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Environmental Threats of Ancient Pb Mining and Metallurgical Activities in the Linares Mining District (Southern Spain) †

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Abstract: Former industrial sites are now dedicated to other land uses in the Linares mining district. Here we selected five residential/farming areas (squares of 1 km^2 each) and sought to evaluate the levels of contamination by Potentially Toxic Elements (PTEs) of the soils, and also to offer an insight into the threat these pollutants may pose to human health or the environment by means of risk assessment. High concentrations especially of Pb, and also of As, Cd, Cu and Zn were found in quantities that are considerably bioavailable. Moreover, risk assessment revealed unacceptable concentrations for Pb and As in all the areas as well as for Cd and Cu in some squares.

Keywords: soil pollution; metal mining area; trace elements; risk assessment; remediation

1. Introduction

The accumulation of chemicals in former mining and metallurgy sites can damage the quality of soils in the nearby areas, leading to undesirable effects risks for living organisms. This scenario is particularly relevant when mechanical weathering like deflation, erosion, and thermal stress act coupled to active chemical weathering, hydration, or hydrolysis of the silicates and carbonates, thus releasing pollutants into the environment [1].

Risk assessment takes into consideration both hazard and exposure, and therefore the bioavailability of compounds. It involves procedures for estimating the probability of occurrence of any given magnitude of adverse health effects over a certain period of time [2]. In this context, baseline human health risk assessment (BHRA) is the analysis of the potential adverse health effects caused by exposure to hazardous substances released from a site in the absence of any measures to control or mitigate their mobility (i.e., under an assumption of no action) [2]. The BHRA model was developed following the Risk Assessment Guidance for Superfund [2] since it is considered that simple site-specific risk assessment offers a reasonable compromise between effort and site-specificity [3].

It is necessary to remediate soils for which concentration of PTEs suppose a risk for human health or environment. Most strategies are based on the isolation and treatment of the polluted soil; these approaches include the following processes [4]: (1) thermal; (2) chemical, by dissolving contaminants in soil particles in washing water, and then treating the water with solidifying agents to produce relatively inert cement-like material; (3) physical, by electrokinetic procedures that remove trace elements by applying an electric current, or by concentrating contaminants into a smaller volume of soil through physical separation processes, thereby reducing the volume of the contaminated material; and (4) biological procedures, which use living organisms for remedial purposes, as is the case of phytoremediation. In all of these approaches it is important to assess soil composition and the mobility, availability and distribution of the pollutants.

All things together, here we sought to:

- Assess the levels of contamination of the areas in question (five sites within Linares mining district).
- Offer an insight into the threat these pollutants may pose to human health and the environment in the study site.
- Discuss the selection of appropriate soil remediation technologies.

2. Materials and Methods

2.1. Study Area

The study area is located in the Linares mining district (Spain). In this area, there were selected five areas (Figure 1):

- **La Garza (square 12):** Soil well developed and cereals are cultivated. There are signs of former mining.
- **La Cruz Foundry (24):** Old facilities of the mining district. Vegetation is not present in this square.
- **San Genaro mine outskirts (25):** Old shaft, now abandoned. Tree plantations are promoted here.
- **Arrayanes (38):** It is located in the vicinity of a former mineral processing plant.
- **Pozo Ancho's mine shaft (51):** This area contains a vast amount of mine waste.

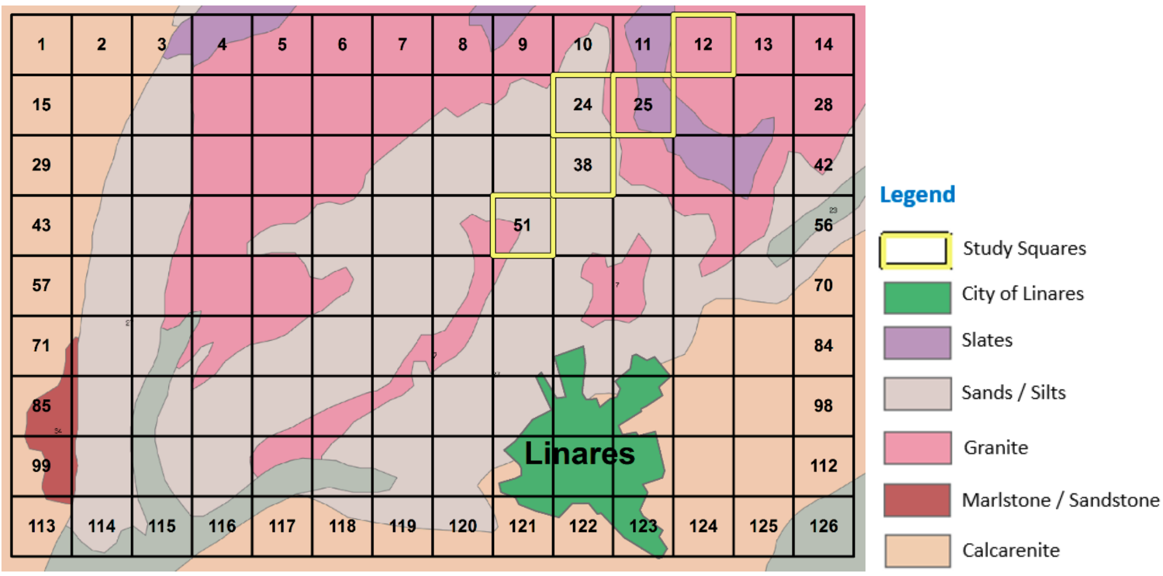

Figure 1. Situation map of the Linares mining district with outcropping lithology and studied grid squares (1 km^2 each).

2.2. Pollution Study

Composite samples of about 50 kg were taken from 0–35 cm depth for each square. Being air-dried and sieved (2 mm), before the chemical analyses that they were subjected:

- pH & Electrical conductivity by glass electrode in soil-water suspension.
- Particle-size distribution by the pipette method.
- Element concentration of As, Cd, Cu, Pb and Zn by ICP-OES
- Sequential Extraction by BCR procedure. Four fractions obtained (Carbonate-bound, Fe-Mn oxide-bound, organic matter-bound and residual fraction). First two are the bioavailable term.
- Other soil parameters (% OM, ECEC, mineral phases, etc…).

This allowed to provide a properly edaphic and chemical characterization of the soil. Afterwards, a Risk assessment by means of the Baseline Human Health Risk Assessment (BHRA) for on-sire receptors was conducted. It was performed for As, Cd, Cu, Pb and Zn taken from exchangeable fractions from BCR. The analysis combines toxicity and exposure assessments and it considers carcinogenic and non-carcinogenic risks following the ISIS guidelines.

3. Results and Discussion

3.1. Analytical Results

Accordingly, the soils in the study area were neutral (square 24, pH = 6.87), slightly alkaline (sample 12, 25 and 51, pH = 7.46, 7.5 and 7.97 respectively) or medium alkaline (sample 38, pH = 8.17). The upper horizon showed low organic matter content (<1.5%). Electrical conductivity was low in samples 12, 25 and 51 (EC < 0.15 dS m^{-1}), while the samples 24 and 38 had higher electrical conductivity (EC = 1.33 and 0.91 dS m^{-1}, respectively), indicating salinization issues. Salinity can have a major effect on soil structure. In this regard, soil structure, or the arrangement of soil particles, greatly affects permeability and infiltration. Soil EC can serve as a proxy for soil chemical properties such as organic matter, clay content, and cation exchange capacity [5]. Moreover, element concentrations and bioavailability results from BCR extraction are summarized in Table 1.

Table 1. Element concentration for each square, expressed in ppm. Values in parenthesis represents bioavailability, corresponding to the first two of fractions of the BCR procedure.

Square	As	Cd	Cu	Pb	Zn
12	18.5 (1.2%)	0.7 (<DL)	67 (20.6%)	5158 (66.1%)	33 (22.6%)
24	139.5 (2%)	18.7 (58.7%)	357 (24.1%)	4244 (46.0%)	694 (51.2%)
25	84.4 (0%)	3.4 (51.2%)	381 (18.5%)	35899 (40.8%)	473 (15.8%)
38	134.5 (19.2%)	2.8 (21.2%)	587 (0%)	9872 (35.6%)	7468 (44.9%)
51	41.6 (0.4%)	1.8 (<DL)	722 (12.5%)	9870 (35.5%)	143 (13.9%)

Regarding element concentrations, Pb concentrations are very high in all the areas, reaching values considered toxic to plants. However, Square 12 is the one that presents low concentrations for the remaining elements, being only affected by these PTEs. Intervention values are surpassed in almost all cases and at least one time for each element analyzed. This means that a soil remediation is required, especially for the high levels of Pb.

This proposal is reinforced by glancing at the sequential extraction results. The bioavailable fraction corresponds to the F1 of the BCR (carbonate-bound). In this respect, equilibrium for metals of this fraction is even possible with the aqueous phase. Therefore they present high relative mobility, thus being easily bioavailable. In general terms, Cd, Cu, Pb and Zn, as opposed to As, were highly available as they were present in the carbonate fraction. The high concentration of these elements in this fraction may be indicative of anthropogenic contamination, as well as recent pollution.

3.2. Risk Assessment Results

Four exposure pathways were considered for this land use, as stated by national legislation; i.e., oral ingestion (dust and soil particles), dermal contact, inhalation (vapor and soil particles), and food consumption (cultivation in polluted soils). For the latter, the soil concentrations of trace elements used for the calculation correspond to the exchangeable fractions from the BCR sequential extraction procedure.

In this regard, the assessment of natural-soil land use introduces As, as in other scenarios, as the element with the largest contribution to overall risk because of its carcinogenic nature. This happens by the fact that it is the only carcinogenic element and it has more restrictive levels. Nevertheless, Cu and Cd also exceeded the maximum accepted risk quotient (HQ = 1) for squares 24, 25 and 51. Pb concentrations in the grids were so high that specific risk assessment showed an unacceptable risk for human health. Inorganic Pb risk assessment was based on predicting PbBs for current and potential future populations in relation to compound exposure. All grids showed PbBs exceeding the limit of 5 μg/dL for both models.

4. Conclusions

The soil of the Linares district present anomalous concentrations of As, Cd, Cu, Pb and Zn, exceeding admisible limits of Pb and As in all the study sites. This is more worrying since a significant proportion of the PTEs (especially Pb) are present in bioavailable forms. This led the risk assessment to unveil a threat to human health; Squares 24, 25 and 51 are priority objectives for soil remediation.

We consider that phyisical separation might be a proper remediation given that most of the pollutants are concentrated in the fine grain size fraction (<63 μm), mainly in squares 12, 38, 51. We suggest gravity and even magnetic separation as complementary procedures given the nature of the minerals and waste found. A second possibility is phytorremediation (phytoextraction or phytostabilization), as the available fractions of soil pollutants are significant.

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