

Correcting field determination of elemental contents in soils via portable X-ray fluorescence spectrometry

Correção da determinação em campo dos teores de elementos em solos via espectrometria de fluorescência de raios-X portátil

Thaís Santos Branco Dijair¹ , Fernanda Magno Silva² , Anita Fernanda dos Santos Teixeira² , Sérgio Henrique Godinho Silva² , Luiz Roberto Guimarães Guilherme² , Nilton Curi^{2*} 

¹Universidade Federal de Lavras/UFLA, Lavras, MG, Brasil

²Universidade Federal de Lavras/UFLA, Departamento de Ciências do Solo/DCS, Lavras, MG, Brasil

*Corresponding author: niltcuri@ufla.br

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ABSTRACT

Portable X-ray fluorescence (pXRF) spectrometry has been useful worldwide for determining soil elemental content under both field and laboratory conditions. However, the field results are influenced by several factors, including soil moisture (M), soil texture (T) and soil organic matter (SOM). Thus, the objective of this work was to create linear mathematical models for conversion of Al_2O_3 , CaO, Fe, K_2O , SiO_2 , V, Ti and Zr contents obtained by pXRF directly in field to those obtained under laboratory conditions, i.e., in air-dried fine earth (ADFE), using M, T and SOM as auxiliary variables, since they influence pXRF results. pXRF analyses in field were performed on 12 soil profiles with different parent materials. From them, 59 samples were collected and also analyzed in the laboratory in ADFE. pXRF field data were used alone or combined to M, T and SOM data as auxiliary variables to create linear regression models to predict pXRF ADFE results. The models accuracy was assessed by the leave-one-out cross-validation method. Except for light-weight elements, field results underestimated the total elemental contents compared with ADFE. Prediction models including T presented higher accuracy to predict Al_2O_3 , SiO_2 , V, Ti and Zr, while the prediction of Fe and K_2O contents was insensitive to the addition of the auxiliary variables. The relative improvement (RI) in the prediction models were greater in predictions of SiO_2 (T+SOM: RI=22.29%), V (M+T: RI=18.90%) and Ti (T+SOM: RI=11.18%). This study demonstrates it is possible to correct field pXRF data through linear regression models.

Index terms: pXRF; soil moisture; soil texture; soil organic matter; prediction models.

RESUMO

A espectrometria portátil de fluorescência de raios-X (pXRF) tem sido útil em todo o mundo para determinar o teor dos elementos no solo em condições de campo e de laboratório. No entanto, os resultados obtidos em campo podem ser influenciados por vários fatores, como umidade (U), textura (T) e matéria orgânica do solo (MOS). Assim, o objetivo deste trabalho foi criar modelos matemáticos lineares para a conversão dos teores dos elementos obtidos por pXRF em campo para resultados obtidos em laboratório, i.e., na Terra Fina Seca ao Ar (TFSA), utilizando U, T e MOS como variáveis auxiliares, uma vez que elas influenciam as leituras. As análises com pXRF foram realizadas em 12 perfis de solo com diferentes materiais de origem, seguidas por coleta de 59 amostras. Leituras com pXRF foram realizadas também em laboratório em amostras de TFSA. Os dados de pXRF obtidos em campo foram utilizados sozinhos ou combinados aos dados de U, T e MOS como variáveis auxiliares, para criar modelos de regressão linear para predição dos resultados de pXRF em TFSA. A acurácia dos modelos foi calculada pelo método *leave-one-out cross-validation*. À exceção de elementos mais leves, as leituras de campo com pXRF subestimaram o teor total dos elementos. Modelos de predição incluindo T apresentaram maior acurácia na predição de Al_2O_3 , SiO_2 , V, Ti e Zr, enquanto a predição dos teores de Fe e K_2O foi insensível à adição das variáveis auxiliares. A melhora relativa (MR) nos modelos de predição foi maior nas predições de SiO_2 (T+MOS: MR = 22,29%), V (U+T: MR = 18,90%) e Ti (T+MOS: MR = 11,18%). Este trabalho demonstrou que é possível a correção dos dados de pXRF obtidos em campo através de modelos de regressão linear.

Termos para indexação: pXRF; umidade do solo; textura do solo; matéria orgânica do solo; modelos de predição.

INTRODUCTION

X-ray fluorescence is a technique capable of providing quantitative data on the content of chemical

elements in the analyzed material (Potts; West, 2008). This technique has been used in different branches of science, such as geochemistry, archeology, forensic science and soil science (Ribeiro et al., 2017; Weindorf; Bakr; Zhu, 2014).

In this technique, a source of energy that emits X-rays hit the atoms of the analyzed material, making electrons to move from inner to outer orbits. Following on, electrons move back to their original orbit emitting energy in the form of fluorescence. Each chemical element emits a characteristic fluorescence when the electron returns to its original orbit, enabling the element identification. The intensity of the fluorescence detected determines the content of that element in the sample (Weindorf; Bakr; Zhu, 2014).

More recently, the portable X-ray fluorescence spectrometer (pXRF) has become a fast, cost-effective and environmentally friendly alternative for the determination of elemental contents in both field and laboratory conditions. pXRF can provide results in a shorter time, with minimal sample preparation and is a non-destructive method (Parsons et al., 2013; Schneider et al., 2016; Weindorf; Bakr; Zhu, 2014). This technique has facilitated different studies, such as evaluation of soil contamination by heavy metals, pedogenesis, soil chemistry, salinity and mapping, among others (Aldabaa et al., 2015; Mancini et al., 2019a, 2019b; O'Rourke et al., 2016; Sharma et al., 2014; Silva et al., 2017; Stockmann et al., 2016a; Weindorf et al., 2015).

However, works have reported that pXRF field data for many elements differ from those obtained under laboratory conditions, i.e. in air-dried fine earth (Silva et al., 2018; Stockmann et al., 2016b), mainly due to differences in moisture, texture, soil organic matter content, and sample roughness (Weindorf; Bakr; Zhu, 2014). This may constrain the use of field data, raising the need for correction of such results.

It is known that soil moisture (M) can absorb or disperse incident X-rays, influencing the results obtained by the equipment (Bastos; Melquiades; Biasi, 2012; Ge; Lai; Lin, 2005; Ribeiro et al., 2018; Sahraoui; Hachicha, 2017; Santana et al., 2019). Soil texture (T) can be associated with soil chemical and mineralogical composition and is capable of influencing various other soil attributes, such as cation exchange capacity, water infiltration rate and porosity, among others (Resende et al., 2014). Soil organic matter (SOM), in turn, promotes many benefits for soils, such as increasing water availability and presents great amounts of C, H, and O; however, SOM can attenuate the X-ray beams, causing decreasing contents of elements detected by pXRF (Hudson, 1994; Ravansari; Lemke, 2018; Shand; Wendler, 2014).

Knowing the factors that may cause interference in the pXRF readings is extremely important for the correction of the field data obtained. Since soil organic

matter is concentrated in the soil surface, some soil classes present a texture gradient in depth and that greater depths tend to maintain soil moisture for a longer time (Resende et al., 2014), the readings carried out with pXRF directly in the field are subject to reading variations caused by these factors (Stockmann et al., 2016a), which may hindrance works whose pXRF analyses have been conducted in both field and lab. Therefore, to demonstrate that it is possible to convert results of field analyses into those obtained in the lab may be very useful for researchers across the world, avoiding the necessity of analyzing the same sample in the field and in the lab. Furthermore, the influence of these soil properties may be variable according to the different elements, but deeper investigations are yet to be carried out in tropical conditions, especially regarding SOM and T, which have not been evaluated yet.

Thus, the objectives of this study were to create and evaluate mathematical models capable of predicting the content of Al, Ca, Fe, K, Si, V, Ti and Zr obtained by pXRF in lab conditions (air-dried fine earth - ADFE) based on pXRF readings conducted in the field, and to assess the influence of M, T and SOM on the prediction of each element evaluated. The hypothesis of this work is that M, T, and SOM can help in the correction of the pXRF results obtained in the field, being possible to convert them into lab-obtained pXRF results without requiring other pXRF analyses in the lab.

MATERIAL AND METHODS

Study area and sample collection

The study area is located in Lavras, Minas Gerais, Brazil, between latitudes 7,650,808 and 7,651,674 mS and longitudes 500,031 and 492,189 mW, zone 23K. The climate of the region has annual average temperature and precipitation of 20.4 °C and 1,460 mm, respectively (Dantas; Carvalho; Ferreira, 2007), classified as Cwa (subtropical with dry winter and rainy summer) according to the Köppen climate classification.

The municipality of Lavras is geologically located at the southern edge of the São Francisco Craton. According to Curi et al. (1990) and Quéméneur et al. (2002), in the region it is common to find gneisses (leuco and mesocratic) cut by mafic rock dikes, represented mainly by gabbro and gabbronorite, while quartzites predominate in the areas of higher altitudes.

The evaluated soils encompassed these different parent materials as described in Table 1, such as the soil

classes and sampled horizons. For this work, 12 soil profiles were described, 59 soil horizons were sampled during two consecutive days within the dry season to assure the actual moisture condition for all soil profiles. Soil profiles were classified at the second and fourth taxonomic levels according to the Brazilian Soil Classification System (Santos et al., 2018) and the US Soil Taxonomy (Soil Survey Staff, 2014), respectively (Table 1). At least one soil profile was described and sampled for each soil class. The main horizons were analyzed *in situ*, including: A, B, C, and Cr for mineral soils and H (or O horizon per Soil Taxonomy) for organic soils.

Soil analyses

The methodological sequence of field and laboratory procedures and the different analyses performed can be seen in Figure 1. First, soil profiles were excavated and the horizons were separated. Then, pXRF analyses were performed in each soil horizon (Table 1) directly on the

soil profile wall in the field (pXRF field) (Figure 1), in three places of the same soil horizon, with ca. 10 cm (horizontally) between the scanning positions. The final pXRF result was obtained by averaging the three scanning results. Then, samples from each horizon were collected from the soil profiles, at the places where the scanings were conducted, in order to determine soil moisture and perform the subsequent lab analyses. For pXRF analysis in the laboratory, a portion (ca. 50 g) of each sample was air-dried, sieved at 2 mm (air-dried fine earth - ADFE) and analyzed by pXRF (pXRF ADFE) by directly placing the equipment aperture at the surface of the samples, making sure the amount of the sample was thick enough (ca. 2 cm) to avoid the X-ray beams both passing through it and reaching the base of the Petri dish containing the sample. A Bruker® pXRF model S1 Titan 600 LE containing the software Geochem was used to perform the analyses and yielding the elemental results. This equipment contains a 50 keV and 100 μ A X-ray Rh tube with silicon drift detector (SSD) <145 eV.

Table 1: Classification, horizons and parent material of the soils sampled in Lavras, Minas Gerais, Brazil.

Parent material	Brazilian Soil Classification System	US Soil Taxonomy	Sampled horizons	Total number of samples
Quartzite	Litholic Neosol	Lithic Ustorthent	A, C, Cr	17
	Regolithic Neosol	Typic Ustorthent	A, Cr	
	Haplic Cambisol	Typic Dystrustept	A, B, C, Cr	
	Yellow Latosol	Xanthic Hapludox	A, B	
Gabbro	Regolithic Neosol	Typic Ustorthent	A, Cr	10
	Haplic Cambisol	Typic Ustorthent	A, B, C	
	Red Nitosol	Rhodic Kandudult	A, B, C	
	Red Latosol	Anionic Acrudox	A, B	
Gneiss	Litholic Neosol	Lithic Ustorthent	A, C, Cr	24
	Regolithic Neosol	Typic Ustorthent	A, Cr	
	Haplic Cambisol	Typic Dystrustept	A, B, C, Cr	
	Yellow Argisol	Inceptic Hapludult	A, B, C	
	Red-Yellow Argisol	Typic Hapludult	A, B, C	
	Red Argisol	Typic Rhodudult	A, B, C	
	Yellow Latosol	Xanthic Hapludox	A, B	
	Red-Yellow Latosol	Typic Hapludox	A, B	
Red Latosol	Rhodic Hapludox	A, B		
Mineral sediments	Haplic Gleysol	Typic Endoaquent	A, C	2
Organic sediments	Haplic Organosol	Typic Udifolist	A, H	6
Total				59

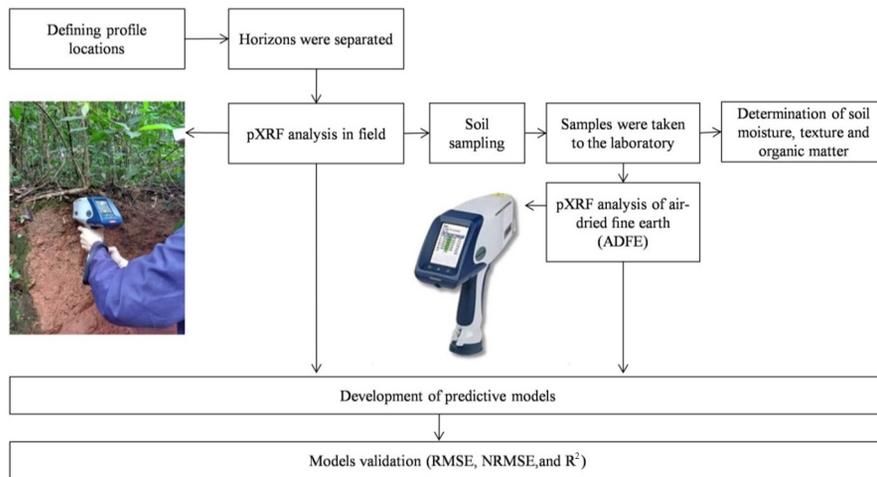


Figure 1: Workflow of the procedures conducted in this study.

Field and laboratory pXRF readings were performed in triplicate during 60s in dual soil mode. To verify the quality of data generated by the equipment, two National Institute of Standards and Technology (NIST) certified samples, 2710a and 2711a, and one sample certified by the pXRF manufacturer (Check Sample) were used. The pXRF results were compared with the certified contents for the elements used in this study. The recovery values (pXRF content / certified content) for 2710a, 2711a and Check Sample were, respectively: Al_2O_3 - 0.96/1.19/0.87; SiO_2 - 0.94/1.08/0.88; Fe - 0.43/0.70/0.89; K_2O - 0.40/0.59/0.86; CaO - 0.18/0.73/0; Ti - 0.51/0.73/0; Zr - 0.98/0/0. The zero value indicates that either there was no quantification in the reference sample or the element was not detected by pXRF.

To determine soil moisture (M), samples were weighted (Wet Mass - WM) and oven-dried at 105°C during 24 hours. After this period, the samples were again weighted to determine the dry mass (DM). Thus, soil moisture (%) was calculated using Equation 1. The collected samples were also subjected to laboratory analysis to determine texture (Gee; Bauder, 1986) and soil organic matter (Walkley; Black, 1934).

$$M\% = \frac{(WM - DM)}{WM} * 100 \quad (1)$$

Statistical analyses

For the prediction of the pXRF results obtained in the laboratory (ADFE) based on the results obtained in the field for each element, linear regression models were created using different combinations of pXRF results

obtained in the field with the independent variables M, T and SOM, according to Equations 2, 3, 4, 5, 6, 7, 8 and 9.

$$y = a1x1 + b \quad (2)$$

$$y = a1x1 + a2M + b \quad (3)$$

$$y = a1x1 + a2T + b \quad (4)$$

$$y = a1x1 + a2SOM + b \quad (5)$$

$$y = a1x1 + a2M + a3SOM + b \quad (6)$$

$$y = a1x1 + a2T + a3SOM + b \quad (7)$$

$$y = a1x1 + a2M + a3T + b \quad (8)$$

$$y = a1x1 + a2M + a3T + a4SOM + b \quad (9)$$

where a is the slope, y is the content of each element to be predicted in the ADFE, x is the content of each element obtained in the field by pXRF, M is soil moisture, T is texture (sand, silt, and clay contents) and SOM is the soil organic matter content.

The accuracy of the predictions of each element content in the ADFE was calculated by the leave-one-out cross-validation method of the “caret” package (Kuhn et al., 2018) in the R software (R Core Team, 2019), through calculation of the following parameters: R^2 , root mean square error (RMSE) (Equation 10) and normalized RMSE (NRMSE) (Equation 11).

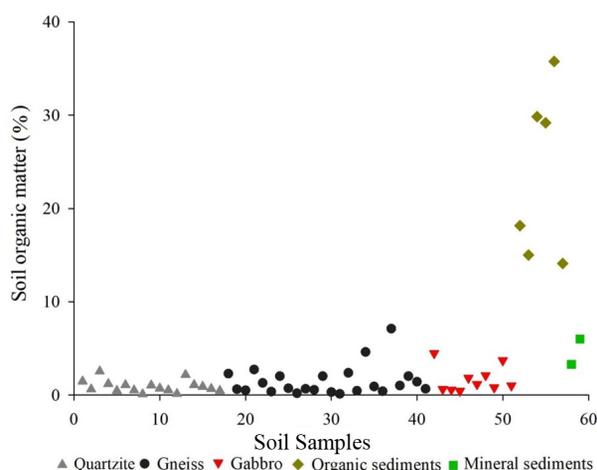


Figure 3: Soil organic matter content in soil samples derived from different parent materials.

Soil moisture (Figure 4) varied according to clay fraction content, SOM content, climatic conditions and land use, and its availability may still be influenced by soil management (Centurion; Andrioli, 2000). The highest moisture content was observed in the Haplic Organosol (Typic Udifolist), related to its position in the landscape and to the higher SOM content, since all the samples were collected in two consequent days within the dry season. Conversely, the soils derived from quartzite, mostly due to their texture rich in sand and lower SOM contents, presented the lowest moisture content.

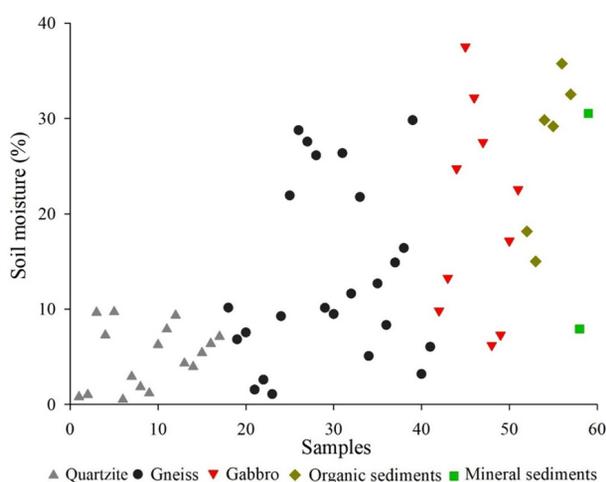


Figure 4: Moisture content in soils derived from quartzite, gneiss, gabbro and organic and mineral sediments.

Variation of soil elemental contents

The soils developed from gabbro presented, on average, higher Fe contents compared to the soils developed from other parent materials (Table 3). This is primarily because the parent rock had a higher Fe content (Monroe; Wicander, 2017) and Fe tends to accumulate in soils. Conversely, quartzite-derived soils presented the highest SiO_2 contents compared to the others, because this rock is basically composed of quartz (SiO_2), a very resistant mineral to weathering (Resende et al., 2019). Also, relationships between the content of certain chemical elements and the different textural fractions of the soil can be made (Zhu; Weindorf; Zhang, 2011). In tropical soils, for instance, greater contents of SiO_2 tend to correspond to soils rich in quartz (SiO_2), dominantly found in greater contents in soils rich in sand (Kämpf; Maques; Curi, 2012; Silva et al., 2019).

The elemental contents of the soil samples varied according to field or laboratory - ADFE (Figures 5 and 6). In general, the contents of all elements or oxides in ADFE were higher than those obtained in the field, with the exception of light-weight elements. This may have occurred because light-weight elements are more influenced by moisture, as also reported by Ribeiro et al. (2018).

The percentage of samples that presented higher contents in ADFE compared to contents of the field analysis was 97% for CaO, Fe, and Ti, 93% for K_2O , 88% for SiO_2 , 86% for Zr, 57% for Al_2O_3 , and 71% for V. Stockmann et al. (2016a; 2016b), evaluating the elemental contents obtained in both field and laboratory (ADFE) conditions by pXRF in Australia, observed that, in general, the contents of Fe, K and Ca were higher in ADFE than those obtained in the field, as found in this work (Figure 6).

Prediction models

The values of R^2_{adj} corresponding to the adjustment of the linear models to predict Al_2O_3 , CaO, Fe, K_2O , SiO_2 , V, Ti, and Zr in ADFE from the results of pXRF field analyses, considering the influence of M, T and SOM are presented in Figure 7. For Fe_{ADFE} and $\text{K}_2\text{O}_{\text{ADFE}}$ predictions, slight differences in R^2_{adj} were observed when adding the auxiliary variables to the models. Stockmann et al. (2016b) reported the small effect of moisture on Fe content obtained by pXRF, similarly to reports of Ribeiro et al. (2018) and the findings of this work. However, here it was noticed that T and SOM also have a very low effect on Fe results.

Table 3: Mean contents of elements (mg kg⁻¹) obtained by portable X-ray fluorescence (pXRF) spectrometer in soils in the field and in air-dried fine earth (ADFE) samples.

Parent Material	Analysis	Al ₂ O ₃	CaO	Fe	K ₂ O	SiO ₂	V	Ti	Zr
Quartzite	Field	86727	242	8686	12554	398872	14	2116	218
	ADFE	84360	1201	14041	17433	520871	6	2990	243
Gneiss	Field	187076	470	25649	3795	262297	10	3402	156
	ADFE	186952	1144	36695	6710	290484	14	5046	179
Gabbro	Field	140314	595	82237	1986	121544	123	4393	122
	ADFE	135228	1786	131419	3151	185700	134	8943	205
Mineral sediments	Field	150515	995	68055	971	168046	54	2594	155
	ADFE	159686	1074	80623	1695	233740	108	10085	188
Organic sediments	Field	104472	770	18864	6016	269845	11	5463	157
	ADFE	120351	75	27293	8697	395594	8	5340	205

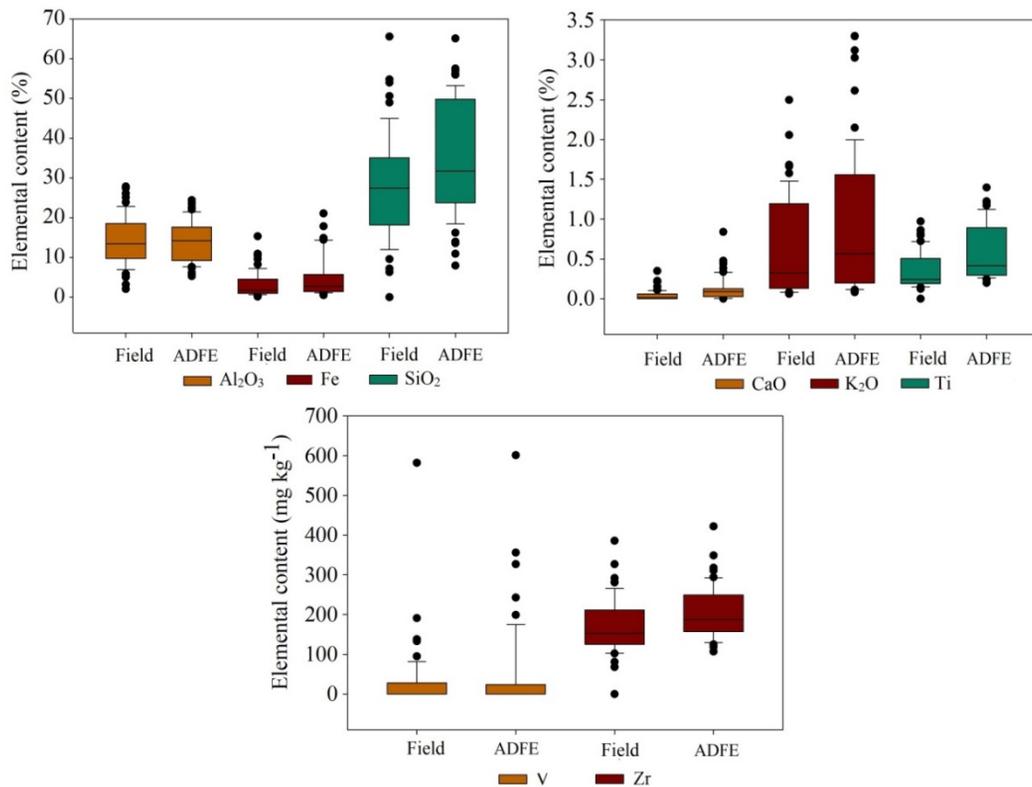


Figure 5: Elemental content obtained by portable X-ray fluorescence (pXRF) spectrometer in soils in the field and in ADFE for Al₂O₃, Fe, SiO₂, CaO, K₂O, Ti, V, and Zr.

The models that considered the soil texture as an auxiliary variable delivered higher values of R²_{adj} for the prediction of SiO₂ and V. SiO₂ predictions reached R²_{adj} of 0.60 using only the data obtained in the field, but it increased

to 0.76 when adding soil texture to the prediction models. The increment of the R²_{adj} values with the addition of the texture data can be explained by the fact that quartz, composed of SiO₂, is the predominant component in the sand fraction of Brazilian

soils (Alves et al., 2013; Araujo et al., 2014). Importantly, the changes in soil moisture did not significantly implied changes in R^2_{adj} for SiO_2 contents, contrary to the findings of Ribeiro et al. (2018). SOM did not improve SiO_2 models either.

For V, R^2_{adj} increased from 0.73 to 0.80 with addition of texture, with a small increase by adding only moisture (0.73 to 0.75) and no improvement when adding soil organic matter as an auxiliary variable. V presents dynamics

similar to Fe and Fe secondary oxide minerals (Aide, 2005; Kabata-Pendias, 2010; Martin; Kaplan, 1998). V^{3+} tends to accumulate along weathering and it can be incorporated into octahedral sites of kaolinite, gibbsite, hematite, and goethite, which are dominant in the clay fraction of most Brazilian soils (Marques et al., 2004). Differences in R^2_{adj} values were minimal for K_2O and Fe prediction by adding moisture, texture and soil organic matter. For K_2O , the model

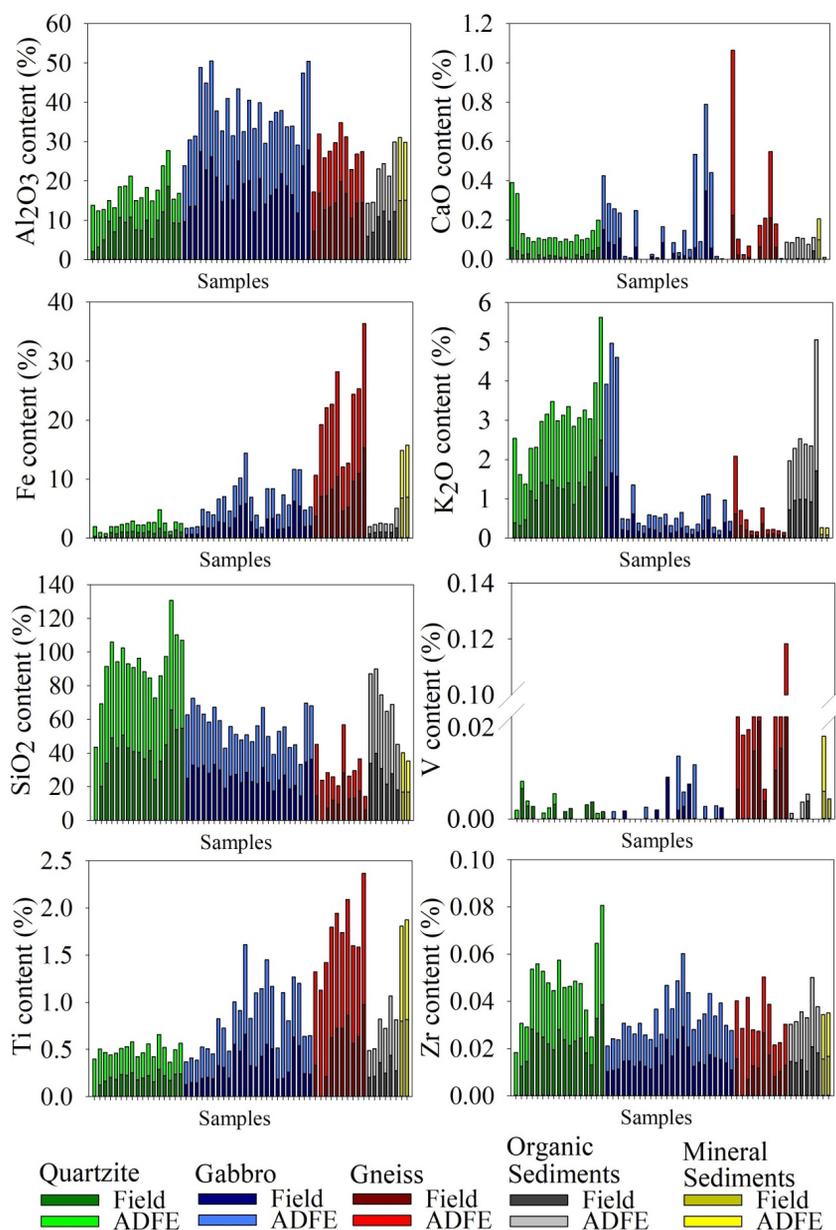


Figure 6: Field and laboratory (air-dried fine earth - ADFE) pXRF results of tropical soils for Al_2O_3 , CaO , Fe , K_2O , SiO_2 , V , Ti , and Zr .

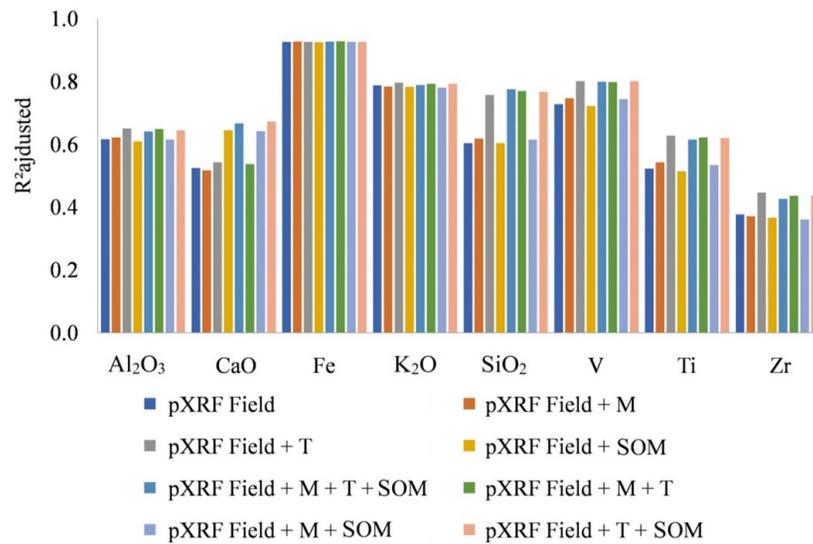


Figure 7: R^2_{adj} corresponding to the adjustment of linear models for the prediction of the Al_2O_3 , CaO, Fe, K_2O , SiO_2 , Ti, V, and Zr contents obtained in the air-dried fine earth (ADFE) from the results of the pXRF analyses conducted in field in association with moisture (M), texture (T) and soil organic matter (SOM).

with pXRF field data coupled with texture provided R^2_{adj} of 0.80 compared with 0.79 using only pXRF field data. For Fe, all the models presented minimal variation, with all the R^2_{adj} achieving values of 0.93.

The model for Al_2O_3 prediction obtained in laboratory with addition of SOM presented the smallest R^2_{adj} (0.61) when compared to the models generated from the addition of texture and moisture. Although a small increase occurred when adding the two latter variables to the models, the R^2_{adj} values reached 0.65 and 0.62, respectively. Texture and moisture, when combined with pXRF data, promoted the same result as the model using only pXRF and texture data. Soil moisture generally underestimates pXRF results (Bastos; Melquiades; Biasi, 2012; Hangen; Vieten, 2016; Lemiere et al., 2014), while texture may affect pXRF analyses due to the range of particle sizes and soil heterogeneity (Berger; Zou; Schleicher, 2009). For Ti prediction, when moisture and texture were added to the model, R^2_{adj} values varied from 0.52 to 0.54 and 0.63, respectively. High and positive correlations (0.78) were found by Zhu et al. (2011) between Ti and clay contents in temperate soils from USA, supporting the importance of texture for Ti prediction models.

For Zr prediction, R^2_{adj} values were the lowest among the evaluated elements. With the addition of texture, R^2_{adj} increased from 0.38 to 0.45, unlike the inclusion of other variables that did not produce considerable improvements. Stockmann et al. (2016b), studying the pedogenesis of soils developed from different parent materials, verified

an increase in Zr content with an increase in clay content. Since Zr is an element commonly found in very resistant minerals, its content tends to relatively increase with soil weathering. Curi and Franzmeier (1987) noted that clay-textured soils (71% clay) developed from basalt showed an increase in soil Zr content relative to rock due to Zr presence in zircon, a weathering resistant mineral. Several studies have highlighted the influence of particle size on pXRF analysis (Berger; Zou; Schleicher, 2009; Parsons et al., 2013; Stockmann et al., 2016b; Zhu; Weindorf; Zhang, 2011). This is explained by the fact that larger particles in the soil may not represent the entire composition contained in the sample (Parsons et al., 2013).

Models validation

In general, good values of the validation parameters of the prediction models were achieved, reaching high R^2 and low NRMSE and RMSE (Figures 8 and 9, and Table 4, respectively). For Fe, the high R^2 value and the lowest value of NRMSE are notorious, showing that the prediction of Fe_{ADFE} yields adequate results under different conditions. However, when analyzing RI (Table 4) for different models using different sets of variables, there is no considerable improvement. Thus, for Fe, only field data is capable to deliver accurate predictions of the values in ADFE, and it is not necessary to add other variables to the prediction models. This enables to perform these analyses even faster and more economical, since adding other variables would increase costs and time.

For SiO_2 and V, the values of R^2 were high (Figure 8) and together with the low NRMSE obtained (Figure 9), indicate a good performance of the model in comparison with most other elements. Also, SiO_2 and V presented a higher RI among all groups, reaching 20.29% and 17.90%, respectively, after adding only the texture as an auxiliary variable. Thus, addition of texture allows better predictions for SiO_2 and V without the addition of other variables. For K_2O , R^2 values were high (0.77) and RMSE values were low and there were no remarkable distinctions regarding the addition of different variables to the models. Also, the highest RI was achieved with the addition of texture only (1.28%). It is possible to state that, due to the small contribution of texture, the field data are sufficient for good predictions. The same happened for Fe, where the RI values were mostly low and negative (-1.52%), except for the model adding SOM and T (2.40%).

Ti presented the highest R^2 (0.60), with a considerable RI (11.18%) in the models to which texture and soil organic matter were added. For CaO, the highest R^2 was 0.48, however, the RMSE presented the highest value (1.141,24) in relation to the other elements (Table 4). This was probably caused by some pXRF readings that did not detect CaO in one of the conditions (field or lab), drastically increasing RMSE. Al_2O_3 models presented values of R^2 between 0.56 and 0.60, not much different from other elements that obtained R^2 near or higher than 0.80, such as Fe, K_2O , SiO_2 , and V. However, the RI for Al_2O_3 was negative for most models, especially by adding texture and SOM (RI = -5.28%), and when all

variables were included (RI = -5.24%). Small positive RI values were obtained by adding only M (0.15%) and M+T (0.97%) (Table 4).

For Zr validation, R^2 was very low and NRMSE was very high. Therefore, it is not advisable to use these models to predict Zr_{ADFE} . Despite of that, it can be observed that adding texture produced a slight improvement over the initial model ranging from 0.30 to 0.35, respectively, indicating that this variable has some positive interference in the prediction of Zr in the ADFE.

Most prediction models were strongly influenced by texture. In tropical soils, the higher sand content tend to positively correlate with SiO_2 content, since this particle size fraction in most soils is dominated by quartz, composed by SiO_2 (Kämpf; Marques; Curi, 2012; Silva et al., 2019). Thus, the use of texture in SiO_2 (and in almost all the other) prediction models improved all statistical parameters evaluated in relation to models that did not use texture as an auxiliary variable. Moisture had less importance than texture in the accuracy improvement of the models, since the reduction in X-ray intensity is proportional to the increase of water content in the sample (Stockmann et al., 2016b). In these tropical soils, soil organic matter did not strongly affect the models, as opposite to the findings of Ravansari and Lemke (2018) in soils from Canada to which three organic materials were added and elemental contents were measured via pXRF after each organic material addition. It is important to re-emphasize that both soil texture and organic matter are factors that directly influence soil moisture.

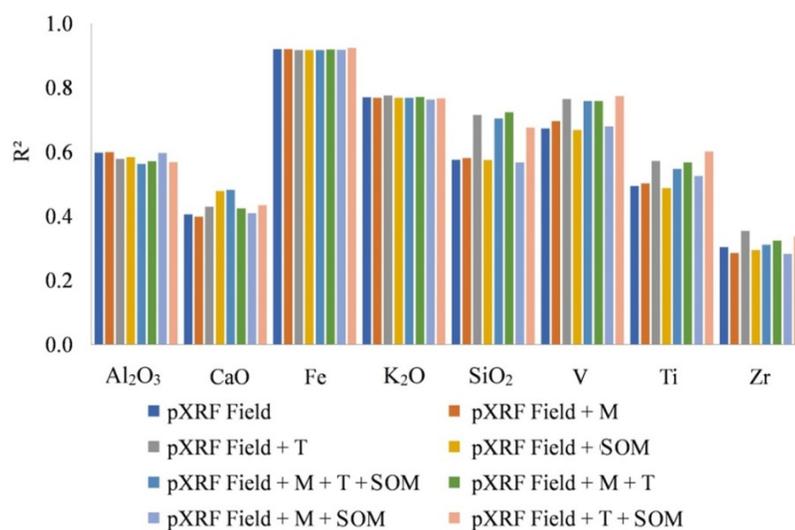


Figure 8: Coefficient of determination (R^2) corresponding to the validation of linear models for the prediction of Al_2O_3 , CaO, Fe, K_2O , SiO_2 , Ti, V, and Zr contents obtained by portable X-ray fluorescence (pXRF) spectrometry on air-dried fine earth (ADFE) based on pXRF analysis in field associated with texture (T), moisture (M) and soil organic matter (SOM).

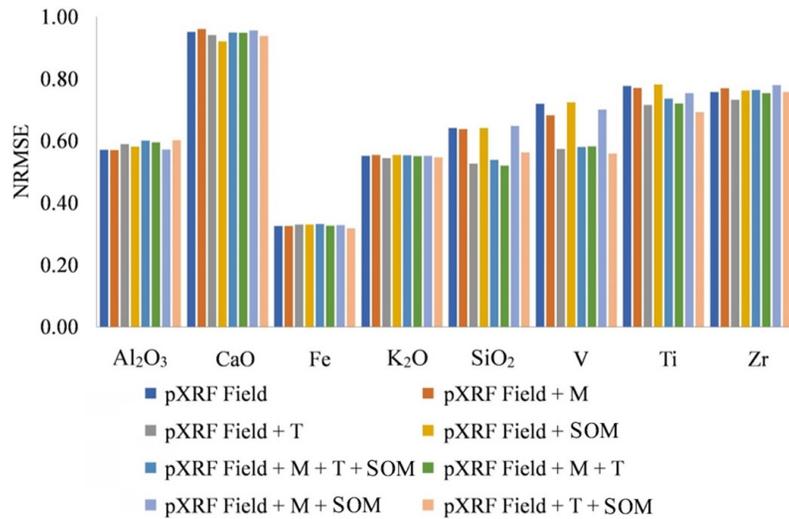


Figure 9: Normalized root mean square error (NRMSE) corresponding to the validation of linear models to predict Al₂O₃, CaO, Fe, K₂O, SiO₂, Ti, V, and Zr contents obtained by portable X-ray fluorescence (pXRF) spectrometer in air-dried fine earth (ADFE) based on field pXRF analysis in field associated with texture (T), moisture (M) and soil organic matter (SOM).

Table 4: Root mean square error (RMSE) and relative improvement (RI) corresponding to the validation of models for the prediction of Al₂O₃, CaO, Fe, K₂O, SiO₂, V, Ti, and Zr contents of the air-dried fine earth (ADFE) by portable x-ray fluorescence (pXRF) spectrometer based on field pXRF analysis associated with texture (T), moisture (M) and soil organic matter (SOM).

Linear Regressions	Al ₂ O ₃	CaO	Fe	K ₂ O	SiO ₂	V	Ti	Zr
RMSE (mg kg ⁻¹)								
pXRF Field	31500	1130	13261	4198	90836	69	2365	53
pXRF Field + M	31454	1141	13257	4217	90303	66	2347	54
pXRF Field + T	32507	1117	13462	4144	74576	55	2180	52
pXRF Field + SOM	32068	1094	13447	4218	90848	70	2381	54
pXRF Field + M + T	32830	1126	13296	4193	73670	56	2193	53
pXRF Field + M + SOM	31524	1135	13360	4194	91808	67	2296	55
pXRF Field + T + SOM	33163	1115	12943	4163	79740	54	2108	53
pXRF Field + M + T + SOM	33151	1128	13506	4213	76333	56	2243	54
RI (%)								
pXRF Field	-	-	-	-	-	-	-	-
pXRF Field + M	0.15	-0.99	0.03	-0.47	5.11	0.59	0.76	-1.63
pXRF Field + T	-3.20	1.13	-1.52	1.28	20.29	17.90	7.80	3.23
pXRF Field + SOM	-1.80	3.19	-1.40	-0.49	-0.59	-0.01	-0.68	-0.70
pXRF Field + M + T	0.97	0.36	-0.26	0.49	19.11	18.90	7.26	0.43
pXRF Field + M + SOM	-0.08	-0.43	-0.75	0.09	2.56	-1.07	3.13	-2.98
pXRF Field + T + SOM	-5.28	1.34	2.40	0.82	22.29	12.21	11.18	-0.10
pXRF Field + M + T + SOM	-5.24	0.19	-1.85	-0.36	19.41	15.97	5.16	-0.94

CONCLUSIONS

The elemental/oxides contents obtained by pXRF in field soil analysis and under laboratory conditions (in ADFE) varied for all analyzed elements/oxides. However, models for prediction of the contents in ADFE could be well adjusted for conversion of the results obtained in field for most elements/oxides. In general, soil texture coupled with field pXRF analyses was more helpful to predicting the elemental content of ADFE results than moisture and soil organic matter. Fe and K_2O contents in ADFE could be satisfactorily predicted from field data, without the addition of soil organic matter, texture or soil moisture. For CaO and Zr, results were less expressive even with the addition of all the auxiliary variables to the models. Thus, through simple models, it is possible to convert the pXRF results obtained in field into those obtained in ADFE for Al_2O_3 , SiO_2 , Fe, K_2O , V and Ti with or without the need to include auxiliary variables (T, M or SOM) according to the element.

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