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Research Article

EFFECT OF SOIL MOISTURE ON TRACE ELEMENTS CONCENTRATIONS USING PORTABLE X-RAY FLUORESCENCE SPECTROMETER

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ABSTRACT

Portable X-ray fluorescence (PXRF) technology can offer rapid and cost-effective determination of the trace elements concentrations in soils. The aim of this study was to assess the influence of soil moisture content under different condition on PXRF measurement quality. For this purpose, PXRF was used to evaluate the soil elemental concentrations for Ca, Mg, Cd, Cr, Cu, Ni, Zn, P, Fe, Mn and Pb in 60 samples in a perimeter irrigated with treated wastewater (Cebala Borj Touil, North-east Tunisia). Scanning was conducted under four moisture conditions: *in-situ*, dried soil at 105°C, 40% moisture content soil and saturated soil. All were then compared relatively to dried sample scans. As expected, the relationship between dried *vs* both *in-situ* and 40% moisture content elements concentrations were linear. However, PXRF readings from saturated samples were significantly underestimated compared to the measurements on dry samples. Furthermore, soil moisture content caused a significant under-reporting of elemental concentrations compared to the scanning on dry samples. PXRF acted differently for each element following the moisture content of soil. In fact, attenuation coefficient σ of Cr, Fe and Mn were the most affected by saturation of soil samples, whilst Ca, Mg and Ni were more affected for 40% moisture content while Cd, Pb, Zn, Cu and P were affected for *in-situ* measurements. Correction equations enhanced the error produced by the water influence moisture content and corrected PXRF measurements.

Keywords: PXRF analysis; Soil; moisture content; trace elements.

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1. INTRODUCTION

Trace elements in soil can be detected by several conventional laboratory methods such as ICP-AES (inductively coupled plasma atomic emission spectrometry), ICP-OES (inductively coupled plasma optical emission spectrometry), AAS (atomic absorption spectrophotometry) and AFS (atomic fluorescence spectrometry). However, these techniques are severely limited by the high costs of analysis, laboratory consumables and time used in laboratory processing [1-2]. Therefore, there is a need for rapid, cost-effective and accurate analytical methods. The portable X-ray fluorescence (PXRF) can rapidly determine element concentrations on sites of interests directly by *in situ* measurements and can be used for quick field screening of potential contaminated soil contamination [3-6].

Previous studies indicated that PXRF analysis was capable of detecting soil trace elements similar to those detected by conventional laboratory methods [3,7,8]. Although PXRF will not replace laboratory techniques such as ICP-OES for high precision analyses, but it offers a number of distinct advantages including *in situ* measurements without pre-treatment and sampling, simultaneous analyses of a wide range of elements, rapid, nondestructive, increased total speed and throughput and accurate identification of many elements simultaneously [3,9,10].

However, several physico-chemical parameters of soil are known to affect the quality and the precision of PXRF reading, essentially sample matrix, surface irregularity, interfering elements, mineralogy, particle size and soil moisture [9,11-18].

Nevertheless in many previous PXRF studies on soil, moisture content has been considered as one of the most influential sources of error, especially when soil moisture content ranges between 40% [19]. Indeed, several authors have shown that water causes an exponential decrease in the intensity of X-rays which lead to a lower precision, poor detection limit and overall lower accuracy [13]. Essentially, water in soil acts as both an absorption layer and a scattering layer, produces an exponential decrease in effective X-ray penetration depth which leads to a lower precision of PXRF scanning [20].

Thus it’s necessary to assessment of precision and accuracy of PXRF for applications to provide results that may be used for a spatial distribution interpretation of trace elements contamination. Therefore certain method has been treated in the literature for correcting the moisture influence on wet soil analysis measured by PXRF [13,21].

Therefore, the aim of this study was to evaluate the influence of soil moisture on the PXRF scanning, in particular Ca, Mg, Cd, Cr, Cu, Ni, Zn, P, Fe, Mn and Pb concentration and apply a moisture correction equations to increase the accuracy of PXRF measurements.

2. MATERIALS AND METHODS

2.1. Field sampling and scanning

Field sampling was conducted from Cebala Borj Touil (North-east Tunisia) (Figure1). The perimeter covers a total area of 3139 ha and irrigated with treated wastewater (TWW) since 1989. The perimeter is irrigated by gravity method witch cause a prolonged stagnation of water in depressions plots, especially in areas where the aquifer flush. In this case, there is a risk of contamination of surface water with TWW.

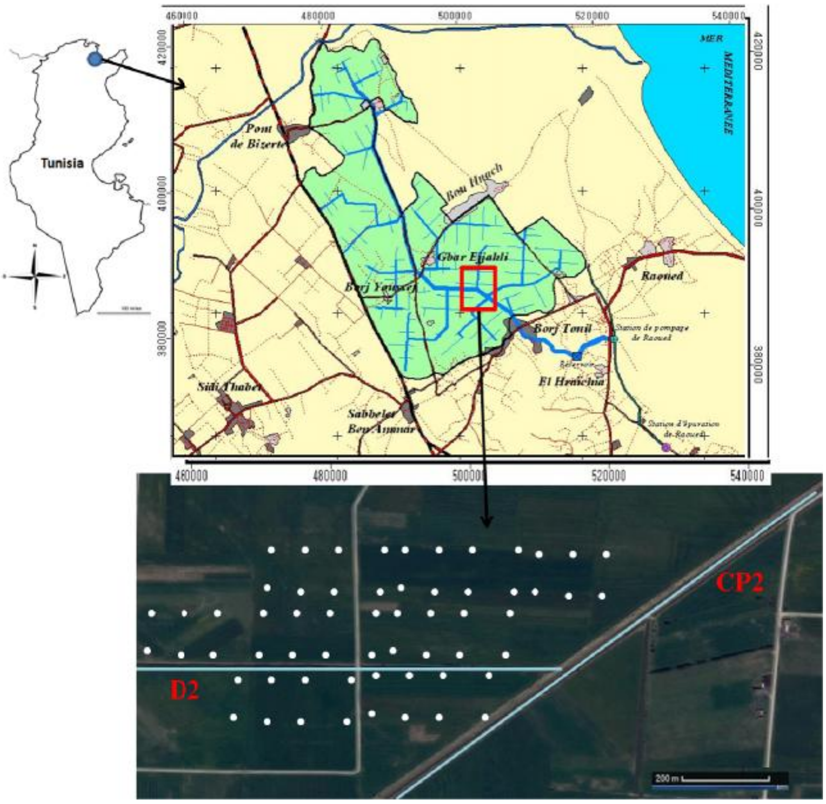

Fig.1. Location of sampling sites in Cebala Borj Touil- Tunisia (Southwestern Tunisia)

A total of 60 soil samples were collected using a stratified random sampling design, from topsoil horizons (0-20cm) for scanning with PXRF under different moisture content conditions and for physicochemical lab analysis.

The soil samples were air-dried and sieved using a 2 mm mesh stainless steel sieve. Soil pH was determined with a pH electrode (Sen Tix 41 (WTW) PLUS) in 1:2.5 distilled water to soil extracts [22]. Electrical conductivity (EC) was also determined from saturated soil-paste with

Tetra 325 electrode (WTW) according to U.S. Salinity Laboratory Staff [23]. Particle size distribution was determined following oxidation of organic matter with hydrogen peroxide, the upper fraction (down to 50 mm) being separated by sieving and the lower one used for subjection to the internationally endorsed procedure [24]. Organic matter (OM) content was determined by soil oxidation with potassium dichromate ($K_2Cr_2O_2$) and concentrated H_2SO_4 [25]. Moisture content was determined by trace system soil moisture equipment TDR (Time Domain Reflectometry) with coated sensors (8 Cm).

For determining trace elements concentration in situ, the samples were scanned with PXRF under field moisture conditions. For laboratory analyses, all scannings were performed with PXRF on pressed pellets (Ø: 3cm). A portable Bruker S1 Titan 600 with calibration range of 37 elements, including light elements Mg, Al and Si was used for determining trace elements concentrations in soil samples. The analyser is characterized by fast SDD® detector and Shield™ detector protecting the sensor window from being punctured by sharp objects under analysis. The analyser was equipped with X-ray tube Rh target operating at a maximum of 50 kV and five position motorized filter changer.

Portable XRF scanning for elemental quantification were chosen for the elements most common on wastewater eventually Ca, Mg, Cd, Cr, Cu, Ni, Zn, P, Fe, Mn and Pb [26]. Scanning was conducted for 30 s per beam, for a total of 60 s per scan.

To assess the influence of soil moisture on XRF signal absorption, the 60 soil samples were analysed by portable XRF with four conditions: *in-situ* scanning, dried soil at 105°C, 40% moisture content soil and saturated soil with distilled water in the sample cups.

2.2. Statistical analyses

Statistical analyses were performed using the software SPSS® for Windows version 20.0. Different measurements of XRF scanning were compared using simple regression to investigate the relationship between the concentrations obtained on dried soil and those measured on different soil treatments. The regression equation, coefficient of determination (R^2), slope and root mean square error (RMSE) were calculated to compare differences between soil treatments. RMSE was calculated by:

$$\mathrm{RMSE} = \sqrt{\sum_{n}^{i=1} \frac{(Xai - Xbi)^2}{n}}$$

*X*a*i* and *X*b*i* are the XRF measurements of *i*th sample with treatments a and b, and *n* is the total number of XRF measurements on the samples with both treatments.

The X-ray intensities emitted from the elements in the wet samples (dI_x) decrease with increasing water content in the soil sample (d_w) due to the X-ray absorption effect of the interstitial water. Equation 2 shows the following relation:

$$\mathrm{d}I_x = -\mu_m\, I_x\, d_w$$

Ge et al. [13] proposed a model for the correction of soil moisture on PXRF measurement based on Lambert-Beer law that the reduction in X-ray intensity is proportional to the increment of water content of the sample:

$$\frac{\mathrm{Cwet}}{\mathrm{Cdry}} = e^{-\sigma w}$$

where C_{wet} is the PXRF elemental concentration with a water content ω, C_{dry} is the PXRF elemental concentration in the dry sample, and σ is the attenuation coefficient due to soil moisture.

3. RESULTS AND DISCUSSION

Descriptive statistics for physico-chemical soil characteristics of analyzed samples were summarized in Table 1. Soil texture estimated to be Silty Clay Loam according to soil textural triangle [27]. The pH did not vary much and was basic (7.90–9.49), which suggests alkaline conditions for all the soil samples. Bulk density and EC showed limited variation. Organic matter content in the soils varied slightly from 0.54% to 1.89%. Soil moisture content was highly variable between 9.12% in dry areas and 22.67% in irrigated areas. Carbonates vary slightly between 35 and 46%. Summarily the soil samples possessed a limited range of physicochemical characteristics which minimize their effect on PXRF scanning accuracy.

Table 1. Basic statistics of physicochemical properties of Cebala Borj Touil soils

	Min	Max	Mean	STD	Median
Sand (%)	2	25	9	7.16	5
Silt (%)	40	81	54	8.64	52
Clay (%)	10	51	38	11.46	42
pH	7.9	9.49	8.48	0.37	8.39
EC (ds/m)	0.24	0.72	0.47	0.14	0.48
BD (g/cm^3)	0.34	1.01	0.46	0.37	0.35
OM (%)	0.54	1.89	0.74	0.14	0.75
MC (%)	9.12	22.67	19.92	11.33	15.91
Carbonates (%)	35	46	38	2.58	37

EC: electrical conductivity, BD: Bulk density, OM: Organic matter, MC: Moisture content

Table 2 summarizes the basic statistics of the investigated trace elements. The PXRF concentrations decreased with increasing water content in soil samples for all studied elements. In fact, standard deviation and CV of the measurements are relatively different particularly between dry soil samples and saturated soil samples for the majority of the elements. Previous researches on the effect of water on XRF scanning have found similar results [9,13-15,18,19].

Variation created an ambiguity in the diagnosis of trace elements concentrations in the studied site between samples of different moisture. For this reason PXRF concentrations in non-dried samples were fitted using the Lambert-Beer equation (Equation 3, Table 3).

Table 2. Basic statistics of trace elements (mg kg^{-1}) in soils of Cebala (n=60)

		Min	**Max**	**Mean**	**STD**	**Median**
Dry	Cd	52	95	70.28	8.74	69
	Pb	26	55	33.60	7.41	30.5
	Zn	17	124	73.57	24.04	77
	Ca	119651	243929	167013	29974	159750
	Cu	34	71	50.03	7.40	49.5
	Cr	53	72	61.65	4.99	62
	Mg	11000	29000	18717	5429	19954
	Ni	78	169	115.20	23.09	110.5
	P	1985	10602	3106	1209	2805
	Fe	25425	48602	37525	5074	37519
	Mn	264	668	428	76	429
In situ	Cd	46	90	63.12	8.66	62.5
	Pb	20	46	27.92	6.04	26
	Zn	15	109	55.02	21.146	56.5
	Ca	93586	198836	142003	23390	141201
	Cu	32	64	43.20	6.265	43.5
	Cr	45	63	55.8	3.7	57
	Mg	9713	25000	13266	3821	12000
	Ni	59	126	86.8	12.92	84
	P	1665	4976	2441	550	2340.5
	Fe	21380	44579	31524	5400	31977
	Mn	255	481	357	58	359

(Continued)

40%	Cd	33	72	53	7	54
	Pb	18	42	24	5	23
	Zn	15	89	40.17	20	42
	Ca	93570	174779	121921	20217	117146
	Cu	15	61	37.7	8	38
	Cr	43	54	48.7	3	50
	Mg	9131	22495	10969	1848	11000
	Ni	49	94	70.35	11.8	70
	P	1410	3748	2039	424	2015
	Fe	17341	38524	26365	4438	25929
	Mn	187	432	299	53	293
Saturated	Cd	22	67	47.4	7.4	49
	Pb	15	33	20.4	3.7	20
	Zn	13	80	26	16.1	17
	Ca	43387	137697	95103	22128	94568
	Cu	13	54	29.4	9.8	31.5
	Cr	27	51	41.75	5.1	41.5
	Mg	3442	12000	8874	1802	9211
	Ni	20	65	41.72	15	48.5
	P	781	2406	1552	352	1539
	Fe	10260	31472	21448.23	4882	20376
	Mn	74	362	235	55	230

The influence of water content on the PXRF measurements and corrected regression equations were presented in Table 3 and figure 2. The PXRF readings were correlated more closely with *in-situ* samples and 40% moisture content samples with similar R^2 values and thus had nominal effects on PXRF accuracy.

Nevertheless PXRF readings were significantly underestimated with saturated samples compared to the readings on dry samples. Correspondingly, moisture-corrected sample PXRF readings provided better correlation to PXRF scans of the dry soil samples as indicated by higher R^2 values, lower RMSE, and slopes closer to 1 in the regression equations for *in-situ* samples and 40% moisture content samples (Table 3).

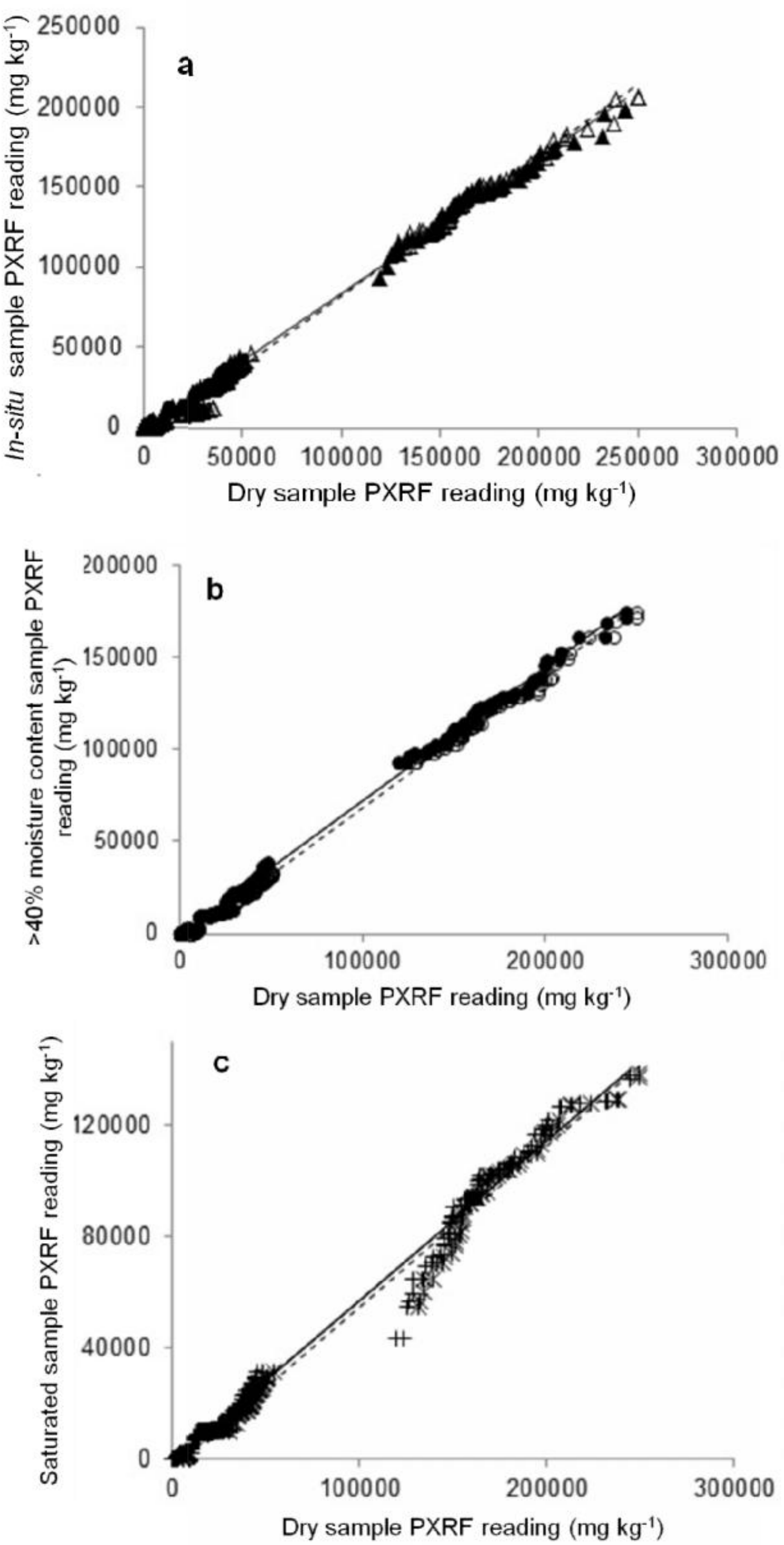

Fig. 2. PXRF readings on soil samples from Cebala Borj Touil under different conditions: *in-situ vs.* dry (a), 40% moisture content sample *vs.* dry (b) and Saturated *vs.* dry (c).

Coefficients in this study were slightly higher than those of Radu and Diamond [3] and Laiho and Perämäki [19]. This is mainly because soils in the study area had lower trace elements distribution variation. Furthermore, these results are consistent with previous findings of Piorek [28] and Laiho and Peramaki [19] for PXRF analysis in 5%–40% moisture soils and showed that soil moisture of >20% caused nominal errors to PXRF elemental measurements and can safely be neglected. In addition, Weindorf et al. [9] noted that even for soil with < 40% moisture contents caused fluorescence denudation and thus a significant amount of variance in PXRF readings.

Table 3. Correlation parameters of portable XRF measurements on soil samples under different conditions (Y) with scanning on in-situ samples, 40% moisture content samples, and saturated samples (X) from Cebala Borj Touil

Soil condition	Regression equation	R^2	RMSE	Cwet/Cdry	σ	Corrected	R^2
In situ	y = 0.8474x - 237.34	0.998	0.538	82.403	0.577	y = 0.8868x - 676.4	0.999
40%	y = 0.7272x - 304.42	0.998	0.711	69.131	0.106	y = 0.7303x - 94.339	0.999
Saturated	y = 0.5744x - 279.33	0.992	0.873	53.777	0.039	y = 0.5799x - 85.82	0.995

As described by Ge et al. [13] the deviations of the PXRF -scan to the dry scan readings are caused by the decreasing of the intensity of characteristic x-rays of analytes as the interstitial water of the sample increases owing to the stronger x-ray absorption by water than by air in fractures and macropores in soil samples.

Also Weindorf et al. [9] noted that when the moisture content of the soil exceeded its field capacity, the pressure inserted by the contact of PXRF during the scanning process could induce the release of interstitial water from macro pores, which might subsequently form a layer of water between the soil and the scanning window of the PXRF. When soil water content was high, a noticeable layer of water covering the window was often observed after the scanning was completed which leads to a lower precision, poorer detection limit and lower accuracy.

In order to further analyze the moisture content effect on PXRF scanning, the measurements under the same scanning conditions of the samples were plotted against scans on dry samples for each element (Table 4, Figure 3). Even at the higher moisture contents in saturated samples, the PXRF was capable of measuring all studied trace elements concentrations in the samples and there is a linear relationship between these concentrations and the moisture content (Figure 3). However, for the scans on the saturated samples, PXRF underestimated almost all the elements owing to moisture, exhibiting a poor relationship with dry scans by the low slopes in the regression equations (ranging from 0.539 for Mg to 0.898 for Cd (Table 4)).

Only Ca, Cr, Fe and Mn showed a significantly close correlation between saturated and dry sample scans ($R^2 \geq 0.905$). Furthermore, the RMSE values of the saturated against dry sample scans were always the highest for all elements.

Most elements of the scans *in-situ* samples acceptably compared to dry sample scans, with R^2 values ranging from 0.791 for Mg to 0.984 for Ca. However, underestimation of the scans on 40% moisture content samples was still quite apparent, as the regression slopes varied between 0.621 for Mg and 0.974 for Ca.

The improved quality of the PXRF-scan data, corrected with Equation 2, is clearly expressed by higher correlation coefficients for almost all elements (Table 3, Figure 3). In fact, after moisture correction using Lambert-Beer equation, R^2 values increased more or less and the slopes in the regression equations shifted much closer to 1, although the RMSE values of some elements slightly increased.

Table 4. PXRF readings of each element under different moisture content conditions *vs.* readings on dried samples

Element	Soil water content	Regression equation	R^2	RMSE	Cwet/Cdry	σ	Corrected	R^2	RMSE
	In situ	y = 0.9805x - 5.7934	0.979	0.044	89.69	0.588	y = 1.0432x - 7.2132	0.983	0.034
	40%	y = 0.7867x - 2.275	0.941	0.069	75.36	0.108	y = 0.7487x + 0.8042	0.945	0.054
	Saturated	y = 0.8038x - 9.0774	0.898	0.080	67.22	0.042	y = 0.7205x - 2.6422	0.921	0.041
Pb	***In situ***	y = 0.7968x + 1.1437	0.955	0.039	83.23	0.578	y = 0.799x + 2.6299	0.970	0.042
	40%	y = 0.6703x + 2.1929	0.947	0.049	73.83	0.108	y = 0.6914x + 1.798	0.963	0.033
	Saturated	y = 0.4572x + 5.0372	0.802	0.060	61.30	0.041	y = 0.459x + 5.0628	0.802	0.033
Zn	***In situ***	y = 0.8579x - 8.0998	0.952	0.071	73.59	0.561	y = 0.887x - 7.6236	0.964	0.069
	40%	y = 0.7752x - 16.86	0.854	0.095	53.17	0.098	y = 0.9074x - 27.753	0.906	0.064
	Saturated	y = 0.5312x - 12.932	0.624	0.112	35.54	0.035	y = 0.6542x - 23.123	0.695	0.059
Ca	***In situ***	y = 0.6691x + 10177	0.984	3.517	73.19	0.107	y = 0.6717x + 10264	0.984	2.348
	40%	y = 0.7701x + 13384	0.974	2.607	85.22	0.582	y = 0.7838x + 17944	0.978	2.338
	Saturated	y = 0.7023x - 22190	0.905	4.457	56.42	0.040	y = 0.667x - 15153	0.921	2.733
Cu	***In situ***	y = 0.8251x + 1.9178	0.952	0.043	86.42	0.584	y = 0.8487x + 2.8674	0.954	0.045
	40%	y = 1.0561x - 15.123	0.930	0.058	74.67	0.107	y = 0.9875x - 11.256	0.945	0.039
	Saturated	y = 1.2295x - 32.118	0.854	0.075	57.33	0.040	y = 1.2249x - 30.831	0.870	0.054
Cr	***In situ***	y = 0.5726x + 13.452	0.960	0.060	79.21	0.109	y = 0.5745x + 13.542	0.976	0.031
	40%	y = 1.0102x - 20.532	0.950	0.074	67.50	0.042	y = 0.9406x - 15.853	0.970	0.044
	Saturated	y = 0.7142x + 11.85	0.928	0.040	90.77	0.590	y = 0.6849x + 16.408	0.960	0.045
Mg	***In situ***	y = 0.2953x + 3347.8	0.791	1.618	48.99	0.039	y = 0.2142x + 5216.5	0.920	0.734
	40%	y = 0.5545x + 2887.5	0.621	1.160	72.97	0.558	y = 0.2126x + 8469.8	0.909	0.802
	Saturated	y = 0.2498x + 6293.1	0.539	1.399	62.05	0.102	y = 0.1927x + 7243.7	0.864	1.384
Ni	***In situ***	y = 0.4934x + 13.515	0.932	0.111	61.46	0.103	y = 0.4752x + 16.245	0.969	0.091
	40%	y = 0.5329x + 25.444	0.906	0.087	76.27	0.567	y = 0.4445x + 38.429	0.938	0.070
	Saturated	y = 0.6164x - 29.289	0.819	0.142	35.11	0.035	y = 0.5987x - 25.617	0.842	0.093

P	***In situ***	y = 0.4255x + 1119.9	0.875	0.405	80.84	0.575	y = 0.6212x + 655.42	0.915	0.372
	40%	y = 0.315x + 1061.4	0.806	0.526	67.63	0.105	y = 0.4871x + 568.02	0.915	0.335
	Saturated	y = 0.2257x + 851	0.599	0.643	51.23	0.039	y = 0.5328x - 25.656	0.898	0.386
Fe	***In situ***	y = 0.9441x - 13980	0.963	2.112	56.47	0.040	y = 0.9347x - 13583	0.968	1.204
	40%	y = 0.8556x - 5742.2	0.957	1.758	70.01	0.106	y = 0.8155x - 4242.8	0.964	1.250
	Saturated	y = 1.0369x - 7387.4	0.949	1.285	83.67	0.579	y = 1.1629x - 10862	0.956	1.188
Mn	***In situ***	y = 0.6856x + 5.457	0.963	0.189	69.86	0.106	y = 0.7483x - 18.589	0.974	0.129
	40%	y = 0.6984x - 63.625	0.936	0.231	54.44	0.040	y = 0.7999x - 104.49	0.972	0.134
	Saturated	y = 0.7413x + 40	0.934	0.138	83.77	0.580	y = 0.8672x + 4.6192	0.958	0.143

(Continued)

Attenuation coefficient σ for each element was determined using the simple regression equations based on the Lambert-Beer law based on the ratio Cwet/Cdry (Table 4). These coefficients are indicators of the moisture content influence on the PXRF elemental concentrations. A high σ value for a given element indicates that an increase in moisture content produced an underestimation in PXRF measurements.

The PXRF measurements of Cr, Fe and Mn were the most affected by saturation of soil samples (Table 3, Figure 3). Their σ values were highest in saturated samples with 0.590, 0.579 and 0.580, respectively. Whilst the σ values for Ca, Mg and Ni for 40% moisture content samples were 0.582, 0.558 and 0.567 indicating that at such moisture content caused an underestimated scanning for these elements. Notably σ values for Cd, Pb, Zn, Cu and P were highest in less moisture content (*in-situ* samples) indicating that PXRF scanning were affected even at low water content. Results are not in covenant with previous studies that showed that the attenuation coefficient σ associated with an increase in moisture content was greater for lighter elements and with atomic number below Z=40 or 26 [13-15,19,29]. Indeed, moisture content affected PXRF scanning differently for each element.

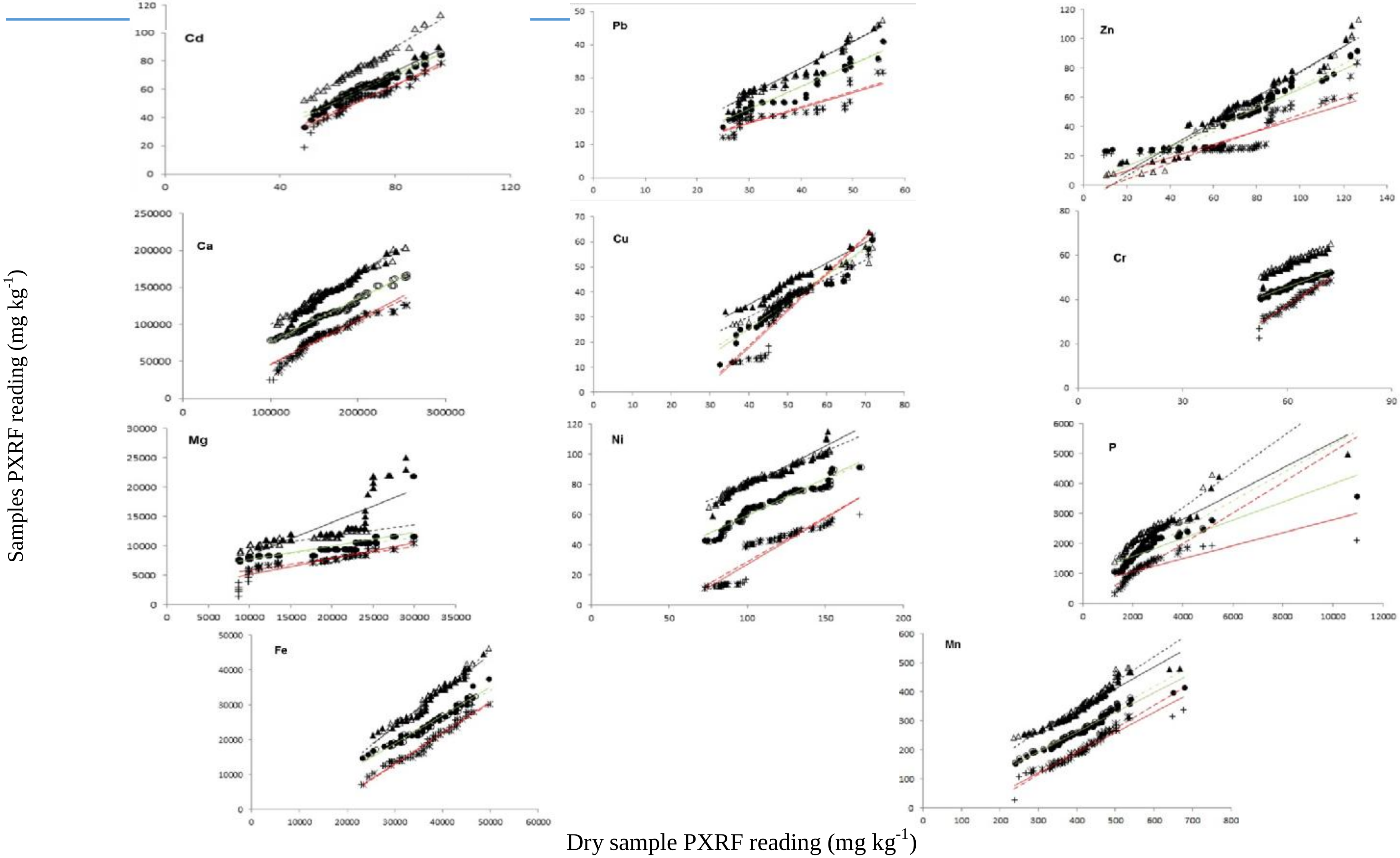

Fig.3. PXRF elemental readings for soils samples under different conditions.

4. CONCLUSION

For each element, an increase in soil moisture content caused a significant decrease in FPXRF concentrations. Each applied moisture content, PXRF measurements presented an underestimation scanning for some elements. Cr, Fe and Mn were the most affected by saturation of soil samples, whereas from 40% moisture content Ca, Mg and Ni scanning were underestimated. While the decrease in Cd, Pb, Zn, Cu and P concentrations were more pronounced in the *in-situ* samples moisture content. Application of Lambert-Beer law significantly improved the error produced by the water influence moisture content and corrected PXRF measurements corresponded much better to the PXRF measurements in dry soils and thus might gradually substitute conventional laboratory methods for the analysis of soil samples. Results of this study could be adopted as a rapid methodology for screening trace elements pollution in irrigated perimeters suffering from water stagnation.

5. ACKNOWLEDGEMENTS

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