Heavy metals distribution in soil particle size fractions from a mining area in the southeast of Spain

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Abstract
The distribution of heavy metals in soil particle size fractions from soils on two representative tailing ponds, El Lirio and El Gorguel, from the southeast of Spain has been studied. In both tailing ponds heavy metal mobility is not enhanced owing to the high pH despite a low buffer capacity. In addition, the materials showed a low fertility and high salinity, which prevent plant colonization and leave their surface unprotected against wind and water erosion. The dominant fraction for both ponds was 425–150 µm, while the finest fraction represented 23 % and 20 % for Gorguel and Lirio tailing ponds, respectively. High concentration of metals occurred in both finest and coarsest fractions due to high surface area and negative charges associated with fine particles and the processes of treatment of the ore. The results showed high pollution of these ponds for all the fractions. However, highest enrichment factors (EFs) were in the finest (<75 µm) and coarsest (2000-425 µm) particles with EFs >10 for Pb; >15 for Cd and >20 for Zn in Lirio and EFs>10 for Pb; >20 for Cd and >30 for Zn in Gorguel.

Key Words
Tailing pond, heavy metals, particle size, mining activities.

Introduction

In Murcia Province, there are 85 mining tailing ponds due to intensive mining activities that occurred during the last century, especially in the Sierra de Cartagena-Union. Although mining activity was abandoned several decades ago, those tailing ponds with high amount of heavy metals still remain in the area. The tailing ponds, due to their composition and location, may create environmental risks of geochemical pollution, negatively affecting soil, water, plant, animal, and human populations, as well as infrastructure. As most of these ponds are not covered by vegetation or any other material, wind and water erode their surface and high amount of material is transported long distances, especially fine particles. Fine particles have high specific area that retains high amounts of metals (Wang *et al.* 2006). In addition, small particles are often soluble and metals are more likely to traverse the gastric mucosa and be more efficiently adsorbed in human tissues than for coarse fractions (Lin *et al.* 1998). The objective of the present study is to evaluate the effect of particle size on the distribution of heavy metals in tailing ponds from a mining area in Southeast Spain.

Methods

Study area and sampling

Mine tailings are located in the Murcia Province (Spain) Cartagena-La Unión Mining District, where much mining activity had been carried out for more than 2500 years, stopping in the nineties.

The climate of the area is a typical Mediterranean with mean monthly temperature of 9.3 °C in January to 24.4 °C in July. Total annual rainfall varies between 279 and 406 mm with on average ~ 275 mm, in autumn and spring. The potential evapo-transpiration rate surpasses 900 mm/y. Two tailing ponds generated by mining activities were selected, El Lirio and El Gorguel. These ponds are representative of existing ponds in Sierra Minera de Cartagena-La Unión, with similar problems and characteristics. The selection of these two ponds was based on access, physico-chemical characteristics (based on previous studies), hydrological conditions, slope, distance from towns, surrounding landscape, etc. Surface soil samples were collected according to a regular sampling grid of 100 m^2 using a Geographic Information System - GIS. Aerial orthophotos were used to design the grid so that sampling was representative of the surface area topography of each pond (Figure 1).

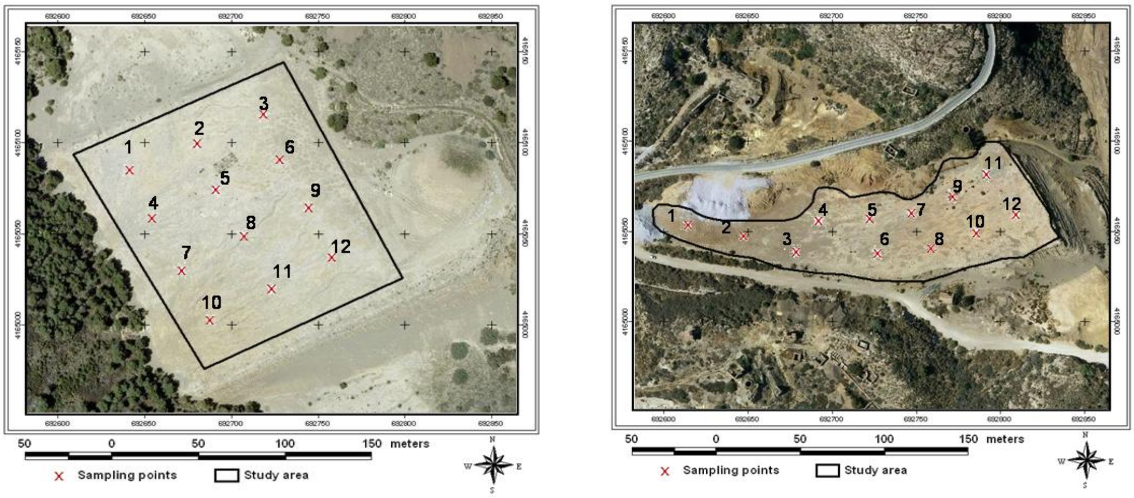

Figure 1. Design of soil surface sampling grids for El Lirio (left) and El Gorguel (right) tailing ponds.

Analytical methods

For the physico-chemical characterization of the surface soil at the two ponds, a sampling was carried out in April 2009 according to the designed sampling grids. Samples were taken from the soil surface (0-15 cm). The collected samples were taken to the lab, air-dried for 7 days, passed through a 2-mm sieve, homogenized, and stored in plastic bags at room temperature prior to laboratory analyses.

The analyses for this study were determined as follow: pH measured in a 1:1 water soil ratio solution according to Peech´s method (1965); soluble salts according to Bower and Wilcox (1965); organic carbon and nitrogen according to Duchaufour (1970), cation exchange capacity following the method of Chapman (1965), particle size analysis carried out by using the FAO-ISRIC system (1990) using a combination of pipette and sieving. The fractionation of bulk soils into five particle size fractions was conducted using sieves with the following sizes: 2000, 425, 150, 106 and 75 µm. For the quantification of the total metals in each fraction, a subset of each particle size fraction was ground, and an acid digestion (nitric-perchloric) was used (Risser and Baker 1990) (210 ºC during 1:3 h and with addition of 0.1 N HCl). Measurement of metals was carried out using atomic an absorption spectrophotometer (AAnalyst 800, Perkin Elmer). We interpritated the amount of metal in the mine waste using an enrichment factor, calculated with respect to highest limit concentration allowed by European regulations (Banat *et al.* 2005; Madrid *et al.* 2002; Chan *et al.* 2001).

Results

Physico-chemical characterization

Mean values of pH in the tailing ponds were 5.39 and 7.41 for Lirio and Gorguel respectively, thus heavy metal mobility is not enhanced at these pH values, although a higher mobility is expected in El Lirio. Additionally, no carbonate was detected for both ponds, indicating that the buffer capacity of these residues is low. Similar contents for organic carbon (O.C.) and total nitrogen (T.N.) were found in both mining ponds, with mean values of 0.37 and 0.42 % O.C. and 0.01 and 0.02 % T.N. for Lirio and Gorguel respectively, which shows the low fertility of these soils. Finally, the residues from both ponds are saline with EC values of 3.6 and 4.8 dS/m for Lirio and Gorguel, respectively.

Table 1. Physico-chemical characteristics of Lirio tailing pond. (unit indicated in the text).

Lirio	pH	E.C.	T.N.	O.C.	C.E.C.	Sand	Silt	Clay
Mean	5.39	3.63	0.01	0.37	16.38	60.17	32.47	7.35
Error	0.38	0.40	0.00	0.05	2.76	7.55	6.32	1.99
Variance	1.78	1.92	0.00	0.03	91.54	684.2	479.5	47.48
Minimum	3.71	2.53	0.00	0.13	0.25	3.00	8.55	1.11
Maximum	7.67	7.39	0.02	0.67	34.77	87.00	70.89	26.11

Fractionation of bulk samples into various particle sizes revealed different behavior between tailing ponds. In Gorguel pond, the dominant fraction was 425–150 µm (32%) (Figure 2); the amounts of the smallest fraction (<75 µm) ranged from 7% to 29% (mean 20%) while the largest fraction (425– 2000 µm) varied from 1% to 31% (mean 9%). On the other hand, samples from Lirio pond showed a heterogeneous particle size distribution; the dominant fraction was 425-150 µm (36%); the smallest fraction represents the 23% of the total, while the coarsest (425– 2000 µm) ranged from 3% to 34%, with a mean value of 16%.

Table 2. Physico-chemical characteristics of Gorguel tailing pond. (unit indicated in the text).

Gorguel	pH	E.C.	T.N.	O.C.	C.E.C.	Sand	Silt	Clay
Mean	7.41	4.80	0.02	0.42	8.39	60.37	30.08	9.55
Error	0.12	0.66	0.01	0.07	1.49	5.14	4.41	1.95
Variance	0.19	5.31	0.00	0.05	26.80	317.51	233.23	45.49
Minimum	6.54	2.67	0.00	0.15	3.73	33.66	6.15	3.16
Maximum	7.90	9.35	0.06	0.71	18.10	88.89	54.84	28.97

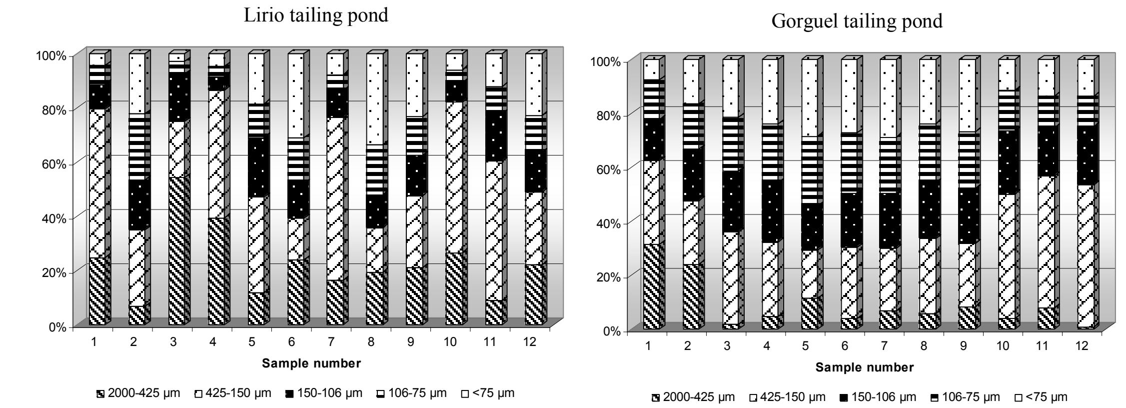

Figure 2. Contents (%) of five particle size fractions in surface soil from Lirio (left) and Gorguel (right) tailing ponds.

Effect of particle size fractions on heavy metal distribution in soil

Mean concentrations (n=12) of metals in five particle size fractions are shown in Figure 3. As can be seen, high concentration of metals occurred in finest fractions due to a highest surface area and negative charges associated with fine particles. However, in contrast to other studies (e.g. Ljung *et al.* 2006) the coarsest fraction had high concentrations of most of the metals except for zinc and cadmium in Lirio tailing pond. This behavior could be due to the process of treatment of the ore, where biggest particles remain enriched with metals probably because they contain minerals such as galena (PbS) and blende (ZnS). It should be highlighted that the Gorguel tailing pond showed a higher concentration of the metals in most of the fractions and higher increment in the coarsest particles than the Lirio pond, indicating a lower recovery of the metals during the treatment of ore.

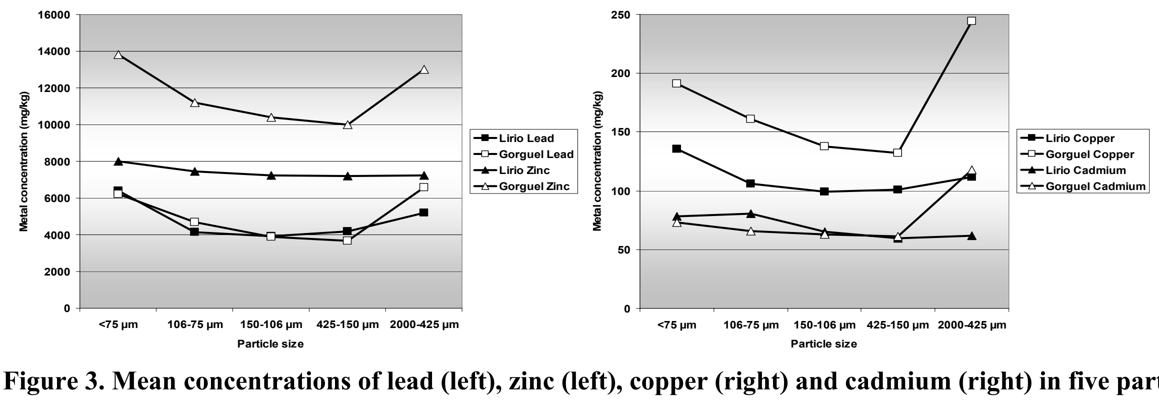

Figure 3. Mean concentrations of lead (left), zinc (left), copper (right) and cadmium (right) in five particle size fractions for soils from Lirio and Gorguel tailing ponds.

Enrichment factor of the metals in particle size fractions

Figure 4 shows the enrichment factors for Cu, Cd, Pb and Zn in each tailing pond for various particle size fractions. In both ponds, metal enrichment factors (EF) >1.0 were found for Cd, Pb and Zn in all samples, while Cu displays an EF <1 in most of the samples for both ponds. Lirio pond had, for all particle size fractions, EF>10 for Pb; EF>15 for Cd and EF>20 for Zn. On the other hand, Gorguel pond had, for all particle size fractions, EF>10 for Pb; EF>20 for Cd and EF>30 for Zn. These results show the high pollution of these pond soils for all the fractions. The highest EFs were found in finest (<75 µm) and coarsest (2000-425 µm) particles, especially for Zn with EFs>40 for Gorguel tailing pond.

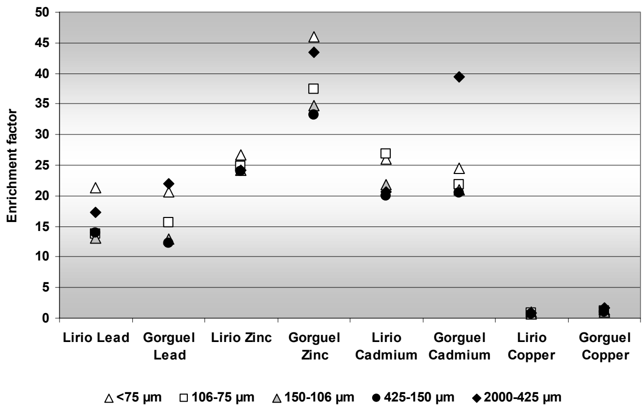

Figure 4. Mean enrichment factors (EF) of metals in five particle size fractions, in soil surface from Lirio and Gorguel tailing ponds.

Conclusion

The characteristics of the studied tailing pond soils prevent plants colonization and leaves their surface unprotected against wind and water erosion, and, as a consequence, pollutants can migrate long distances. This research has showed that high concentration of metals occurred in both finest and coarsest fractions due to high surface area and negative charges associated with fine particles and the processes of ore treatment. The results showed the high pollution of these ponds for all the fractions with enrichment factor (EF)>1. However, highest EFs were for the finest (<75 µm) and coarsest (2000-425 µm) particles with EFs >10 for Pb; >15 for Cd and >20 for Zn in Lirio and EFs>10 for Pb; >20 for Cd and >30 for Zn in Gorguel.

Acknowledgements

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