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

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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 Al₂O₃, CaO, Fe₂O₃, SiO₂, 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 Al₂O₃, SiO₂, V, Ti and Zr, while the prediction of Fe and K₂O contents was insensitive to the addition of the auxiliary variables. The relative improvement (RI) in the prediction models were greater in predictions of SiO₂ (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.

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 hinder 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 of 20.4 ºC 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 scannings 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 μA 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       | Lithic Neosol                       | Lithic Ustorthent| A, C, Cr         | 17                     |
|                 | Regolithic Neosol                   | Typic Ustorthent | A, Cr            |                        |
|                 | Haplic Cambisol                     | Typic Dystrustep | 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 Kandiudult| A, B, C          |                        |
|                 | Red Latosol                         | Anionic Acrudox  | A, B             |                        |
| Gneiss          | Lithic Neosol                       | Lithic Ustorthent| A, C, Cr         |                        |
|                 | Regolithic Neosol                   | Typic Ustorthent | A, Cr            |                        |
|                 | Haplic Cambisol                     | Typic Dystrustep | A, B, C, Cr      |                        |
|                 | Yellow Argisol                      | Inceptic Hapludult| A, B, C         |                        |
|                 | Red-Yellow Argisol                  | Typic Hapludult  | A, B, C          | 24                     |
|                 | 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**                 |
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: Al₂O₃ - 0.96/1.19/0.87; SiO₂ - 0.94/1.08/0.88; Fe - 0.43/0.70/0.89; K₂O - 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).

\[ M\% = \left( \frac{WM - DM}{WM} \right) *100 \]  

(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.

\[ y = a1x1 + b \]  
\[ y = a1x1 + a2M + b \]  
\[ y = a1x1 + a2T + b \]  
\[ y = a1x1 + a2SOM + b \]  
\[ y = a1x1 + a2M + a3SOM + b \]  
\[ y = a1x1 + a2T + a3SOM + b \]  
\[ y = a1x1 + a2M + a3T + b \]  
\[ y = a1x1 + a2M + a3T + a4SOM + b \]  

(2) to (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).

\[ \text{RMSE} = \sqrt{\frac{1}{n} \sum (y_i - \hat{y}_i)^2} \]  
\[ \text{NRMSE} = \frac{\text{RMSE}}{\text{Max}(y_i)} \]  

(10) and (11)
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\[ \text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (e_i - m_i)^2} \]  

(10)

\[ \text{NRMSE} = \frac{\text{RMSE}_{\text{with treatments}}}{\sigma} \]  

(11)

where \( n \) is the number of observations, and \( i \) is the element content predicted by pXRF in ADFE through the models, \( e_i \) is the estimated content of elements, and \( m_i \) is the content of elements obtained by pXRF in ADFE.

In addition to these parameters, the relative improvement (RI) (Equation 12) of the models in relation to the simple linear model of Equation 2 was calculated. Thus, it was possible to define if the auxiliary variables M, T and SOM contribute to the prediction of the content of each element obtained by pXRF in ADFE, based on the contents obtained by pXRF in the field.

\[ RI = \frac{\text{RMSE}_{\text{field}} - \text{RMSE}_{\text{with treatments}}}{\text{RMSE}_{\text{field}}} \times 100 \]  

(12)

**RESULTS AND DISCUSSION**

**Characterization of the soil moisture, texture and organic matter**

The values of minimum, maximum, mean, standard deviation (SD), and coefficient of variation (CV) for texture (clay, silt, and sand contents), M and SOM of the studied soils are presented in Table 2. The substantial range of the values reflects the different soil classes and the parent materials in which the samples were collected.

| Soil property | Minimum | Maximum | Mean | SD  | CV  |
|---------------|---------|---------|------|-----|-----|
| Clay (%)      | 5       | 70      | 32   | 18.3| 2.4 |
| Silt (%)      | 5       | 59      | 26   | 12.9| 1.7 |
| Sand (%)      | 14      | 68      | 42   | 13.7| 1.8 |
| SOM (%)       | 0.1     | 14.1    | 1.7  | 2.2 | 0.3 |
| M (%)         | 0.5     | 37.5    | 13.6 | 10.6| 1.4 |

The highest SD values were obtained for texture, as there is great variability between the soil classes, horizons, parent materials (Resende et al., 2014) (Figure 2). Additionally, different degrees of weathering and erosion rate of soils influence soil texture (Zhang et al., 2019), helping to explain the results.

In general, the clay content increases in the following order: quartzite < gneiss < gabbro. The higher the quartz content in the parent material the smaller the soil clay content, which is associated with the high quartz resistance to weathering mostly present in the sand particle size fraction.

The variation in SOM contents (Figure 3) was probably caused by different land uses and practices of soil management (Foley et al., 2005), as well as the depth of the sample, clay content, mineralogy, climate, moisture regime, among others (Resende et al., 2014). The highest contents of SOM were observed in the Haplic Organosol (Typic Udifolist), due to the paludization pedogenetic process (Santos et al., 2018). For the other soil classes, the highest SOM content was observed in the superficial horizon. The soils derived from quartzite presented lower SOM contents probably due to their higher sand content and the dominance of sparse grasses in the area, causing little deposition of organic matter. The soils derived from gneiss and gabbro, due to their higher clay contents among other factors, presented higher accumulation of SOM.
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.

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 SiO₂ contents compared to the others, because this rock is basically composed of quartz (SiO₂), 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 SiO₂ tend to correspond to soils rich in quartz (SiO₂), 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 K₂O, 88% for SiO₂, 86% for Zr, 57% for Al₂O₃, 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 Al₂O₃, CaO, Fe, K₂O, SiO₂, 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 K₂O$_{ADFE}$ 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.
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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 | \(\text{Al}_2\text{O}_3\) | CaO  | Fe   | \(\text{K}_2\text{O}\) | \(\text{SiO}_2\) | 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 \(\text{Al}_2\text{O}_3\), Fe, \(\text{SiO}_2\), CaO, \(\text{K}_2\text{O}\), Ti, V, and Zr.

The models that considered the soil texture as an auxiliary variable delivered higher values of \(R^2_{\text{adj}}\) for the prediction of \(\text{SiO}_2\) and V. \(\text{SiO}_2\) predictions reached \(R^2_{\text{adj}}\) 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 \(R^2_{\text{adj}}\) values with the addition of the texture data can be explained by the fact that quartz, composed of \(\text{SiO}_2\), 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 imply changes in $R^2_{\text{adj}}$ for SiO$_2$ contents, contrary to the findings of Ribeiro et al. (2018). SOM did not improve SiO$_2$ models either.

For V, $R^2_{\text{adj}}$ 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 $R^2_{\text{adj}}$ 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$_2$O$_3$, CaO, Fe, K$_2$O, SiO$_2$, V, Ti, and Zr.
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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; Viiten, 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 NMRSE 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 SiO₂ and V, the values of R² 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, SiO₂ 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 SiO₂ and V without the addition of other variables. For K₂O, R² 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 R² (0.60), with a considerable RI (11.18%) in the models to which texture and soil organic matter were added. For CaO, the highest R² 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. Al₂O₃ models presented values of R² between 0.56 and 0.60, not much different from other elements that obtained R² near or higher than 0.80, such as Fe, K₂O, SiO₂, and V. However, the RI for Al₂O₃ 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, R² was very low and NRMSE was very high. Therefore, it is not advisable to use these models to predict Zr⁴⁺. 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 SiO₂ content, since this particle size fraction in most soils is dominated by quartz, composed by SiO₂ (Kämpf; Marques; Curi, 2012; Silva et al., 2019). Thus, the use of texture in SiO₂ (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 (R²) corresponding to the validation of linear models for the prediction of Al₂O₃, CaO, Fe, K₂O, SiO₂, 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).](attachment:figure8.png)
Correcting field determination of elemental contents in soils via portable x-ray fluorescence spectrometry

Figure 9: Normalized root mean square error (NRMSE) corresponding to the validation of linear models to predict $\text{Al}_2\text{O}_3$, CaO, Fe, $\text{K}_2\text{O}$, $\text{SiO}_2$, V, Ti, 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 $\text{Al}_2\text{O}_3$, CaO, Fe, $\text{K}_2\text{O}$, $\text{SiO}_2$, 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 | $\text{Al}_2\text{O}_3$ | CaO | Fe | $\text{K}_2\text{O}$ | $\text{SiO}_2$ | V | Ti | Zr |
|--------------------|-----------------|-----|----|-----------------|----------------|---|----|----|
| 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 (%)

| RI (%) | pXRF Field | pXRF Field + M | pXRF Field + T | pXRF Field + SOM | pXRF Field + M + T | pXRF Field + M + SOM |
|--------|------------|----------------|----------------|------------------|--------------------|---------------------|
|        | -0.15      | -0.99          | -0.03          | -0.47            | 5.11               | 0.59                |
|        | 0.76       | -1.63          | -3.20          | 1.13             | -1.52              | -1.28               |
|        | 2.56       | 0.43           | 3.19           | -1.40            | -0.49              | -0.59               |
|        | 0.09       | -2.98          | 0.97           | 0.36             | -0.26              | -0.01               |
|        | -0.36      | 1.34           | -0.75          | 2.40             | 0.82               | 19.11               |
|        | 11.18      | 15.97          | 10.24          | -1.85            | 0.36               | 19.41               |
|        | -0.70      | -2.98          | -0.10          | -0.36            | 15.97              | 5.16                |
|        | -0.94      | -0.94          |               |                  |                    |                     |

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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$_2$O 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$_2$O$_3$, SiO$_2$, Fe, K$_2$O, V and Ti with or without the need to include auxiliary variables (T, M or SOM) according to the element.

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