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Portable X-ray fluorescence (pXRF) spectrometry applied to the prediction of chemical attributes in Inceptisols under different land uses

Espectrometria portátil de fluorescência de raios-x (pXRF) aplicada à predição de atributos químicos de Cambissolos sob diferentes usos

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ABSTRACT

Portable X-ray fluorescence (pXRF) spectrometry has been increasingly adopted for varying studies worldwide. This work aimed at characterizing effects of soil management on the content of chemical elements detected by pXRF in managed and unmanaged areas of Inceptisols, and evaluating the potential of using pXRF data to generate prediction models for soil fertility attributes, evaluating the effect of land uses on such models. Samples were collected in A, B, and C horizons of soils under native forest, native Cerrado, coffee crops with 1 and 5 years of implantation and eucalyptus. Soil fertility attributes were determined through laboratory analyses, whereas, elemental contents were obtained through pXRF analysis. PXRF data were used for modeling (regressions) and validation of soil fertility attributes and necessity of lime (NL) application, with or without distinction between managed and unmanaged areas. Management practices on coffee crops increased the levels of Sr, CaO, P_2O_5, Cu, and Zn. CaO content was efficient for prediction of exchangeable Ca^{2+} contents (R^2 = 0.91), pH (R^2 = 0.88), base saturation (R^2 = 0.89) in managed areas. General models presented adequate results to predict exchangeable Ca^{2+} (R^2 = 0.92), pH (R^2 = 0.85), and base saturation (R^2 = 0.90). Models for unmanaged areas were less effective. PXRF detected modifications in elemental contents caused by management practices and provided reliable predictions of soil fertility attributes.

Index terms: Soil property modeling; soil management; soil fertility; Brazilian Cerrado; proximal sensor.

RESUMO

Espectrômetria portátil de fluorescência de raios-X (pXRF) tem sido crescentemente adotada para estudos sobre solos. Este trabalho objetivou caracterizar efeitos do manejo do solo no teor de elementos químicos detectados pelo pXRF em Cambissolos manejados e não manejados e avaliar o potencial de uso de dados do pXRF para gerar modelos de predição da fertilidade do solo. Amostras foram coletadas em floresta nativa, Cerrado nativo, cafeeiros com 1 e 5 anos de implantação e eucalipto, nos horizontes A, B e C. Atributos de fertilidade do solo foram determinados por análises laboratoriais, enquanto o teor dos elementos foi obtido pelo pXRF. Dados do pXRF foram utilizados para modelagem (regressões) e validação de atributos de fertilidade do solo, além da necessidade de calagem (NL), com ou sem distinção entre áreas manejadas e não manejadas. Práticas de manejo dos cafeeiros aumentaram os teores totais de Sr, CaO, P_2O_5, Cu e Zn. Os teores de CaO foram eficientes para predição de teores trocáveis de Ca^{2+} (R^2 = 0,91), pH (R^2 = 0,88) e saturação por bases (R^2 = 0,89) nas áreas manejadas. Modelos gerais foram adequados para predizer teores trocáveis de Ca^{2+} (R^2 = 0,92), pH (R^2 = 0,85) e saturação por bases (R^2 = 0,90). Modelos para áreas não manejadas foram menos eficazes. O pXRF detectou modificações no teor dos elementos causadas pelas práticas de manejo e possibilitou predições adequadas de atributos relacionados à fertilidade do solo.

Termos para indexação: Modelagem de atributos do solo; manejo do solo; fertilidade do solo; Cerrado brasileiro; sensor próximo.

INTRODUCTION

Technological advances in varied branches of research have led to large increases in crop productivity in the past decades. Increased productivity is a result not only of the efficient use of agricultural inputs, but also of machinery and equipment that improve soil management and turn places formerly with low agricultural potential into high productivity areas (Lopes; Guilherme, 2016).

Inceptisols are the second largest soil class on the planet in terms of occupied area, covering ~15% of the Earth's ice-free surface (Eswaran; Reich, 2005). These soils are weakly developed and can pose some physical limitations to plant growth. Moreover, in cases of inappropriate management, they can be easily subjected to erosion and degradation (Resende et al., 2014). Despite those constraints, these soils have been used for agricultural purposes, allowing food production for ~20% of the world's population (McDaniel, 2018). In Brazil, areas of Inceptisols have been cultivated with eucalyptus for wood and cellulose production, sugarcane, and coffee (Serafim et al., 2013; Silva et al., 2018).

Brazil is the largest coffee producer in the world (Alvarenga; Arraes, 2017) and it is estimated that coffee production in 2018 in the country will range from 54 to 58 million bags (60 kg) of benefited coffee (CONAB, 2018). The state of Minas Gerais is the largest producer in the country, producing ~30 million bags in a planted area of 1,243,833 ha (CONAB, 2018). According to Bernardes et al. (2012), 10% of the total area cultivated with coffee plants in Minas Gerais are areas of Inceptisols. However, studies on the management of coffee crops in these soils are rare and mainly concern aspects related to soil physics and conservation (Lima et al., 2009, 2010; Serafim et al., 2013; Silva et al., 2016).

Among the advances that have emerged in recent years and are potentially applicable in improving agricultural management, the portable X-ray fluorescence (pXRF) spectrometer stands out by detecting contents of chemical elements in a few seconds and without the production of sample waste (Ribeiro et al., 2017; Weindorf; Bakr; Zhu, 2014). PXRF can be used directly in the field or in the laboratory to detect total elemental content of the Periodic Table from Mg to U in soil samples and other materials (McGladdery et al., 2018; Pearson et al., 2017; Ribeiro et al., 2017; Weindorf; Bakr; Zhu, 2014). Some studies have shown good results for predicting soil chemical properties, such as pH (Sharma et al., 2014) and cation exchange capacity (Sharma et al., 2015), but few have attempted to predict available nutrient contents from pXRF analyses (Silva et al., 2017; Pelegrino et al., 2018). However, several factors can affect soil elemental contents, such as soil parent material, the degree of weathering-leaching, and management systems (Araujo et al., 2014; Curi; Franzmeier, 1987; Lopes; Guilherme, 2016; Resende et al., 2014; Schaetzl; Anderson, 2005). Thus, modeling pXRF results to predict the availability of plant nutrients in soils must consider soil variability and ongoing management practices. For example, areas of Brazil under native vegetation compared with those under cultivation in the Cerrado region present remarkable contrasting conditions of nutrient availability to plants (Lopes; Guilherme, 2016).

Thus, the objectives of this work were to: a) characterize the effects of management on the contents of several chemical elements detected by pXRF along the A, B, and C horizons of Inceptisols under different land uses; and b) develop models from pXRF data for predicting soil fertility attributes and necessity of lime application, comparing the effect of land uses (native vegetation vs. cultivated areas) on model accuracy. We hypothesize that pXRF elemental data and appropriate statistical modeling will provide solid predictive capability for multiple soil chemical parameters.

MATERIAL AND METHODS

Study area

This study was carried out at Santa Luzia farm, in Campos Altos county, Minas Gerais state, Brazil. The area presents five land uses distributed across 17 ha; two are under natural vegetation: native Cerrado and native forest, which have not undergone anthropic interference, and hereafter are referred to as *unmanaged areas*. The other three areas have been subjected to different management practices and land uses, hereafter named *managed areas*. They consist of two areas planted with coffee (*Coffea arabica* Lineu) with 1 and 5 years of implantation and one area planted with eucalyptus (*Eucalyptus* spp.) with 5 years of implantation (Figure 1).

The five areas are on clayey-skeletal, kaolinitic, subactive, thermic, shallow, Typic Dystrustepts, developed from phyllite (Silva et al., 2018). The dominant minerals present in this rock are feldspars, micas (mainly muscovite), and quartz (Silva et al., 2006; Batista et al., 2018). The managed areas were initially submitted to conventional soil tillage by plowing to 20 cm depth. The liming application was carried out to raise the base saturation percentage to 60%, as recommended by Alvarez and Ribeiro (1999). Three months after liming, the soil was furrowed for planting.

The coffee area with 5 years of implantation received lime and fertilizer application annually per Guimarães et al. (1999). The 1-year-old coffee area was fertilized at planting and received an additional application of N, P, and K per Guimarães et al. (1999). The areas planted with coffee have received annual application of chicken and cow manure as well as coffee husks. The eucalyptus plantation received the conventional fertilization at planting with fertilizers containing N, P, and K after lime application.

The unmanaged area of native Cerrado has native vegetation named "*Open Cerrado*", dominated by grasses and scarce shrubs. The native forest area is mostly composed of large, secondary and late trees.

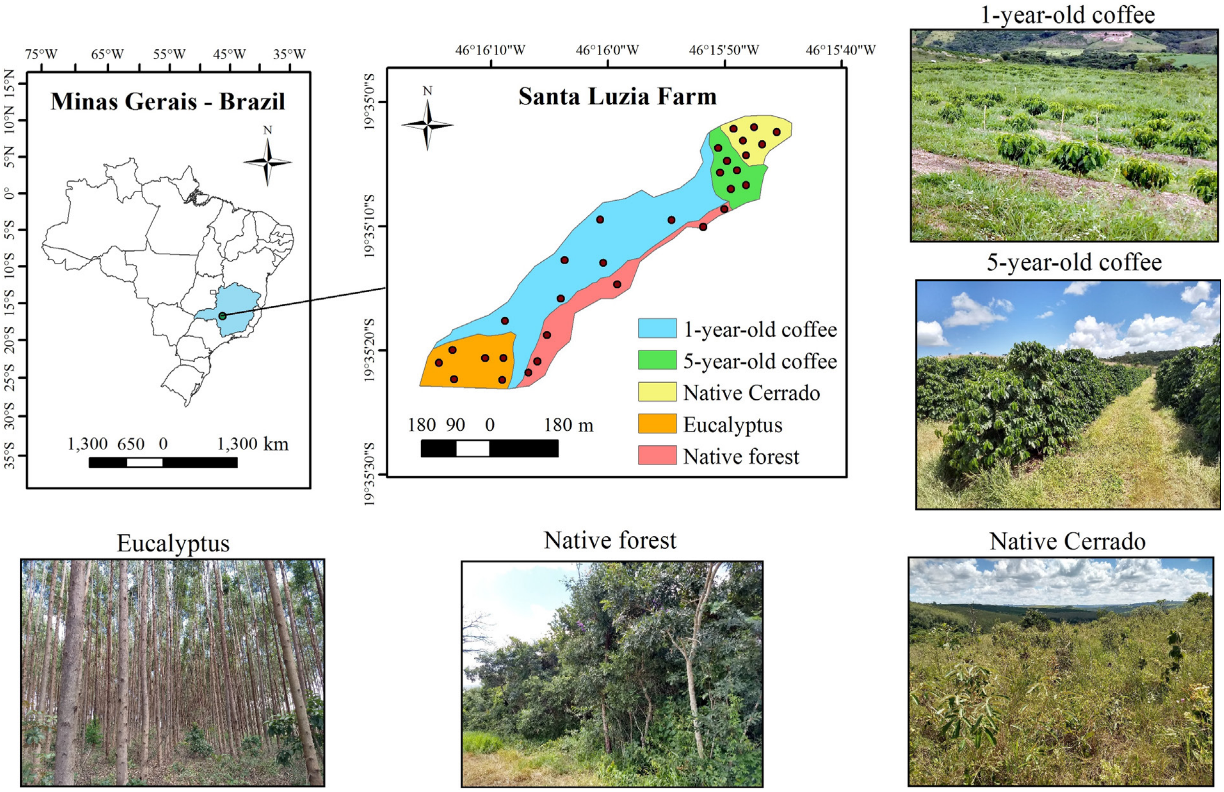

Figure 1: Study area, sampled locations and corresponding land uses in Campos Altos, Minas Gerais, Brazil.

Soil sampling, laboratory and statistical analyses

Six sites were randomly distributed in each of five areas and sampled at depths equivalent to the A, B, and C horizons of the Inceptisols (Figure 1), comprising 90 total samples. The samples were air-dried, passed through a 2 mm sieve and subjected to laboratory analyses.

The following analyses were performed: pH in water; H + Al (Shoemaker et al., 1961); available P and K^+ (Mehlich, 1953), exchangeable Ca^{2+}, Mg^{2+}, and Al^{3+} extracted with 1 mol L^{-1} KCl (Mclean et al., 1958); organic carbon (Walkley; Black, 1934) and remaining P (Alvarez; Fonseca, 1990). The values of sum of bases (SB), base saturation (V%), aluminum saturation (m%), and effective (t) and potential (T) cation exchange capacity were also calculated. Necessity of liming (NL) was calculated according to the method of raising base saturation to 60% (Alvarez; Ribeiro, 1999). These results were subjected to analysis of variance and Scott-Knott test at a significance level of 5% to assess differences of these soil properties between different land uses in Sisvar software (Ferreira, 2014).

PXRF analyses and elemental contents variability with soil depth

After air-drying and sieving, the soil samples were analyzed by a pXRF (Bruker® model S1 Titan LE) featuring a Rh X-ray tube of 4W, 15-50 keV, and 5-100-µA, silicon drift detector (SDD) with a resolution of <145 eV. All soil samples were analyzed in triplicate, for 60 seconds each in *Trace* mode (dual soil), and using the software Geochem, according to Weindorf and Chakraborty (2016). The accuracy of the equipment was assessed through comparisons of elemental contents present in samples certified by the pXRF manufacturer (check sample - CS) and samples certified by the National Institute of Standards and Technology (NIST) (2710a and 2711a) with elemental contents obtained by pXRF for such samples. The percentage of recovery (recovery % = 100 x content obtained/content certified) are presented in Table 1. The elements/oxides that were detected in all the samples and used in this study were: V, Al_2O_3, Pb, Sr, Cl, Zn, Cu, Ni, Fe, Mn, CaO, P_2O_5 and K_2O. Mean elemental content in each soil horizon was plotted to show the variability with depth and relative difference between land uses.

Table 1: Percentage of recovery of element contents by portable X-ray fluorescence (pXRF) spectrometer of samples certified by the National Institute of Standards and Technology (NIST)(2710a and 27111a) and pXRF manufacturer check sample (CS). The percentages of recovery of the samples are shown only for the elements that were used in this work and were present in the certified samples.

Certified Material	Al	P	K	Ca	Mn	Fe	Ni	Cu	Zn	Sr	V	Pb	Cl
	%												
2710a	82.7	385.8	57.4	33.4	70.1	74.1	-	73.1	88.5	98.0	51	107	-
2711a	69.5	580.2	44	41.4	59.3	66.7	69.1	71.4	79.7	90.9	29	109	-
CS	95.5	-	86.2	-	83.4	89.4	89.7	90.2	-	-	-	101	-

Modeling and validation of available nutrient contents and necessity of lime application from pXRF data

Simple linear, polynomial, and logarithmic regression models were adjusted for prediction of available/exchangeable contents of Ca^{2+}, P, K^+, Al^{3+}, pH, V%, and NL from pXRF results (CaO for predicting exchangeable Ca^{2+}, pH, NL, and V %; K_2O for predicting available K^+; P_2O_5 for predicting available P; Al_2O_3 for predicting exchangeable Al^{3+}). Regressions were created in two ways: general, by grouping data of managed and unmanaged areas; and specific, by analyzing managed and unmanaged areas separately. The models were calibrated using 75% of the data, chosen randomly and regardless of the soil horizons to which they belong. The models (general and specific) with high coefficient of determination (R^2) were validated with the remaining 25% of the data, through calculations of R^2, root mean square error (RMSE) (Equation 1), and mean error (ME) (Equation 2) between real (reference) and predicted contents:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(ei - mi\right)^2} \quad (1)$$

$$ME = \frac{1}{n}\sum_{i=1}^{n}\left(ei - mi\right) \quad (2)$$

where *n* is number of observations (soil samples), *ei* refers to the values estimated by the models, and *mi* corresponds to the observed values obtained from laboratory analyses.

RESULTS AND DISCUSSION

Soil fertility properties in different land uses

Table 2 shows the mean values of soil laboratory results for different land uses in A, B, and C horizons. The managed areas (except for eucalyptus) presented significant differences in soil fertility properties compared with unmanaged areas in all soil horizons indicating superior conditions for plant development due to the frequent application of corrective soil amendments and fertilizers for coffee production. Soils under coffee plantations in Southern Minas Gerais tend to present low pH, available P contents, and base saturation, with most of the plantations containing high contents of available K^+ (Figueiredo et al., 2013). The complete characterization of cultivated soils is important so that fertility correction recommendations can be properly made. Considering soil stoniness, texture, and depth can further help in decision making on application of soil amendments and fertilizers, reducing leaching loss (mainly for available K^+) which is strongly required by coffee plants and highly susceptible to leaching in tropical environments (Bley et al., 2017).

Even with intensive coffee management, which includes addition of manure and coffee husks besides corrective amendments and fertilizers, there was no significant difference between organic matter contents of managed and unmanaged soils in the surface horizon. Also, it seems the application of these sources of organic matter on coffee areas did not contribute to increasing organic matter content with depth. Organic matter contents in forest areas were greater than those in other land uses.

In the areas cultivated with coffee for 5 years, mean pH values were >7. This is likely due to farmers not considering the stoniness of those soils (66%) in the calculations of the amount of lime needed and, hence, in its application. Very high available P contents were also observed as well as the tendency of K^+ leaching; available K^+ contents in the C horizon increased in coffee areas in relation to the two areas of native vegetation.

Areas planted with eucalyptus showed low fertility soils, even with lower contents of some nutrients than the native Cerrado area as evidenced by low exchangeable Ca^{2+}, Mg^{2+}, and available K^+ and P in all horizons. Low availability of nutrients is attributed to fertilizer application

Table 2: Mean values of soil fertility analyses in managed (coffee after 1 and 5 years of implantation and eucalyptus) and unmanaged (native forest and native Cerrado) areas of Inceptisols in Campos Altos, Minas Gerais, Brazil.

	pH	K^+	P	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	SB	t	T	V	m	SOM	P Rem
Land use	H_2O	-----mg dm^{-3}----		------------------------------cmol$_c$ dm^{-3}------------------------------							---------%----------		dag kg^{-1}	mg L^{-1}
							A Horizon							
Coffee 1	6.58 a	133.47 b	97.92 b	4.34 b	0.90 a	0.13 d	1.59 c	5.59 b	5.34 b	7.46 b	71.61 a	2.88 c	3.93 a	34.89 b
Coffee 5	7.03 a	206.44 a	1256.53 a	5.97 a	1.53 a	0.00 d	1.86 c	8.03 a	8.03 a	9.62 b	82.50 a	0.00 c	4.92 a	42.89 a
Native Cerrado	5.00 b	110.48 b	1.91 b	0.21 c	0.16 b	1.65 c	7.59 b	0.66 c	2.31 c	8.24 b	7.91 b	71.85 b	3.53 a	20.59 d
Eucalyptus	4.70 b	47.12 c	1.89 b	0.11 c	0.10 b	2.58 b	7.31 b	0.33 c	2.92 c	7.64 b	4.48 b	88.50 a	2.55 a	28.60 c
Native Forest	4.88 b	100.57 b	2.67 b	0.22 c	0.16 b	2.98 a	12.59 a	0.61 c	3.62 c	13.20 a	4.76 b	82.93 a	4.34 a	19.46 d
							B Horizon							
Coffee 1	5.76 a	152.99 a	7.88 b	2.26 a	0.71 a	0.58 c	3.04 c	3.36 b	3.95 b	6.41 b	50.79 a	20.54 b	2.64 b	30.73 b
Coffee 5	6.43 a	234.87 a	639.35 a	4.00 a	1.19 a	0.08 c	2.51 c	5.78 a	5.87 a	8.29 b	68.01 a	2.17 c	2.95 b	36.71 a
Native Cerrado	5.03 b	73.16 b	2.08 b	0.10 b	0.10 b	1.63 b	6.61 b	0.39 c	2.02 c	7.00 b	5.64 b	80.72 a	2.57 b	20.39 c
Eucalyptus	4.92 b	39.89 b	1.39 b	0.10 b	0.10 b	2.63 a	7.15 b	0.30 c	2.93 c	7.45 b	4.07 b	89.57 a	2.04 b	23.35 c
Native Forest	4.83 b	83.62 b	2.10 b	0.10 b	0.10 b	3.25 a	12.65 a	0.41 c	3.67 b	13.07 a	3.33 b	88.49 a	3.73 a	16.07 d
							C Horizon							
Coffee 1	5.20 b	138.53 b	3.14 b	0.77 b	0.29 b	0.98 d	3.83 c	1.41 b	2.39 b	5.24 b	26.80 b	42.78 b	1.59 b	28.02 b
Coffee 5	5.90 a	252.28 b	362.25 a	2.36 a	0.62 a	0.55 d	3.39 c	3.63 a	4.18 a	7.02 b	48.68 a	20.87 c	2.01 b	33.14 a
Native Cerrado	5.20 b	56.74 b	1.89 b	0.10 b	0.10 b	1.48 c	5.36 b	0.34 b	1.83 b	5.70 b	6.22 c	81.18 a	2.16 b	23.27 c
Eucalyptus	5.01 b	30.65 b	1.10 b	0.10 b	0.10 b	2.35 b	6.03 b	0.28 b	2.63 b	6.30 b	4.46 c	89.37 a	1.60 b	22.26 c
Native Forest	4.93 b	69.16 b	1.50 b	0.10b	0.10 b	3.06 a	11.05 a	0.37 b	3.44 a	11.44 a	3.42 c	89.02 a	2.95 a	14.55 d

P Rem: remaining phosphorus; SB: sum of bases; t: effective cation exchange capacity; T: potential cation exchange capacity; V: base saturation; SOM: soil organic matter. Means followed by the same lower case letters in columns compare different land uses.

only being carried out at implantation, five years before the soil samples were collected. Uptake of nutrients by eucalyptus roots was another source of loss. Leite et al. (2010) noted that the management of eucalyptus plantations, regardless of the previous land use, tends to decrease nutrient contents in soils. The substitution of native Cerrado vegetation for eucalyptus plantations without fertilizer input through the cultivation period highlights the need for adequate long-term management to avoid soil nutrient exhaustion. This is especially true after the eucalyptus harvest (export), which could cause nutritional deficiencies in plants that will subsequently grow in the same area. In the case of eucalyptus regrowth without fertility correction, low wood production may ensue depending on the level of nutrient stress to which the plants would be subjected (Gonçalves et al., 2013).

For unmanaged areas, soil nutrient contents and other conditions regarding fertility properties are much worse for plant development than those found in the managed areas, as expected. It highlights the contrasting natural low fertility conditions of Brazilian Cerrado soils, even for Inceptisols, compared with managed soils. The values of pH, exchangeable Ca^{2+} and Al^{3+}, available P, H+Al, T, and SOM found in the native Cerrado and native forest are similar to the values reported by Skorupa et al. (2012) in other areas of Cerrado and seasonal semi-deciduous forest.

It is possible to notice that the longer the period the area has been managed, the greater the downward mobilization of bases within the soil profile, especially for the areas cultivated with coffee. Soil fertility generally improves with depth, which is particularly important in these Inceptisols that present lower natural nutrient contents than those required by most crops. The improvement of soil conditions with depth for plants causes greater and easier development of the root system, directly and indirectly improving plant nutrition and water absorption by crops (Santos et al., 2014; Silva et al., 2015).

Element contents obtained by pXRF with soil depth

Regarding element contents obtained by pXRF, V did not present a constant variation along the soil profile among land uses (Figure 2). The highest contents were found with eucalyptus, whilst the lowest ones were found cultivated with coffee. The same areas that presented similar V values (e.g., 1-year-old coffee and native forest; 5-year-old coffee and eucalyptus) also presented similar Al_2O_3 and Pb contents with depth. The similar variation of V, Al_2O_3 and Pb contents obtained by pXRF between neighboring areas, regardless whether they are managed or not, may be related to variations in the parent material of these sites. According to COPAM (State Council of Environmental Policy of the Minas Gerais state) Normative Resolution number 166, of June 29th, 2011, the reference values for these elements are: 19.5 mg kg^{-1} for Pb (72 mg kg^{-1} prevention and 180 mg kg^{-1} research), and 129 mg kg^{-1} for V (no values for prevention and research). The values found did not exceed the reference values, although in this study they were obtained by pXRF instead of ICP equipment after semi-total digestion of the reference samples. As Inceptisols are weakly developed soils which have not yet undergone long-term weathering and leaching, slight variations in parent material can be easily indicated by pXRF analysis. Thus, these elements are possibly indicators of small variations in parent material.

In the A horizon, the contents of Sr (Figure 2) were much higher in managed areas than in unmaneged areas. While in the area with eucalyptus the contents did not change appreciably with depth, the B horizon of the area with 1-year-old coffee and the B and C horizons in the 5–year-old coffee area showed Sr decrease with depth. For unmaneged areas, the variation of Sr with depth was minimal compared to managed areas. The increase of Sr content in the A horizon in areas of intensive management may be related to the application of lime in coffee plantations since the occurrence of this element along with Ca has been reported (Myrvang et al., 2017).

P_2O_5 contents remained practically constant with depth in unmanaged areas, while higher contents were observed in A horizon in areas with coffee (Figure 3) due to the contribution of both fertilizers and organic matter. In 5-year-old coffee areas, the P_2O_5 contents were much higher than those of other areas, even at depth. Available P contents (Table 2) showed the same trend, reflecting long-term P-fertilizer application.

Similar behavior to P_2O_5 was observed for CaO, which presented greater contents in areas with coffee than in the other areas. The unmanaged areas and the area with eucalyptus presented similar CaO contents and were practically constant with depth. The contents of K_2O varied more with depth in areas cultivated with coffee. However, this trend does not agree with available K^+ (Table 2). In such areas the K_2O contents are greater, but a decrease in available K^+ occurs with depth, probably due to a greater amount of K-bearing minerals such as muscovite with depth in these soils (Silva et al., 2018). The contents obtained by pXRF are total contents present in the soil samples. As Inceptisols are soils with low degree of weathering-leaching, much of the Al and K reported by pXRF are likely part of the crystalline structure of phyllosilicate minerals common in these soils such as kaolinite ($Al_2Si_2O_5(OH)_4$), muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) and K-feldspars ($KAlSi_3O_8$) (Araujo et al., 2014; Silva et al., 2018).

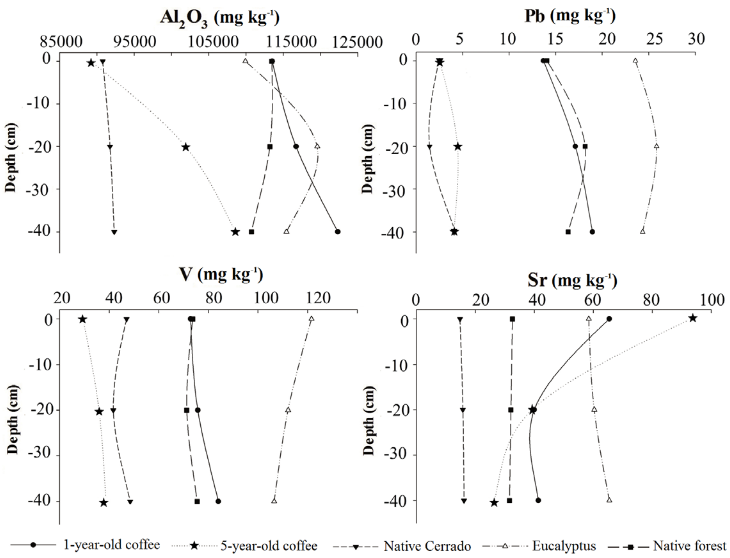

Figure 2: Variation of elements obtained by portable X-ray fluorescence (pXRF) spectrometry in areas with different land uses in Campos Altos, Minas Gerais, Brazil.

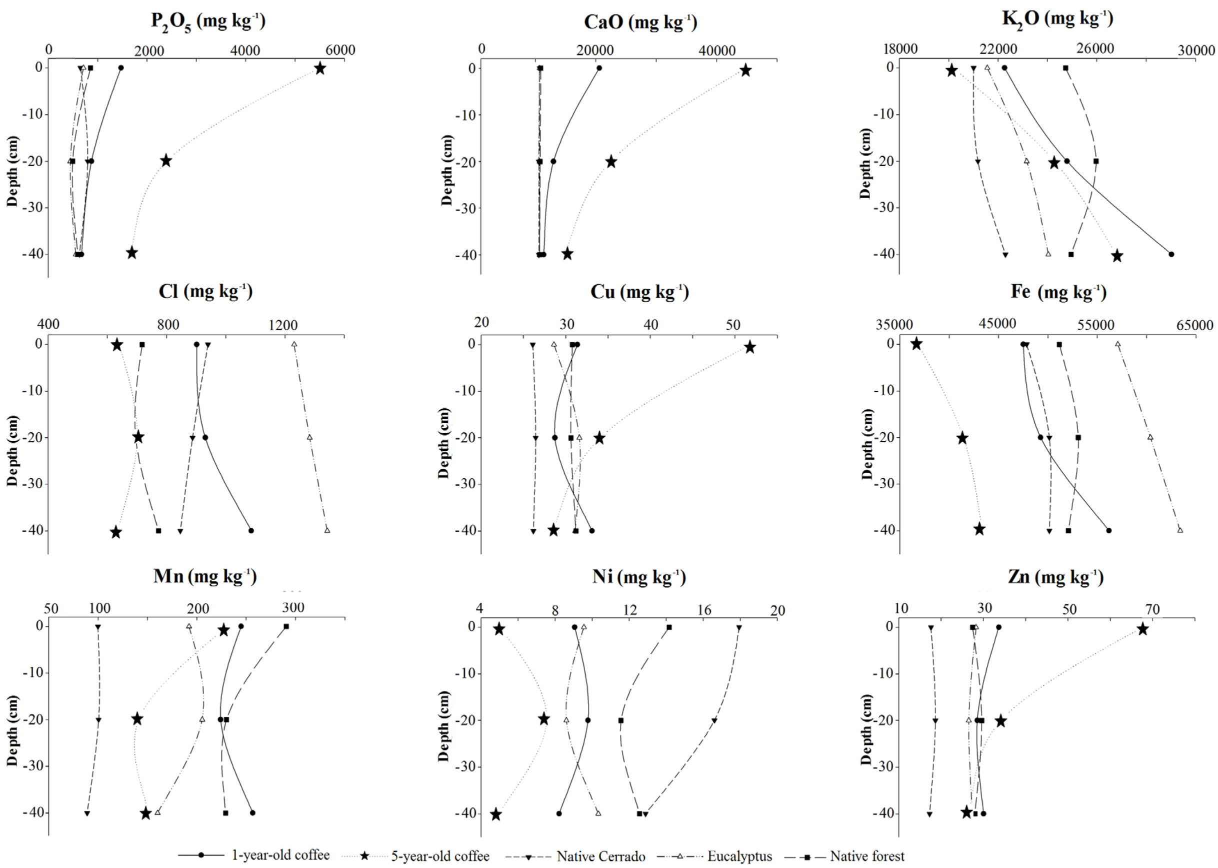

Figure 3: Variation of elements contents obtained by portable X-ray fluorescence (pXRF) spectrometry in areas with different land uses in Campos Altos, Minas Gerais, Brazil.

The micronutrients Zn and Cu (obtained by pXRF), as well as CaO and P_2O_5, also presented higher values in the surface horizon of the 5-year-old coffee area relative to other areas. Fe contents tended to increase with depth in the managed areas, while Ni, Mn, and Cl contents did not present a well-defined pattern of variation according to management or soil depth. Although the available contents of micronutrients in the soil were not the focus of this study, it is also possible to observe higher values of Cu and Zn in the coffee crop areas. Such values result from the application of fertilizers containing micronutrients indicating the possibility of using pXRF for modeling and prediction of micronutrient availability to plants.

Predictions of nutrient content availability and necessity of liming using pXRF data

Without considering management practices, general prediction models (Table 3) presented adequate results with R^2 >0.60 for prediction of exchangeable Ca^{2+} (R^2 = 0.93), V % (R^2 = 0.89), pH (R^2 = 0.84), and NL (R^2 = 0.62) from CaO contents obtained by pXRF and for prediction of available P (R^2 = 0.90) from P_2O_5 contents obtained by pXRF. Although studies have demonstrated the efficiency of pXRF data for predicting soil properties in temperate regions (Aldabaa et al., 2015; Sharma et al., 2014, 2015), regional calibration of models for different soil classes under different land uses and management is preferable. Notably, gypsum was not applied in the study areas as it can influence the CaO readings by pXRF (Weindorf et al., 2013). Therefore, further studies should be carried out in areas amended with gypsum to develop appropriate alternate predictive models. Modeling of exchangeable Ca^{2+}, NL, V %, and pH in managed areas showed high predictive accuracy, but the same did not occur for unmanaged areas, probably due to the CaO contents variability being not directly related to the variations of exchangeable Ca^{2+}, V %, and pH in these areas.

Table 3: Equations to predict values of soil chemical analyses and necessity of liming from portable X-ray fluorescence (pXRF) spectrometer and respective coefficients of determination (R^2) in Campos Altos, Minas Gerais, Brazil.

Predicted variable	pXRF data	Model	Equation	R^2
		Managed	$y = 1.5386\ln(CaO_{pXRF}) - 9.9191$	0.93
Exchangeable Ca^{2+} ($cmol_c\ dm^{-3}$)	CaO	Unmanaged	$y = 0.0003{*}CaO_{pXRF} - 0.0742$	0.36
		General	$y = 1.4999\ln({*}CaO_{pXRF}) - 9.627$	0.93
		Managed	$y = 22.196\ln(CaO_{pXRF}) - 134.76$	0.89
V (%)	CaO	Unmanaged	$y = -0.0023{*}CaO_{pXRF} + 6.403$	0.08
		General	$y = 22.596\ln(CaO_{pXRF}) - 139.77$	0.89
		Managed	$y = 0.7108\ln(CaO_{pXRF}) + 0.148$	0.88
pH	CaO	Unmanaged	$y = -0.0004{*}CaO_{pXRF} + 5.2745$	0.21
		General	$y = 0.6478\ln(CaO_{pXRF}) + 0.6884$	0.84
		Managed	$y = -1.669\ln(CaO_{pXRF}) + 14.315$	0.90
Necessity of liming ($t\ ha^{-1}$)	CaO	Unmanaged	$y = -4E\text{-}06CaO_{pXRF}^2 + 0.0142CaO_{pXRF} - 1.9205$	0.64
		General	$y = -1.944\ln(CaO_{pXRF}) + 17.235$	0.62
		Managed	$y = -1E\text{-}05CaO_{pXRF}^2 + 0.3932CaO_{pXRF} - 291.22$	0.92
Available P ($mg\ dm^{-3}$)	P_2O_5	Unmanaged	$y = 0.0007CaO_{pXRF} + 1.5385$	0.11
		General	$y = -1E\text{-}05CaO_{pXRF}^2 + 0.3593CaO_{pXRF} - 254.44$	0.90
		Managed	$y = 0.004CaO_{pXRF} + 40.839$	0.03
Available K^+ ($mg\ dm^{-3}$)	K_2O	Unmanaged	$y = 0.0019CaO_{pXRF} + 38.032$	0.12
		General	$y = 0.0042CaO_{pXRF} + 16.033$	0.04
		Managed	$y = 1E\text{-}05CaO_{pXRF} - 0.32$	0.04
Exchangeable Al^{3+} ($cmol_c\ dm^{-3}$)	Al_2O_3	Unmanaged	$y = 3E\text{-}05CaO_{pXRF} - 0.3905$	0.35
		General	$y = 6E\text{-}06CaO_{pXRF} + 1.061$	0.01

For prediction of both available K^+ from K_2O and exchangeable Al^{3+} from Al_2O_3, the R^2 values were very low (0.04 and 0.01, respectively). The same nutrients that presented high R^2 in the general models also presented high R^2 values for validation (Figure 4). However, RMSE and ME values for available P (227.78 and -47.74, respectively) and V % (10.83 and -2.34, respectively) were very high (Table 2).

When the models were generated only for unmanaged areas (Table 3), the R^2 values were very low and only NL presented a respectable R^2 of 0.64. However, the validation of NL for unmanaged areas (Figure 5) delivered an R^2 value of 0.09, indicating that the model did not generate satisfactory predictions, although the RMSE and ME values were not high (1.89 and 0.70, respectively).

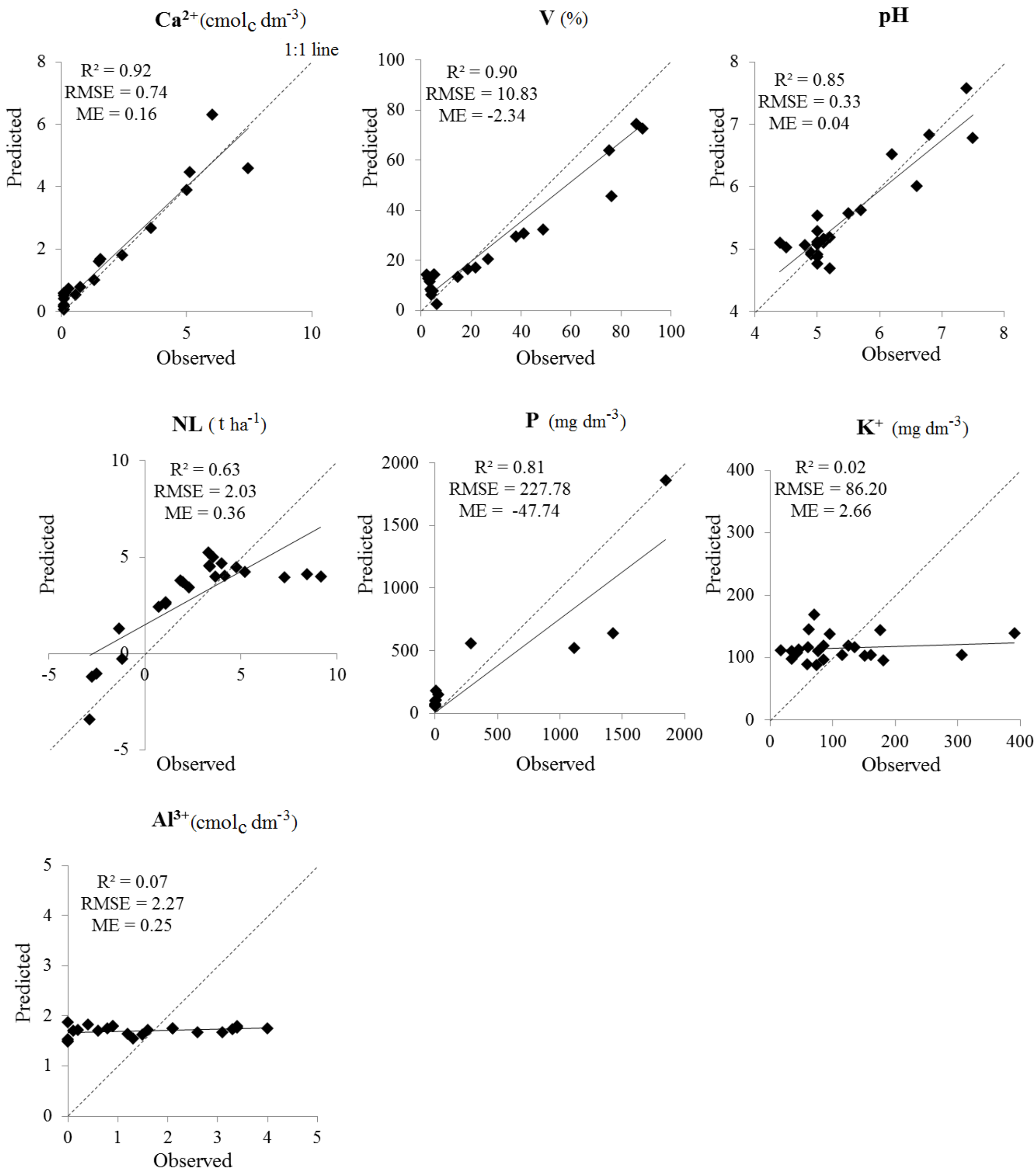

Figure 4: Validation of general models for managed and unmanaged areas in Campos Altos, Minas Gerais, Brazil.

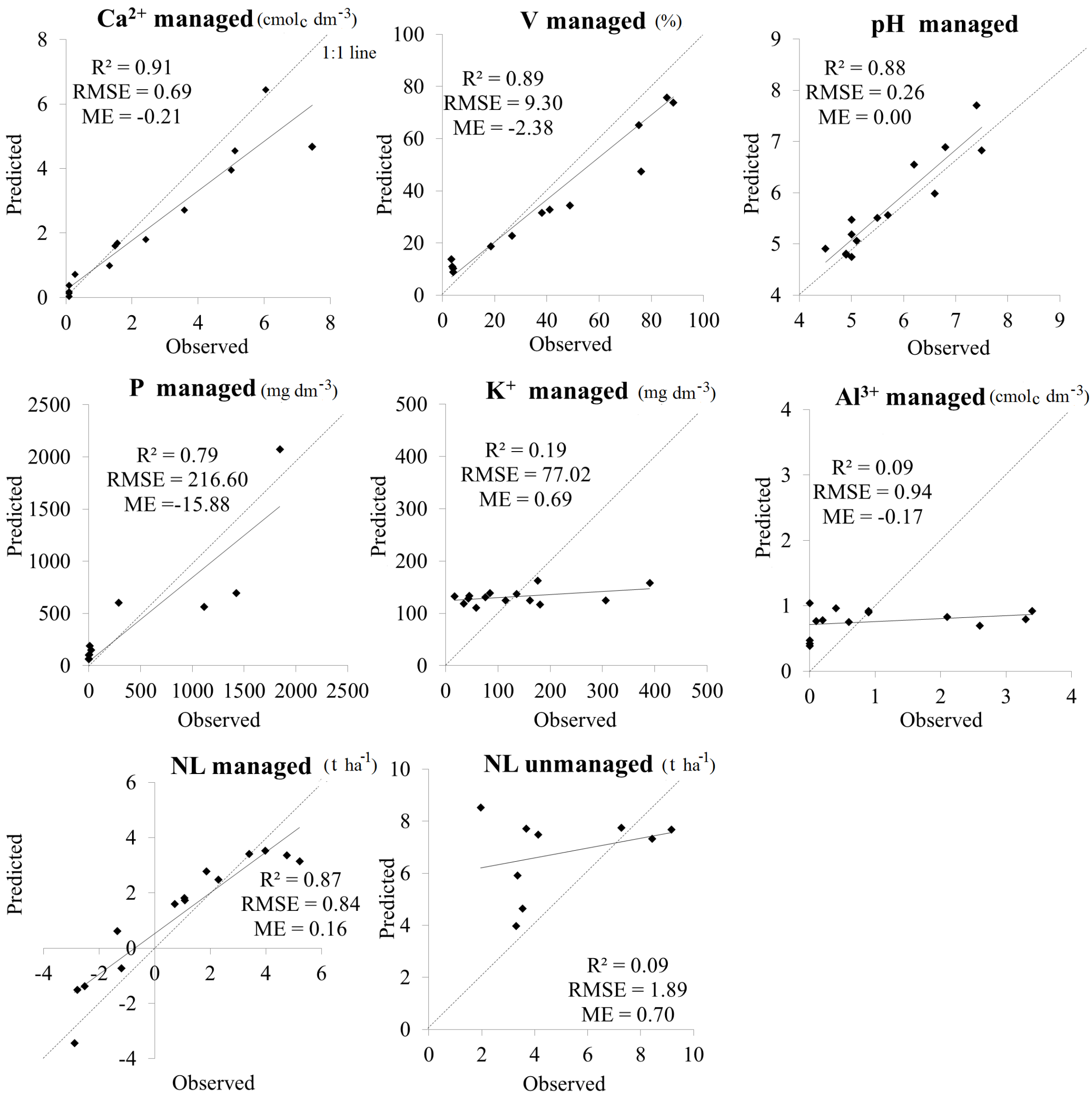

Figure 5: Validation of models for managed areas and necessity of liming model for managed and unmanaged areas in Campos Altos, Minas Gerais, Brazil.

The models for predicting exchangeable Ca^{2+} (R^2 = 0.93) and V % (R^2 = 0.89) in the managed areas outperformed the general models. However, for predicting pH (R^2 = 0.88), NL (R^2 = 0.90), and available P (R^2 = 0.92), both the general models and the models for managed areas presented similar R^2 (Table 3). Furthermore, validation models demonstrated high predictive accuracy for exchangeable Ca^{2+}, V % and pH, confirming the possibility of using pXRF for easily and rapidly estimating such data (Figure 5).

In general models for managed areas, P_2O_5 results generated adequate data for predicting available P. However, the validation values of these models were low, as evidenced by high RMSE and ME values.

General models failed to adequately predict available K^+ and exchangeable Al^{3+} from pXRF K_2O and Al_2O_3. The R^2 values were very low and insignificant, with the highest ones found for the models of unmanaged areas (R^2 = 0.12 for available K^+ and R^2 = 0.35 for exchangeable Al^{3+}) due to their presence in the crystalline structure of minerals, as aforementioned.

The models generated in this work verified relationships between elemental contents obtained by pXRF and soil fertility properties related to these elements (e.g., CaO and exchangeable Ca^{2+}) and absence of this relation for other elements (e.g., Al_2O_3 and exchangeable Al^{3+}; K_2O and available K^+). The adequate models generated in this work may be used as the basis for both further studies on the prediction of soil fertility properties and for easily assessing soil properties in areas under similar environmental conditions to the ones of this study area without performing wet chemistry analyses. More specifically, these models can also be applied in this same area for monitoring soil fertility attributes.

CONCLUSIONS

The assessment of various elemental contents, i.e. V, Al_2O_3, Pb, Sr, Cl, Zn, Cu, Ni, Fe, Mn, CaO, P_2O_5 and K_2O, can be achieved with pXRF, helping identify differences in their concentrations between managed and unmanaged areas (under native vegetation) caused by application of corrective soil amendments and fertilizers in soils. In managed areas cultivated with coffee plants and eucalyptus, it is possible to accurately predict attributes related to soil fertility, such as exchangeable Ca^{2+}, V %, and pH, through the use of simple models with pXRF data as predictor variables. For unmanaged areas, those predictions were not accurate and require further investigation.

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