Environmental Impact of an Abandoned Cinnabar Mining Exploitation (Usagre, Spain)

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INTRODUCTION.

Over the world, several cinnabar mining districts have been investigated concerning the consequent Hg pollution of surrounding ecosystem compartments. Among those gathering more attention, there are the Almadén and Mieres mining districts in Spain (Loredo et al., 1999; Higueras et al., 2003, 2006; Fernández-Martínez, et al., 2006; Millán et al., 2006), which are the largest and the eighth largest Hg mining districts in the world, respectively. Apart from these, in Spain there are other Hg mining areas extensively exploited up to quite recently, and whose environmental consequences have not been investigated so far. This is the case of the Usagre mining district.

The Usagre mining district belongs to the Ossa-Morena Zone, the Iberian Massif geotectonic unit that displays the greatest variety of types of mineralisation and the largest number of ore deposits. Particularly, the Usagre district is characterised by epithermal Hg-(Cu-Pb-Ba) replacements in limestones (Variscan age). The most important deposit of this type is the Sultana-Mariquita mine, an Hg-rich deposit (size: 0.11 Mt and grade: 5-7 % Hg) worked intermittently from 1631 to 1971 (Tornos et al., 2004).

The aim of the present work is to study the Hg content and distribution in soils and plants in the Usagre mining area in order to establish its Hg pollution degree, and, therefore, to assess the derived environmental risks.

MATERIALS AND METHODS.

Study Area.

The studied mining area is located 2 km western of Usagre village, southern of Badajoz province (Spain). The mineralization of this mining district is constituted by cinnabar (HgS), which represents the dominant sulphide phase, and $Hg°$, with barite ($BaSO_4$) as the main gangue mineral. There are also traces of galena (PbS), pyrite (FeS_2), tetrahedrite ((Cu,Fe)$_{12}Sb_4S_{13}$), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), realgar (AsS) and gold. Some abandoned mining sites and an inactive smelting plant are the main remains of the past extraction and processing of Hg mineral resources.

Sampling.

Soils and plants sampling was carried out in five different sites in the studied abandoned mining area. Three of these sites (U-1, U-2 and U-3) were located near the inactive smelter at distances about 75, 50 and 25 m, respectively. Such places are partially covered with HgS residues and smelting wastes. The other two sampling sites (U-4 and U-5) were situated in the close environs of two abandoned mining sites. Soil sampling included surface soils (0-20 cm). Four sampling points were randomly selected at the five sites, and single composite soil samples corresponding to each one of sampling sites were generated. Plant sampling involved the aerial part of the characteristic plant species growing in the five mentioned sampling sites. Perennial as well as annual plant species of different size and leaf morphology were sampled. Three plant specimens of the different plant species were collected at the different sampling sites. Plant samples were washed with fresh water, then cleaned using an ultrasonic bath to remove dust contamination, and finally rinsed with deionised water.

Mercury Analysis.

The analysis of total Hg contents was performed on finely powdered soil and plant samples using a Hg Milestone analyser (Milestone Instruments, Sorisole, Italy), model DMA-80. $Hg°$ in soil samples was evaluated by means of a pyrolisis technique, following the method of Biester & Scholz (1997). The exchangeable Hg in soil samples was determined following the DIN V 19730 procedure.

RESULTS AND DISCUSSION.

Hg in Soils.

The content of total, elemental and exchangeable Hg in soil samples are indicated in figure 1.
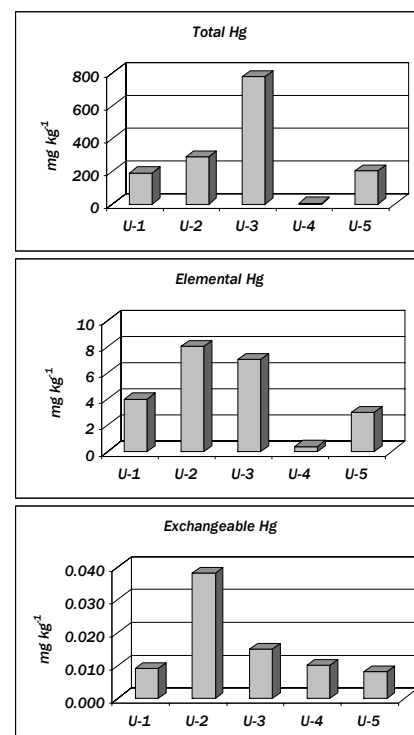

fig 1. Total, elemental and exchangeable Hg concentrations of sampled soils in the Usagre mining area.

Soil samples show a wide range of total Hg concentrations, from 5 mg kg^{-1} (U-4) to 778 mg kg^{-1} (U-3). These concentrations can be considered critical (concentration above which Hg toxicity is considered to be possible). & and Pendias (1992), the Hg critical content is 0.3-5 mg kg^{-1}.

The exchangeable Hg fraction in the studied soils is very low, ranging from 0.008 to 0.038 mg kg^{-1}. This is consistent with the low solubility of cinnabar and the low reactivity of Hg° (Rytuba, 2003). Moreover, in these soils this behaviour could be enhanced by their carbonate content and their soil pH values. It has been reported that when carbonates are present in host rocks cinnabar solubilisation is even more limited. Besides, high soil pH favours the retention of Hg in the form of cinnabar (Higueras, 2003). On the other hand, the low content of pyrite (traces) and the important presence of carbonates prevent acid drainage, which in turn severely limits cinnabar solubilisation. Mercury mines that release mine drainage can generate very high concentrations of iron-rich mercury-bearing precipitates that can be a significant source for bioavailable Hg (Rytuba, 2000).

The Hg° content in the studied soils ranges between 0.4 and 8 mg kg^{-1}. Such values are low in relation to the corresponding total Hg contents, representing a fraction comprised in the range 1-8%. Higher Hg° values are found in the closest sites to the smelter (U-1, U-2 and U-3), and in those in the way of the favourable wind direction (U-5).

Hg in Plants.

The Hg concentrations in the aboveground biomass of the natural plant species collected in the sites near the inactive smelter and near the mining sites are represented in Table 1.

Hg plant contents vary in a wide range (from 0.057 to 37.6 mg kg^{-1}), though most plant specimens display Hg concentrations comprised in the range 0.1-10 mg kg^{-1}. The frequency distribution is as follows: 28% (0.05-0.1 mg kg^{-1}), 22% (> 0.1-1 mg kg^{-1}), 44% (> 1-10 mg kg^{-1}) and 6% (> 10 mg kg^{-1}). Thus, an important proportion of collected plant samples (50%) shows to surpass the Hg critical concentration in plants, this is the level above which toxicity effects are likely, (1-3 mg kg^{-1}; Kabata-Pendias & Pendias, 1992). The high Hg values found in this large amount of plant specimens are of great

concern, not only for the high risk of toxicity to plants, but also for the great risk of Hg incorporation in the trophic chain. Vegetation growing in this polluted area is employed as pasture for livestock. According to the Directive 2002/32/EC on undesirable substances in animal feed, the maximum Hg level allowed in animal feed in order to avoid its transfer and further accumulation in the higher trophic levels of food chain is 0.1 mg kg^{-1}.

U-1

	mg kg^{-1}
Centaurea calcitrapa L.	1.58
Cirsium arvense (L.) Scop.	2.32
Hirschfeldia adpressa Moench.	0.059
Hordeum murinum L.	0.320
Malva rotundifolia L.	2.34
Medicago muricata Benth.	0.941
Plantago media L.	3.16
Trifolium fragiferum L.	3.98
Xanthium spinosum L.	0.385

U-2

	mg kg^{-1}
Agrostis setacea Curtis	1.42
Centaurea calcitrapa L.	0.816
Cirsium arvense (L.) Scop.	2.22
Hirschteldia adpressa Moench.	0.217
Hordeum murinum L.	1.03
Koeleria phleoides (Vill.) Pers.	3.30
Lamarckia aurea (L.) Moench.	1.63
Malva rotundifolia L.	4.69
Trifolium angustifolium L.	9.01

U-3

	mg kg^{-1}
Marrubium vulgare L.	37.6
Cynara humilis L.	3.28
Centaurea calcitrapa L.	1.99
Bromus madritensis L.	12.7

U-4

	mg kg^{-1}
Bromus madritensis L.	0.080
Cynara humilis L.	0.099
Dactylis glomerata L.	0.062
Eryngium campestre L.	0.078
Lolium rigidum Gaudin	0.059

U-5

	mg kg^{-1}
Carlina corymbosa L.	0.092
Dactylis glomerata L.	0.095
Echium plantagineum L.	0.151
Scabiosa columbaria L.	0.057
Trifolium angustifolium L.	0.130

Tabla 1. *Mercury contents in the aboveground tissues of plant species collected near the smelter and the mining sites located in the Usagre mining area.*

CONCLUSIONS.

The Usagre mining area shows critical total Hg soil concentrations in the close environs of pollutant sources. Also high levels of Hg° are found in such places, especially around the smelting plant (up

to 8 mg kg^{-1}). Conversely, soils display quite low exchangeable Hg contents (0.008-0.038 mg kg^{-1}).

The Hg concentrations in the aboveground tissues of the natural plant species collected in the mining area vary in a wide range (from 0.057 to 37.6 mg kg^{-1}), though most plant specimens display contents comprised in the range 0.1-10 mg kg^{-1}, with a great proportion (50%) showing critical contents. The high Hg values found in this large amount of plant specimens are of great concern because of the great risk of Hg incorporation in the trophic chain.

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