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# Single extraction tests for risk assessment of arsenic and heavy metals in polluted soils from mining activities

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## Introduction

Mining activities are one of the most important sources of metalloids and/or heavy metals contamination in soils. However, environmental risk is better assessed on the basis of the element mobility and bioavailability than total concentration in soils, which are commonly evaluated by single extraction protocols [1, 2]. In this work, three single extraction methods based on the use of neutral salt solutions, weak acid medium or chelating agents, have been applied to polluted soil samples collected from the Mónica mine surroundings (NW Bustarviejo, Madrid, Spain). Correlations between extracted and total concentrations of As and heavy metals (specifically Cd, Cu, Pb and Zn) in soils were studied by linear regression analysis, in order to assess the usefulness of the different leaching tests for risk assessment of the different elements.

## Experimental

Arsenic and heavy metals in soil samples were extracted by both mechanical shaking (MS) and ultrasonic focused probe (UPS), under the experimental conditions showed in Table 1. The extracts were analyzed by ICP-AES, using Rh as an internal standard. The certified reference materials (CRMs) BCR 483 and BCR 700 were used for validation of the extraction methods. On the other hand, the total element concentrations in soil samples were also determined by ICP-AES, after microwave digestion with aqua regia [2].

Soil amount (g)	Extractant			Time	
	Type	Concentration (mol L <sup>-1</sup> )	Volume (mL)	MS (h)	UPS (min)
2	CaCl <sub>2</sub>	0.01	20	2	2
0.75	CH <sub>3</sub> COOH	0.43	30	16	15
2	EDTA	0.01	20	1	1.5

Table 1. Experimental conditions for extraction of soil samples.

## Results and Discussion

The results obtained by the extraction methods applied (MS and UPS), for both CRMs and soil samples, were statistically comparable. Therefore, the UPS method is recommendable due to the considerable reduction in the time required for sample extraction.

		As	Cd	Cu	Pb	Zn
<b>Total concentration (µg g<sup>-1</sup>)</b>		3·10 <sup>2</sup> -3·10 <sup>4</sup>	1.3-53.5	26-3·10 <sup>3</sup>	12.4-2.7·10 <sup>3</sup>	94-1.6·10 <sup>4</sup>
<b>CaCl<sub>2</sub></b>	µg g <sup>-1</sup>	0.2-4.8	0.01-3.2	2-29	0.02-9.5	1.2·10 <sup>2</sup>
	%	0.01-0.08	1-29	0.1-13	0.01-1.1	0.1-15.8
<b>CH<sub>3</sub>COOH</b>	µg g <sup>-1</sup>	10.7-1.8·10 <sup>2</sup>	0.03-6.4	1.7-1.5·10 <sup>2</sup>	0.6-2.9·10 <sup>2</sup>	0.2-1.9·10 <sup>2</sup>
	%	0.4-4.8	1.7-48	0.2-29	0.04-20	0.2-7
<b>EDTA</b>	µg g <sup>-1</sup>	7.4-3.2·10 <sup>2</sup>	0.003-4.4	1.8-1.3·10 <sup>2</sup>	2-3.2·10 <sup>2</sup>	1.8-1.4·10 <sup>2</sup>
	%	0.4-4.1	0.2-37	3-30	1-24	0.3-16.4

Table 2. Total and extracted concentrations, in µg g<sup>-1</sup>, and extraction percentage ranges found in soil samples (n=16).

Soil samples presented generally elevated total concentrations of Cd, Cu, Pb and Zn and very high levels of As (Table 2), probably due to the former arsenic mining activities. However, element extraction percentages were generally low, except for some elements in some soil samples and depending on the extracting agent. Therefore, this seems to indicate an overall low mobility of elements. However, due to the high total concentrations, low percentages sometimes correspond to elevated extractable concentrations, so that environmental risk is relevant to consider.

The mobility degree, in terms of CaCl<sub>2</sub> extraction percentages, was found to be Cd>Zn>Cu>Pb>As, which can be associated to elements present in the exchangeable fraction in soils. Acetic acid induces also hydroxides and carbonates extraction and thus overall metal solubility increases, whereas EDTA is assumed to extract the previous fractions together with organically bound compounds. Therefore, from the higher percentages found for Cu in acetic acid and Pb in EDTA, these elements are likely to be bound to carbonates and organic matter, respectively.

From the Pearson's coefficients obtained, good correlations were found for Cd and Zn, for all extractants evaluated, probably due to their higher mobility. A highly significant correlation ( $P < 0.01$ ,  $n = 16$ ) was observed between total and CaCl<sub>2</sub> extractable element concentrations in soils, except for Cu, which presented a better correlation when acetic acid or EDTA were used for extraction. However, As and Pb showed worse correlations in these extractants. Therefore, the use of CaCl<sub>2</sub> as extracting agent seems to be adequate for risk assessment of most of elements studied. On the other hand, total element concentrations in soils seem to be the most relevant factor for element mobility.

	As	Cd	Cu	Pb	Zn
<b>CaCl<sub>2</sub></b>	0.76	0.89	0.33	0.69	0.84
<b>CH<sub>3</sub>COOH</b>	0.44	0.91	0.82	0.54	0.93
<b>EDTA</b>	0.54	0.90	0.86	0.48	0.88

Table 3. Pearson's coefficients obtained for linear regression analysis between extracted and total element concentrations in soil samples ( $n = 16$ ).

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