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Could an abandoned mercury mine area be cropped?

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ABSTRACT

The Almadén area (Spain) is known for its high natural mercury background as well as for the anthropogenic impact due to mining activities. After the end of these activities, appropriate alternative use of the soil has to be found, and agricultural activities stand out as an environmentally-friendly and potentially profitable alternative, giving to the soil a sustainable use without risks for human or animal health according to current legislation.

Experiments performed at different scales (involving hydroponics, growth in pots and lysimeters) allow recommendations to be made regarding the adequacy of cultivation of different crops for animal or human consumption before they are sown in the field. Regarding crops for animal feeding, mercury accumulation in vegetative organs represents a higher potential risk for animals. Nevertheless, seeds and fruits can be used, both for human and animal consumption. Finally, this work will lead the way to obtain a scientific basis for elaborating a list of recommendations on sustainable and safe alternative land use, according to current international legislation.

1. Introduction

European mercury mining districts in Almadén (Spain), Idrija (Slovenia), and Monte Amiata (Italy) have produced more than half of the total mercury (Hg) extracted and commercialized in the world and near the total amount of the Hg mined in Europe. Among them, Almadén has been considered the largest and oldest mercury mining area and its production represented above one third of the total Hg extracted and produced in the world. Mercury has been exploited in Almadén since the Roman times and, apart from occasional disasters, the extraction has been continuous till recently, when the closure of the mine was decided. In 2002, mining activity at the Almadén mine ceased, but significant quantities of ore were stockpiled prior to that time and retorting of the ore was not discontinued until February 2004 (Hernández Sobrino, 2007). For centuries, the economy of this area was thus dependent on the mining activities and as a consequence, once the mine has closed, the entire region has suffered an economic depression in the last decades. In order to mitigate this situation, it is necessary to find appropriate socio-economical alternatives for the local population, including the implementation of alternative land use.

Some previous studies have been focused on the Almadén mining district (Berzas Nevado et al., 2003; Ferrara, 1999; Gray et al., 2004; Higueras et al., 2003), but there are not many that evaluate Hg accumulation in the edible parts of food crops. The use of such plants for fodder could also pose a health risk by allowing Hg to enter the food chain, so that Hg concentration in the edible parts of crops needs to be evaluated. Regarding total Hg concentration in Almadén soil, studies carried out by different authors show values between 0.5 and up to >1700 mg kg^{-1} where the maximum is obtained near the mine (Huckabee et al., 1983; Lindberg et al., 1979; Millán et al., 2011; Sanchez et al., 2005). Values like these must be considered normal for a region rich in mercury deposits and with an intense and prolonged mining activity (Gray et al., 2004; Higueras et al., 2004). The soluble mercury levels range from <0.02 to 1.04 mg kg^{-1}. The concentrations of exchangeable mercury vary between 0.15 and 7.3 mg kg^{-1} (Millán et al., 2006). These results obtained from sites directly affected by ore extraction, sites close to mining and processing activities, and areas unaffected by any such activity (particularly open forest areas—known as *dehesas* in Spanish—where natural Mediterranean vegetation grows in the presence of agrosilvopastoral activities). In order to study the Hg accumulation ability of different crops, as well as the concentration in the edible organs, preliminary tests have to be carried out under controlled conditions before their cultivation in the area. This work summarizes the experimental work carried out in the last decade in order to assess on the cultivations to be

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implemented in the area. Results of different types of study are reported here: (1) *hydroponic experiments*, used to simulate different Hg concentrations in the soil solution; (2) *experiments performed in pots under greenhouse conditions*, using soil from the Almadén area, and (3) *lysimeter experiments* using undisturbed soil monoliths from a test plot located near Almadén, used for agricultural and farming purposes. Lysimeter experiments make it possible to work under close-to-real conditions due to the advantage of preserving the soil horizon characteristics. Results from field plots are included where available. Several crops, either currently cultivated in the Almadén area or the close surroundings have been selected. Therefore, the main objective of this work is to obtain a scientific basis for elaborating a list of recommendations on sustainable and safe alternative land use, without risks for human or animal health, according to current international legislation.

2. Materials and methods

2.1. Plant growth (for hydroponic and pot experiments)

Seeds were surface-sterilised in 10% v/v sodium hypochlorite for 15 min, rinsed thoroughly with deionised water and germinated in darkness at 28 °C for 3 days on water-moistened filter paper. The seedlings obtained were placed in plastic containers with half strength, continuously aerated nutrient solution. The composition of the nutrient solution was as follows: 1.5 mM $Ca(NO_3)_2$, 4.0 mM KNO_3, 1.5 mM KH_2PO_4 and 1.0 mM $MgSO_4$. Micronutrients were supplied as 36 μM Fe-EDDHA, 33 μM $MnSO_4H_2O$, 1.6 μM $ZnSO_4$ 7·H_2O, 1.6 μM $CuSO_4$ 5·H_2O, 46 μM H_3BO_3 and 0.1 μM $(NH_4)_6Mo_7O_{24}$ 4·H_2O. The pH of the nutrient solution ranged from 5.5 to 6.0.

2.2. Hydroponic experiments

When plants reached four developed leaves, they were transferred to plastic pots (10 L perlite in the upper compartment and 2 L of solution in the lower compartment or only 4 L of nutrient solution for pure hydroponics). Mercury was added as $HgCl_2$ to the nutrient solutions to give concentrations ranging from 0 to 5 μM Hg. Deionised water was used for preparing all solutions and was added to replace transpiration losses every two days. The entire nutrient solutions were changed weekly. All plants were grown in a glasshouse under the following environmental conditions: night/day temperature 12–28 °C, relative humidity 50–80% and a photosynthetic photon flux density of 500-μmol m^{-2} s^{-1}. All experiments were performed in triplicate or quadruplicate following a randomised block design.

At harvest, the roots and shoots of each plant were separated and their fresh weight recorded. They were then thoroughly washed, first with tap water, followed by rinsing three times with deionised water. To determine dry weights while avoiding Hg losses, plant matter was dried at room temperature for at least two weeks until a constant weight was reached. The samples were then ground and sieved to a size of less than 50 μm for Hg determination.

2.3. Pot experiments

When the prepared plantlets (for species see below) reached the four-leaf stage, they were transferred to 15 L plastic pots (for numbers per pot see below) containing a mixture of soil, perlite and sand in equal proportions. The soil was collected close to the village of Almadenejos, in the Almadén district. Almadenejos lies in a river valley of mainly slate and sandstone lithology; the main land use is grassland pasture (Millán et al., 2006). This soil is classified as a Mollic Haploxeralf according to USDA Soil Taxonomy criteria. Only soil from the horizons Ah and Bt1—i.e., to a depth of 40 cm (that of shallow ploughing)—was used in these experiments. The aggregates in the substrate were broken down and the soil sieved to 2 mm. Plants were harvested coinciding with the beginning of flowering (harvesting time for forage use) and full maturity (harvesting of seeds for human consumption). Only shoots were collected at the first sampling stage, while whole plants were collected at the second. The samples, where appropriate, were separated into roots, stems plus leaves, husks and grains or fruits and the fresh weights recorded. The aerial parts of the plants were washed as described for the hydroponic experiment, while roots were placed in individual beakers, rinsed several times with deionised water and cleaned using an ultrasonic bath to remove external contamination (5 cycles of 5 min). Dry weights were determined by drying the samples at room temperature for at least two weeks, until a constant weight was reached. The samples were then ground and sieved to a size of less than 50 μm for Hg determination. All plants were grown under the above-mentioned glasshouse conditions. This experiment was performed in quadruplicate.

2.4. Lysimeter experiments

Lysimeter experiments represent an intermediate stage between greenhouse and full-scale field experiments. The lysimeters used consisted of a cubic meter ($1 \times 1 \times 1$ m^3) of an unaltered soil monolith placed within a metallic structure. Lysimeters were extracted northeast of Almadenejos, in the same area described above. All lysimeter experiments were performed under cover at the CIEMAT research facilities in Madrid. The climatological conditions of the Almadén area and Madrid are similar. Each lysimeter was instrumented with a set of sensors to monitor soil parameters: pH, Eh, soil temperature, volumetric water content and water matrix potential (Schmid et al., 2004). The electrodes and sensors were set at different depths (15, 25 and 50 cm) in the lysimeters. In order to carry out a monitoring of the soil properties, an electronic data collector was implemented to obtain data for each sensor every 30 min. The exception was the pH sensor, where the signal is too weak to be obtained by the data collector. The pH was therefore obtained with a standard pH meter (Schmid et al., 2004). Irrigation was carried out according to the mean annual precipitation data over a period of 30 years for the region of Almadén (Carrasco et al., 2001).

Soil samples were collected from two soil profiles marking the extreme perimeter where the soil monoliths were extracted. The soil profiles showed an upper organic horizon (Ah) and a lower mineral horizon (Bt) where the pH was near neutral (6.8–7.0). The upper horizon contained 4 to 6% and 10 to 13% of organic matter and clay content, respectively. In contrast the lower horizon contained 0.5 to 1.3% and 17 to 46% of organic matter and clay content. The soil has been classified as Mollic Haploxeralf according to the USDA Soil Taxonomy (Soil Survey Staff, 1999) and is representative of "dehesa" soil in the Almadén area (Schmid et al., 2003). Total Hg content ranged between 14 and 22 mg kg^{-1} in the upper horizon and a maximum content of 44.61 ± 3.67 mg kg^{-1} was reached within the upper part of the lower horizon (Sanchez et al., 2005).

Seeds (for species see below) were directly sown in the lysimeter soil and the plants raised following the typical agricultural practices of the Almadén area. Samples were taken at the beginning of flowering (harvesting time for forage use) and at full maturity (the time when seeds are harvested for human consumption). The plants taken at the first sampling stage were separated into shoots and roots, while those taken at the second stage were separated into roots, leaves plus stems, husks and grains. Fresh weights were recorded for all samples. Sample washing and processing was similar to that described for the pot assay. This experiment was performed in triplicate.

2.5. Plant species

2.5.1. White lupin (Lupinus albus L.)

White lupin cv. Marta plants were grown in hydroponics, pots filled with soil and lysimeters (Zornoza et al., 2010). In hydroponics (0; 1.25; 2.50 and 5 μmol L^{-1} Hg) 6 plants per pot were grown for 10 weeks without reaching flowering or fruit, but in soil (25 plants per pot) and lysimeter experiments (30 plants m^{-2}), the plants were grown until maturity. White lupin has several uses. On one hand, the seeds are used for human consumption as snack food and as raw material for the production of lupin flour used in a variety of goods like bread or gluten free products. On the other hand, it is also cultivated as fodder for animals. Regarding this latter use, these plants could be consumed in several forms; livestock could graze these plants as fresh green forage (at the beginning of the flowering stage) or consume them as silage. Moreover, lupin flour is used for fish and bird meal (Hernández and León, 1994; Pulse Western Australia, 2012). Sampling periods corresponding to the different uses are shown in Table 1. Results presented in this paper collect data from one harvest in hydroponics and pot experiments and four consecutive harvests in lysimeter experiments.

2.5.2. Chickpea (Cicer arietinum L.)

Chickpea plants cv. Eulalia were cultivated in hydroponics, pots filled with soil and lysimeters. In hydroponics (1.25; 2.50 and 5 μmol L^{-1} Hg) 4 plants per pot were grown for 110 days to reach maturity. Plants in the pots (25 plants per pot) and lysimeter experiments (36 plants m^{-2}) were also grown and harvested at maturity stage. This crop is used both for human and animal consumption. Cooked and roasted chickpea seeds as well as young shoots are used for human consumption, and chickpea flour (besan) is used in cooking, especially in Middle Eastern countries (Hernández and León, 1994; Pulse Western Australia, 2012). They are also cultivated for animal feed. Livestock can graze these plants as fresh green forage (at the beginning of the flowering stage), and the seeds form part of the diets of poultry, pigs, cows and fishes (FAO, 2012). Table 1 shows the sampling periods corresponding to these different uses. The results represent data from one harvest for all types of experiment.