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X-ray fluorescence and gamma-ray spectrometry combined with multivariate analysis for topographic studies in agricultural soil

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HIGHLIGHTS

- Characterization of topographic sequence of two hillslopes from agricultural soil.
- Employment of EDXRF and gamma-ray spectrometry data combined with PCA.
- The combination of green analytical methodologies with chemometric studies allowed soil differentiation.
- The innovative methodology is promising for direct characterization of agricultural catchments.

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ABSTRACT

Physical and chemical properties of soils play a major role in the evaluation of different geochemical signature, soil quality, discrimination of land use type, soil provenance and soil degradation. The objectives of the present study are the soil elemental characterization and soil differentiation in topographic sequence and depth, using Energy Dispersive X-Ray Fluorescence (EDXRF) as well as gamma-ray spectrometry data combined with Principal Component Analysis (PCA). The study area is an agricultural region of Boa Vista catchment which is located at Guamiranga municipality, Brazil. PCA analysis was performed with four different data sets: spectral data from EDXRF, spectral data from gamma-ray spectrometry, concentration values from EDXRF measurements and concentration values from gamma-ray spectrometry. All PCAs showed similar results, confirmed by hierarchical cluster analysis, allowing the data grouping into top, bottom and riparian zone samples, i.e. the samples were separated due to its landscape position. The two hillslopes present the same behavior independent of the land use history. There are distinctive and characteristic patterns in the analyzed soil. The methodologies presented are promising and could be used to infer significant information about the region to be studied.

1. Introduction

Soil characterization in a catchment is an important factor for agriculture and environmental conservation. Soil is not homogenous and depends on morphological variables for its classification. Physical and chemical properties of soils play a major role in the evaluation of different geochemical signature, soil quality, discrimination of land use type, soil provenance and soil degradation (Franz et al., 2013; Melquiades et al., 2013; Hernández et al., 2007).

Elemental composition of soils and sediments are widely used to establish the origin of heavy metals, evaluate anthropogenic influence and the geochemistry of sediments and soil environments (Walling, 2013; Glasby et al., 2004). Besides the major elements, the trace elements and natural radionuclides are essential to many environmental studies (Navas et al., 2007).

Among the several analytical techniques used for soil analysis, the ones that minimize sample preparation, the time consumed in measurement and could be considered green techniques, are more versatile. It is very common to use non-destructive methodologies

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like gamma-ray spectrometry and X-ray spectrometry for soil characterization (West et al., 2013; Kuang et al., 2012). Furthermore, because of advances in analytical instrumentation, it is now possible to generate large data sets that are difficult to evaluate using simple univariate statistical methods, especially due to their complexity and to their multivariate nature (Luo, 2006). Consequently, multivariate methods have been widely applied to investigate and interpret the large amounts of data generated by current spectrometric methods (Bagur-González et al., 2009; Dragovic and Onjia, 2006). Therefore, synergies obtained by the simultaneous study of multivariate statistics and elemental composition data, allow robust interpretations in geochemical and geological aspects (Gallego et al., 2013; Sielaff and Einas, 2007).

Recently, some researchers used Energy Dispersive X-Ray Fluorescence (EDXRF) allied to multivariate statistical methods of analysis with different objectives, for example precision agriculture, soil quality parameters determination, soil provenance and soil classification (Barsby et al., 2012; Kaniu et al., 2012; Figueroa-Cisterna et al., 2011; Comero et al., 2011; Wastowski et al., 2010; Ye and Wright, 2010; Bramley, 2009; Thomaz and Melquiades, 2009; Herpin et al., 2002; Sena et al., 2002). Also, the use of multivariate analysis, combined with gamma ray spectroscopy is growing (Charro et al., 2013; Fajkovic et al., 2013; Nenadovic et al., 2012; Okeji et al., 2012, Dragovic and Onjia, 2007; Dragovic and Onjia, 2006).

The aim of this study is to describe a methodology to obtain characteristic soil patterns combining spectroscopic techniques with multivariate analysis for direct characterization of agricultural catchments. This will be obtained by (a) the soil elemental characterization and (b) its differentiation in topographic sequence and depth of two hillslopes in a catchment, using EDXRF and gamma-ray spectrometry data combined with PCA analysis.

2. Experimental

2.1. Study area

Boa Vista catchment is located at Guamiranga municipality in the Center South of Paraná state, Brazil (25°09′23″S and 50°54′46″W), Fig. 1. It has an area of ~6 km^2 and tobacco planting is the main culture. The lithology consists of diabase intrusion formed mainly of pyroxene and calcic plagioclase. The forest cover is Araucária Forest and the soil type is an association of Ferralsols and Nitisols with clay texture located at well-drained hillslope sectors and Gleysols restricted to the riparian zone (FAO, 2006).

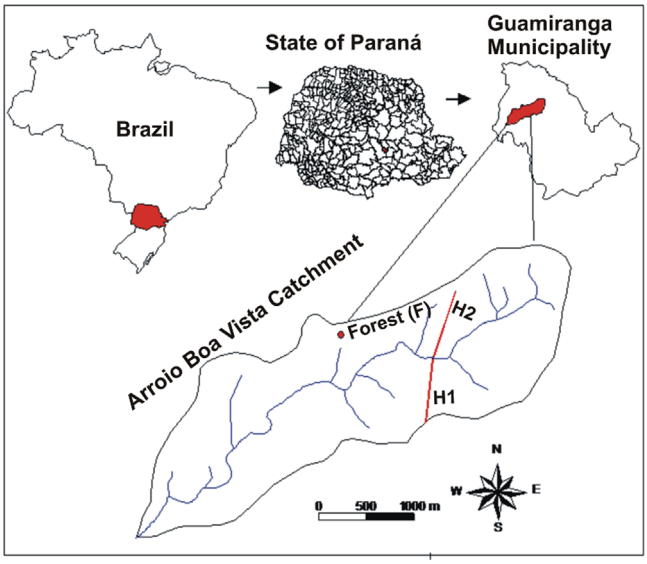

Fig. 1. Arroio Boa Vista Catchment. The two hillslopes studies are indicated as H1 and H2 and the reference forest profile as F.

2.2. Sampling and preparation

Soil samples from the two hillsides of the catchment, were collected. One hillslope was cultivated exclusively with tobacco culture (*Nicotiana tabacum*) for more than 30 years. The other hillslope was occupied with mate (*Ilex paraguariensis*), oat and tobacco crop. In addition, a reference profile at the summit position from a native forest was sampled.

From hillslopes H1 and H2 were collected 8 and 6 samples respectively, each of which was composed of 5 representative subsamples. It was studied over 5 depths: 0–5, 0–10, 10–20, 20–30 and 30–40 cm. Metal rings of 100 cm^3 were used for 0–5 samples collection. The other depths were collected using a conventional auger with 1 m length and with a scoop of 10 cm. Cross contamination was avoided by cleaning the auger and the border of the hole before each collection. Each sample was composed of 5 subsamples collected at the same altitude along the hillslope. Therefore, 70 samples were collected from the two hillslopes. From the forest reference profile, 9 more samples were collected, at the following depths: 0–5, 0–10, 10–20, 20–30, 30–40, 40–50, 50–60, 60–70 and 70–80 cm. The altitude and codes of samples are detailed in Table 1.

Samples were dried at 60 °C for 48 h, ground with a mortar and sieved for grain size smaller than 125 μm for EDXRF and 1 mm for gamma-ray spectrometry.

2.3. Instrumentation

EDXRF analysis was performed using the EDX-700 (Shimadzu Inc.) in two measurement conditions. The first condition was 50 kV, 1 mA, air atmosphere, 100 s and without filters. In this case the spectra present explicitly the scattering peaks. The second condition was used for elements concentration determination. So, a routine containing two ranges of elements were established 15 keV, 184 μA, 200 s and Ti filter for Na–Sc and 50 keV, 250 μA, 100 s and Zr filter for Ti–U range. Three grams of sample in powder form were placed in XRF cells covered with Mylar film. Each cell was measured 3 times. For quantitative evaluation, calibration curves were constructed with the following certified reference materials: NIST-1632, NIST-2702, CRM-008, CRM-029, RTC-408, SEM-1646-a, SRM-2711, NRCC-HISS-1, NRCC-MESS-2, CANMET-SO-2, IAEA-04, IPT-42, IPT-51, IPT-57, IPT-63 and IPT-134.

The radionuclides analysis, K, Th and U, was conducted employing a Na(Tl) scintillation detector (76 mm × 152 mm), model GammaRad5 (Amptek Inc.) with 8 cm of Pb shield. The samples were placed in acrylic recipients containing around 180 g of soil and sealed for 30 days to reach secular equilibrium. The measurement time was 86,400 s. Samples from 0–10 cm to 30–40 cm depths were analyzed. The efficiency calibration was accomplished with the International Atomic Energy Agency (IAEA) RG-Set certified samples, following the calibration procedure indicated by the same agency. The peaks used for the estimates of radionuclides concentrations were 2614 keV of Tl-208 (Th-232 series), 1764 keV of Bi-214 (U-238 series) and 1460 keV of K-40. Since uranium and thorium concentrations were based on the assumption of equilibrium conditions, they were reported as "equivalent uranium" (eU) and "equivalent thorium" (eTh) (IAEA-TECDOC-1363, 2003).

The deviations were determined calculating the standard deviation from the analysis repetition. Detection and quantification limits were determined according to Currie (1968).