



## Use of portable XRF: Effect of thickness and antecedent moisture of soils on measured concentration of trace elements

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### ABSTRACT

The use of portable X-ray fluorescence (PXRF) for rapid measurements of concentrations of trace elements in soils is increasing. The purpose of this study was to assess in a systematic way the influence of soil moisture and sample thickness on concentrations of Ni, Zn, Cd, and Pb in a mixture of glass beads as well as Windsor loamy sand and Webster loam soils. The Windsor soil was collected from near Lebanon, NH, and the Webster soil was sampled from Story County, IA. In this context, the efficacy of the Compton Normalization (CN) calibration method to correct for changes in soil moisture was determined. Despite CN calibration, an inverse correlation between PXRF measured concentrations and soil moisture was observed. The magnitude of this effect depends upon the energy of the characteristic X-ray fluorescence of each element, with those emitting lower energy X-ray fluorescence being more greatly influenced. Moisture contents ranging from 0.09 to 0.26 cm<sup>3</sup> cm<sup>-3</sup> were found to generate trace element concentrations with no statistical difference, with significantly lower concentrations reported at greater moisture contents. In addition, measured concentrations of each trace element increased with increasing sample thickness until a constant measured concentration was attained, which was also correlated with the energy of the characteristic X-ray fluorescence of the corresponding trace element. Ni, with the lowest energy fluorescence, obtained constant measured concentration at 3 mm for all matrices, whereas a sample thickness of up to 10 mm was needed for Cd. In order to account for energy differences across a range of trace elements and matrices, the use of PXRF should be limited to soil samples having a thickness of at least 10 mm.

### 1. Introduction

The occurrence and persistence of trace elements in the soil-water environment is of major concern at both the local and national levels. Traditional site characterization methods require time and labor intensive sampling as well as costly laboratory analysis. Recently there has been a trend towards the use of handheld portable X-ray fluorescence instruments for in situ analysis of soil samples. This method allows for rapid sampling and reasonably accurate measurements of trace elements. These coupled with subsequent laboratory analysis have the potential to lead to more efficient management and remediation strategies.

A major limitation in field and laboratory use of PXRF is due to antecedent soil moisture content, which is well documented in the literature. USEPA (2007) Method 6200, a commonly cited method for PXRF analysis of soils, states that soil moisture contents > 20% will have a significant impact on PXRF measured concentrations of trace elements. Imanishi et al. (2010) evaluated the effect of moisture content

using a large benchtop XRF instrument and found that soil moisture contents > 12% resulted in significant reduction in the measured concentrations of Sr, Fe, Ti, and Ca. Argyraki et al. (1997) applied a correction coefficient to PXRF measured concentrations of lead in soils with moisture contents ranging between 6.83 and 19.09%, and was able to considerably improve the correlation between PXRF and ICP-AES measured concentrations. Lemiere et al. (2014) illustrated that it is even possible to estimate concentrations of Pb, Zn, Cu, and As from PXRF measurements on dredged sediment samples with moisture contents of up to 50%. Additionally, Parsons et al. (2012) found that a 1% increase in moisture content resulted in a 1.15–1.75% reduction in analyte concentration. As such, several approaches to correct PXRF data for changes in soil moisture have been proposed (Ge et al., 2005; Bastos et al., 2012).

Innov-X Systems for example, the manufacturer of the instrument used in this study, suggests that calibration using the Compton Normalization (CN) method described in their instrument manual (Innov-X Systems, 2010, pg. 87) corrects for changes in the soil matrix

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and therefore soil moisture will not be a significant factor in the accuracy of measured concentrations, i.e. PXRF results would be directly comparable to measurements obtained with competing techniques undertaken on dry soil. The underlying principle of this calibration method is that the standard data are normalized to the Compton peak. The Compton peak exists in the spectrum of every sample and results from the incoherent backscattering of X-ray radiation from the excitation source (i.e. the scattering of the characteristic tube lines). The intensity of the Compton peak is inversely related to the sample mass attenuation coefficient and therefore provides a basis for the correction of the X-ray fluorescence effects of the matrix. Hence, this calibration method has the potential to correct for changes in the soil matrix, leading the manufacturer to claim that soil moisture will not be a significant factor in the accuracy of measured concentrations. However, there is little work presented in the literature to lend credibility to the robustness of the CN calibration applied to wet soils. It has recently been stated that Innov-X Systems is one of three dominant PXRF providers (Weindorf et al., 2014), so it is therefore reasonable to expect that these instruments are extensively used by professionals in research and in industry. Given the widespread use of Innov-X instruments, it is imperative that the efficacy of this calibration be evaluated. Consequently, a major goal of this study is to validate the assertion that effects due to soil moisture may be minimized using the CN calibration.

In addition to EPA Method 6200 (2007) mentioned above, a literature search reveals that several other methods for PXRF analysis of soils have been introduced over the past ten years. The USDA Natural Resources Conservation Service has recently published a PXRF method in the most up to date Soil Survey Field and Laboratory Methods Manual (Soil Survey Staff, 2014), and several international methods are also commonly cited (British Standards Institute, 2009; Peinado et al., 2010; European Committee for Standardization, 2011). These methods provide a comprehensive overview of procedure and potential limitations involved with PXRF analysis of soils, however, there is little emphasis given to sample thickness, although this effect has been previously addressed in the literature.

Using mass as a proxy for sample thickness, Parsons et al. (2012) reported that measured concentrations generally increase with increasing mass in a sample cup for a suite of trace elements with characteristic X-ray fluorescence energies ranging from 5.900–10.543 keV ( $K\alpha$  spectral line). However, they did not relate this information to an ideal or minimum sample thickness to be recommended for PXRF measurements. Imanishi et al. (2010) evaluated the effect of sample thickness on measured XRF concentrations. Using elements with characteristic X-ray fluorescence energies ranging from 6.405–23.173 keV ( $K\alpha$  spectral line), they recommended a minimum sample thickness of 10 mm be used when analyzing soil samples. Therefore, the second goal of this study was to evaluate the effect of sample thickness on PXRF measured concentrations of trace elements across a broad range of characteristic X-ray fluorescence energies, in order to confirm the recommendation of Imanishi et al. (2010) and to provide supplemental information to these methods.

## 2. Methods

In this study, several experiments were carried out on a mixture of glass beads and two soils having different physiochemical properties. The glass bead mixture consisted by weight of 30% beads with diameters ranging from 10 to 25  $\mu\text{m}$  and 70% 300–500  $\mu\text{m}$  diameter beads such that a silt loam texture was roughly approximated. This mixture of glass beads was included in the study as a relatively homogenous (mineralogical composition and geometric structure) non-reactive porous medium, which serves as an effective reference material against heterogeneous reactive soil matrices. The composition of the beads is primarily quartz ( $\text{SiO}_2$ ) which is expected to be an abundant mineral within both soils. The bulk pore and particle geometry is taken as an ideal representation of what would conceptually be expected within the

**Table 1**  
Physical and chemical properties of the soils used in the study.

Soil		Webster loam	Windsor loamy sand
Taxonomic classification		Fine-loamy, mixed, mesic Typic Endoaquoll	Mixed, mesic, Typic Udipsamment
Source Location		Iowa	New Hampshire
Total organic carbon	%	4.02	2.03
Cation exchange capacity	$\text{cmol kg}^{-1}$	27.0	2.0
Sand (2.00–0.05 mm)	%	39	77
Silt (0.05–0.002 mm)	%	39	20
Clay (< 0.002 mm)	%	22	3

soils. Applied trace elements are assumed to exist within the glass bead matrix as surface precipitates.

Two soils were used in this study. Windsor loam is a loamy sand formed on glacial outwash plains collected near Lebanon, NH. Webster loam formed in glacial till or local alluvium derived from till on uplands and was sampled from Story County, IA. Select properties obtained from a previous study by Liao and Selim (2010) are listed in Table 1. These were previously prepared by air drying and passing through a 2 mm sieve, and were then impregnated with solutions of known concentrations of Cd, Ni, Pb, and Zn. This was achieved by applying an aqueous solution of nickel(II) nitrate (Fisher Scientific, Waltham, MA), cadmium nitrate tetrahydrate, lead nitrate and zinc nitrate hexahydrate (Sigma Aldrich, St Louis, MO) such that the final concentration of each trace element was 200  $\text{mg kg}^{-1}$  of each matrix. Impregnated samples were allowed to air dry at room temperature until volumetric moisture contents were < 0.01  $\text{cm}^3 \text{cm}^{-3}$ , and were then homogenized by manually stirring for 10 min. Characteristic emission lines measured for the concentration of trace elements ranged between 7.480 keV for Ni to 23.273 keV for Cd.

### 2.1. Soil moisture

For each homogenized matrix, impregnated dry samples were evenly spread on to a wooden 20.5 cm  $\times$  30.5 cm tray to a uniform thickness of 3 mm. The tray had no background concentrations of the trace elements of interest. Deionized water was applied to each matrix via a spray bottle at a volume of 90% of the calculated pore space, and samples were left to equilibrate for 3–4 h at room temperature to attain approximately uniform moisture content. PXRF readings commenced every 4–5 h as the samples continue to naturally decrease in soil moisture (drying) to produce measured concentration values over a range of moisture contents. Moisture contents were determined by weighing the tray with its contents, subtracting the mass of the dry matrix and tray, dividing by the mass of the dry matrix and then multiplying by the bulk density of the matrix. Bulk density was determined by weighing a known volume of soil compacted to the same degree as would be expected in the experiments. At each moisture content, measurements were taken at five different points in the tray. The same five points were measured throughout the study. In order to determine the moisture content at which no statistical difference from the dry samples occurred, a comparison was made between the average values attained at each sampling. This was done using the Tukey pairwise comparison procedure with  $\alpha = 0.10$ , and was carried out with SAS® 9.4 statistics software.

### 2.2. Sample thickness

Air dried, homogenized samples were spread out on a single sheet of wax paper placed atop an acrylic platform at thicknesses of 1, 2, 3, 4, 5, 10, and 20 mm. PXRF measurements at each thickness were duplicated five times. Again, the Tukey pairwise comparison procedure with

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