

Elemental composition of soils and sediments by using portable X-ray fluorescence (pXRF) spectroscopy: a preliminary study



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Portable X-ray fluorescence spectrometry (pXRF) provides rapid and low-cost analysis in laboratory and field conditions for a wide range of environmental applications. Its successful application in soils requires a good instrument calibration and the possibility to implement custom calibrations and methods using known samples as well as reference materials.

The aim of this work was to verify and find the best instrument setup for the specific matrix, elements and their concentration range with the purpose of using the pXRF technique directly *in situ* for the screening of sites potentially polluted.

pXRF setup:
8 mm spot size; 90 sec of time scan (30 sec x 3 phases); phase 1 30 kV, phase 2 50kV, phase 3 15 kV
Meuse valley - standard factory calibration for soil applications
Marradi basin - standard factory calibration for soil applications + custom calibration for P, S, Ca, and Fe quantification with coefficient correction method

Detection and quantification of the element species:

Al	K	Ba	Pb
Si	Mn	Cd	Sb
Ca	P	Co	Sn
Fe	S	Cr	Sr
Mg		Cu	Zn
		Mo	

by using pXRF TRACER 5i made by Bruker

Study areas
Two sample sets were analysed

1) pedogenized sediments from MARRADI BASIN (n=13)

2) agricultural land from MEUSE VALLEY (n=10)

Element concentrations results were compared with analytical results from aqua regia digestion (AQ) followed by ICP-OES analysis

Samples preparation:
the air-dried fine earth fraction has been further crushed (<0.5 mm); for pXRF analysis, the dry soil powders have been packed (sample size: 3.5 cm of diameter x 2 cm of height) into a sample cup

	Marradi				Meuse valley			
	mean	std. dev.	min	max	mean	std. dev.	min	max
Main physico-chemical properties								
pH	8.1	0.5	7.5	8.7	7.1	0.4	6.5	7.6
CaCO ₃ g kg ⁻¹	192	49	67	270	-	-	-	-
Sand	624	147	349	788	-	-	-	-
Clay	97	18	69	123	-	-	-	-
Organic C	30.4	30.0	2.7	100.7	15.9	3.7	12.1	21.8
Elemental composition (*)								
Al	17.9	3.0	14.4	26.0	17.6	3.3	13.1	21.5
Fe	14.5	1.6	12.6	18.0	24.1	5.5	14.8	30.4
Ca	49.0	6.6	36.8	58.4	4.7	1.7	2.6	8.4
Mg	9.7	1.4	8.1	13.7	3.3	1.2	1.6	5.6
K	5.5	1.1	4.2	7.8	3.9	1.3	2.2	5.7
Mn	339	44	252	405	682	162	452	1053
P	381	63	291	507	-	-	-	-
S	869	539	338	2054	-	-	-	-
Ba	123	23	92	175	-	-	-	-
Cd	0.13	0.03	0.09	0.19	11.8	13.1	1.9	32.6
Co	7	1	6	9	11	2	7	14
Cr	97	22	62	125	29	5	22	38
Cu	13	4	9	21	27	10	12	42
Mo	2	1	1	3	-	-	-	-
Pb	13	2	10	17	292	320	52	830
Sb	1	0.2	1	2	-	-	-	-
Sn	1	0.2	1	2	-	-	-	-
Sr	239	37	173	302	-	-	-	-
Zn	50	9	39	68	811	835	169	2138

(*) Elemental composition refers to AQ-ICP method

pXRF vs AQ results

CLASS 1 – ELEMENT CONTENTS STRONGLY CORRELATED (0.84<r<0.99, p<0.001)

The elements related to the organic matter (P and S, $r^2>0.60$), carbonates (Ca, $r^2>0.55$) and oxy(hydr)oxides (Fe and Mn) have comparable concentrations between pXRF and AQ. Preliminary results showed that portable XRF could quickly provide data for some elucidations of important pedogenic processes involving many elements in the studied soils. Alternative methods offer results after expensive and time-consuming analytical procedures. For environmental and human health purposes, the pXRF should be a valid tool for a rapid screening of heavy metals, such as Zn and Pb. Cu and Cr concentrations detected by XRF are, on the average, two-fold than those measured by AQ and, for Cu the XRF overestimation is systematically greater in the case of poorer C-samples ($r=-0.830$, $p<0.001$). For Cu and Cr a larger set of soil samples and further custom calibration corrections will be tested.

CLASS 2 – ELEMENT CONTENTS WEAKLY CORRELATED (0.67<r<0.78, p<0.01)

pXRF overestimated the element contents with respect to AQ extraction. A larger set of soil samples and further custom calibration will be tested.

CLASS 3 - ELEMENTS NOT EVALUABLE BECAUSE THEIR CONCENTRATION WAS BELOW THE pXRF DETECTION LIMIT (Co, Mo, Cd, Sn, Sb, Ba)

GENERAL CONCLUSIONS

Our preliminary results showed that pXRF had a good performance in the determination of several elements concentration, both for pedogenic and environmental studies, in soil matrix with contrasting properties. For certain elements, such as Zn and Pb, the pXRF can be used in a large range of concentration using standard instrument setup. The pXRF however is not suitable for trace elements (<10 mg kg⁻¹). The instrument calibration appears however as a critical point which must be taken into account in the pXRF applications, because pXRF results are affected by both "matrix" (i.e., different calibration setup for P, S, Ca and Fe in our two sample sets) and "element" (i.e., Cu, Cr, Mg and Sr) effect.