

SUPPLEMENTARY INFORMATION

Assessment of field portable X-ray fluorescence spectrometry for the *in situ* determination of heavy metals in soils and plants

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This document provides extended results and information of the work presented in the main article. Table 1 shows results corresponding to section 3.1.4 *Precision study*. Here, the coefficients of variation of the 12 repeated measurements of three soil reference standards and three samples with different preparations are shown.

Table 1 Variation of repeated records on the soil samples^a

Element	Standards		"Pressed" samples		"Sieved" samples	
	Mean CV	Range	Mean CV	Range	Mean CV	Range
As	9	3 - 19	19	13 - 23	20	7 - 37
Cd	2		8	7 - 9	14	5 - 22
Cu	16	5 - 21	6	2 - 12	14	2 - 32
Fe	1	1 - 1	2	2 - 3	5	2 - 10
Mn	8	5 - 13	6	3 - 9	9	5 - 17
Ni	10	4 - 16	17	11 - 23	22	13 - 34
Pb	9	5 - 13	7	2 - 17	11	4 - 27
Zn	11	8 - 13	4	3 - 8	6	4 - 9

^a CV - coefficient of variation (%); "pressed" samples - samples sieved, ground and pressed as described in the text

Tables 2 shows the time needed (according to our experience) for sample preparation for ICP-OES analysis. In addition, table 3 presents a list of prices for digesting and analyzing heavy metals in soil and plant samples. Both tables indicate the big expenses of money and time that are necessary for characterizing heavy metal polluted sites by this analytical technique.

Table 2 Approximate time needed (working days) to prepare soil and plant samples for ICP-OES determination

Soil sample	Task			Total time (days)
	Drying at room temperature	Sieving	Agate mortar grinding	
Copper mine 1 (n=22)	1 (+5 drying)	1.5	1	3.5
Copper mine 2 (n=12)	0.5 (+5 drying)	1	0.5	2
Silver mine (n=20)	1 (+5 drying)	1.5	1	3.5
Landfill 1 (n=48)	2 (+5 drying)	3	2	7
Landfill 2 (n=12)	0.5 (+5 drying)	1	0.5	2
Plant samples	Washing	Oven-drying and weighting	Grinding	
Above-ground (n=63)	2	1.5 (+2 drying)	2.5	6
Roots (n=11)	1	0.5 (+2 drying)	0.5	2

^a Soil drying and sieving time depends on water content, stoniness and soil aggregates.

Table 3 List of prices for digestion and ICP-OES element determination per soil or plant sample

Task	Price
Acid digestion	4.5 €
Determining 1 st element	3.0 €
Determining 2 nd and subsequent elements	1.8 €

By using this system, we intend to save on cost, time, resources and wastes in the initial characterization of potentially heavy-metal polluted sites. The results were highly comparable to those obtained by ICP-OES, and here we demonstrated it by a comparison of maps where FPXRF and ICP-OES results are spatially represented. Zn and Cu concentration (ICP-OES and FPXRF) data of one of the landfills was used to create a pollution distribution map. The IDW interpolating tool of the ArcMap™ software (v. 9.3.1., ESRI) was used. Data was grouped in increasing levels of element concentrations related with reference limits for soils established by the Spanish law (table 4).

Table 4 Reference levels of Zn and Cu for soils according to RD 1310/1990^a.

Soil pH	Zn	Cu
pH < 7	150	50
pH > 7	450	210

^aRD 1310/1990. Real Decreto 1310/1990 de 29 de octubre, por el que se regula la utilización de los lodos de depuración en el sector agrario. Boletín Oficial del Estado del 1 de noviembre de 1990.

Figure 1 Spatial distribution of Zn in one of the landfills determined by FPXRF (on the top) and by ICP-OES (on the bottom).

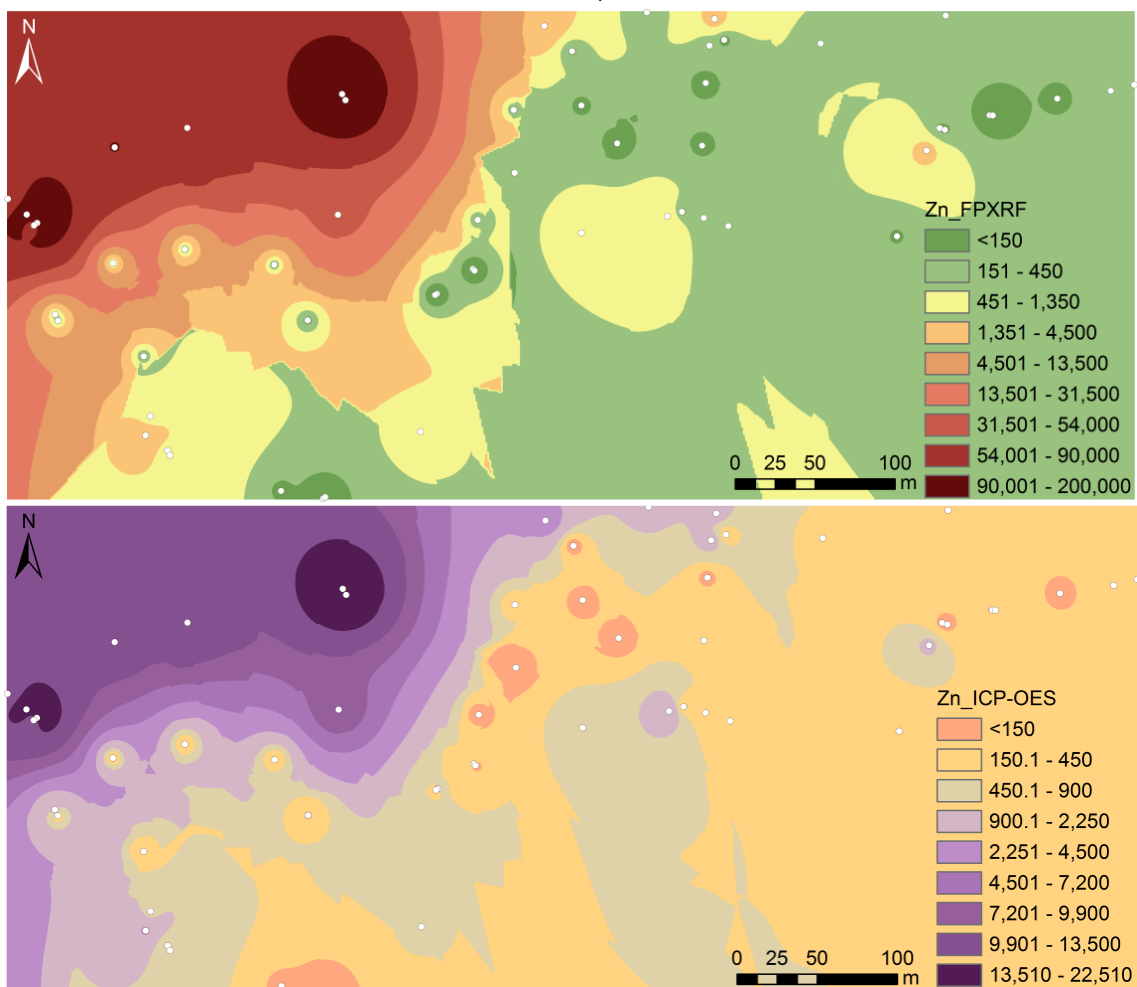


Figure 2 Spatial distribution of Cu in one of the landfills determined by FPXRF (on the top) and by ICP-OES (on the bottom).

