hg concentrations were obtained with Hg associated to water-soluble phases, exchangeable fraction, carbonates and amorphous oxyhydroxides were determined as the lowest concentrations.

Marrubium vulgare could be a good candidate for phytoextraction techniques due to its capacity to accumulate high Hg content in shoot.

Not one of the analysed soil microbial activity parameters indicate any type of stress or disruption over soil superficial samples of Almadenejos either when comparing the values obtained for all the analysed soil samples in Almadén or when possible comparing to external standards. This may be explained by a low microbial availability of Hg and to some extent the physical and chemical characteristics of the soils in the Almadenejos plot that show optimum values related with critical parameters such as organic matter.

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