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

Alberti R. 1, Falsone G. 2*, Gironda M. 1, Aresi N. 1, Lienard A. 1, Colinet G. 3, Minardi G. 4, Franciosi O. 2

1 KXlab srl, Milano, Italy; 2 DIPSA, Alma Mater Studiorum University of Bologna, Bologna, Italy; 3 Department of BIOSystem Engineering, Soil-Water-Plant Exchanges, University of Liège, Gembloux, Belgium; 4 Consorzio di Bonifica della Romagna Occidentale, Faenza, Italy
*gloria.falsone@unibo.it

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 50 kV, 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

**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

**Study areas**
Two sample sets were analysed

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

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

2) agricultural land from **Meuse valley** (n=10)

For Cu and Cr a larger set of soil samples at variable concentration levels of Cu and Cr were also tested

**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, r²>0.60), carbonates (Ca, r²>0.55) and oxides/hydroxides (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 affect 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.