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Predicting potentially toxic elements in tropical soils from iron oxides, magnetic susceptibility and diffuse reflectance spectra

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A B S T R A C T

Environmental impacts can be more accurately assessed with the aid of spatial characterization of potentially toxic elements (PTEs). In fact, developing cost-effective, environmentally friendly spatial characterization methods for PTEs can facilitate the expeditious, accurate, detailed diagnosis of soil in large areas. In this study, we used three geomorphic surfaces of Oxisols to assess the ability of chemical and X-ray diffraction analyses of iron oxides, diffuse reflectance spectroscopy (DRS) and magnetic susceptibility (MS) measurements to predict the contents in PTEs (Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb and Zn) and their spatial variability. Magnetic susceptibility and diffuse reflectance spectroscopy allowed well-calibrated prediction models for Ba, Co, Cu, Mn and Ni to be developed, whereas DRS-calibrated methods afforded more accurate prediction of Ba and Mn contents, and magnetic susceptibility-calibrated methods of Co and Ni contents. The correlation between PTEs and free iron contents, and their spatial pattern, testifies to the goodness of the proposed methods for predicting the contents of potentially toxic elements in soils.

1. Introduction

Agriculture is a major source of potentially toxic elements (PTEs) in soil worldwide, but particularly in heavily cultivated areas (Alloway, 1995). Characterizing the spatial distribution of PTEs in farming areas is crucial to assessing the environmental impact of soil contamination (Cattle et al., 2002). Geostatistics at different scales is one commonly used tool for this purpose (Burak et al., 2010; Lin et al., 2014; Nanos and Martín, 2012). In fact, geostatistical maps are useful for identifying contaminated areas to assist decision-making. However, geostatistical analyses of large areas require using also large numbers of samples, which makes laboratory determinations of PTEs contents unfeasible for obvious economic and time-related reasons. A need for cost-effective, environmentally friendly methods for the spatial characterization of element contents therefore exists to facilitate the rapid, accurate diagnosis of large areas at a detailed level.

Prediction models can be highly useful for characterizing spatial variability in continuous variables such as soil attributes, which involves using large numbers of samples with conventional methods (Lagacherie and McBratney, 2007). Because they co-precipitate with, and specifically adsorb, Co, Cr, Cu, Mn, Mo, Ni, Zn and As from solution (Alloway, 1995), iron, aluminium and manganese oxides play a central role in PTEs chemistry and behaviour. PTEs contents can thus be expected to change in parallel with iron oxides, and iron oxides to be effective PTEs predictors for highly weathered soils such as Oxisols — the predominant soil order in tropical regions.

Magnetic susceptibility (MS) is an effective technique for predicting soil attributes influenced by iron oxides such as adsorbed phosphorus (Camargo et al., 2016), and also for assessing metal contamination of soil (Morton-Bermea et al., 2009).

Diffuse reflectance spectroscopy (DRS) provides a rapid, inexpensive, non-destructive prediction tool for the simultaneous characterization of various soil attributes (Camargo et al., 2015; Colombo et al., 2014; Guerrero et al., 2016; Viscarra-Rossel et al., 2010; Viscarra Rossel et al., 2016). Although low concentrations of PTEs preclude observation of their spectral features, PTEs contents can be predicted by examining the relationship between soil attributes such as iron oxides and spectral features (Stenberg et al., 2010; Wu et al., 2007). The

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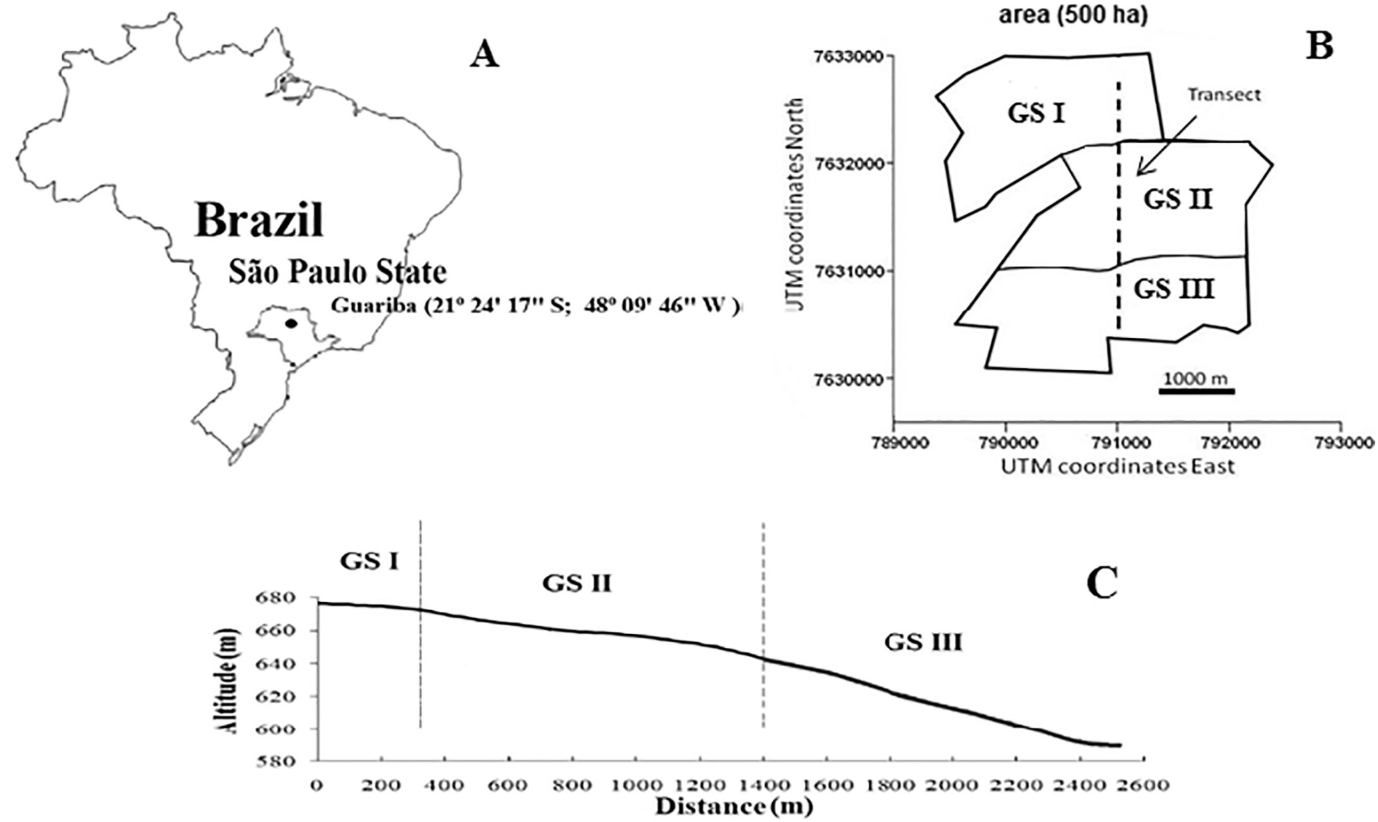

Fig. 1. Study site. A) Location of the city of Guariba (São Paulo, Brazil); B) Sample collection area (500 ha) and transect; and C) Transect profile. GS geomorphic surface. (Adapted from Camargo et al., 2015).

Table 1
Physical and chemical properties of the soil profile in each geomorphic surface (GS) (Adapted from Camargo et al., 2014 and 2016).

Profile	Depth	Horizon	Color	pH		OM	Ca	Mg	K	SB	CEC	V	CS	FS	Silt	Clay	S/C	Fe_2O_3	Al_2O_3
	m		Moisture	H_2O	KCl	g kg^{-1}	mmol$_c$ kg^{-1}					%	g kg^{-1}					g kg^{-1}	
GS I – Typic Hapludox (Soil Survey Staff, 2010)																			
1	0–0.15	A1	5YR 4/6	7.4	6.6	32.84	57.3	7.40	1.41	66.11	78.07	84.69	387	262	58.5	292.5	0.20	48.1	35
	0.90–1.40	Bw2	5YR 4/4	5.0	4.3	11.33	4.5	2.30	0.80	7.60	38.44	19.78	286	284	69.5	360.5	0.19	58.1	55
GS II – Typic Hapludox (Soil Survey Staff, 2010)																			
2	0–0.20	Ap1	5YR 4/5	6.0	4.9	19.37	16.80	5.60	1.72	24.12	51.87	46.50	307	304	74.5	314.5	0.24	59.4	40
	1.20–1.60	Bw2	5YR 4/6	5.1	4.4	10.91	1.90	1.00	3.97	6.87	37.71	18.23	328	228	64.5	379.5	0.17	65.8	55
GS II – Typic Eutrudox (Soil Survey Staff, 2010)																			
3	0–0.15	Ap1	5YR 4/4	6.5	5.7	21.21	24.20	10.70	2.94	37.84	58.08	65.16	367	298	77.5	257.5	0.30	46.9	30
	0.85–1.00	Bw2	5YR 4/5	6.1	5.6	10.68	8.50	2.40	0.80	11.70	28.10	41.65	333	269	59.5	338.5	0.18	50.6	45
GS III – Typic Eutrudox (Soil Survey Staff, 2010)																			
4	0–0.15	Ap1	2.5YR 4/6	6.1	5.1	27.12	32.20	9.30	2.33	43.83	78.09	56.13	312	192	98	398	0.25	82.1	50
	1.00–1.40	Bw2	2.5YR 5/6	6.5	5.9	9.62	18.20	2.90	0.19	21.29	39.51	53.90	264	182	76	478	0.16	96.2	55

OM = Organic matter, SB = Sum of bases, CEC = cation-exchange capacity, BS = Base saturation, CS = coarse sand, FS = fine sand, S/C = silt/clay ratio.

potential of spectroscopic techniques for PTE prediction has been the subject of some recent reviews (Horta et al., 2015; Shi et al., 2014).

The primary aims of this study were (a) to predict the contents in PTEs (Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb and Zn) from iron oxide contents, magnetic susceptibility (MS) and diffuse reflectance spectra (DRS); and (b) to characterize the spatial variability of PTEs in Brazilian Oxisols.

2. Materials and methods

2.1. Study site

The study site spanned an area of 500 ha under a sugarcane plantation located near Guariba, in the North–East of the São Paulo state in Brazil (Fig. 1a). One hundred soil samples (Series 1) were collected from depths of 0–25 cm at 25 m intervals along a transect spanning three different geomorphic surfaces (GSs) (Daniels et al., 1970; (Fig. 1b). Also, another 206 soil samples (Series 2) were collected from subareas each representing 2.5 ha around the transect in order to predict unknown values.

The most evolved geomorphic surface, GS I, is a depositional surface occupying 400 m of the hillside; it has slopes of 0–4% (Fig. 1c) and Typic Hapludox soil (Soil Survey Staff, 2010). The boundary between GS II and GS III is approximately 1400 m from the top of the hillside. GS II has a gentle slope and its soils are Typic Hapludox and Typic Eutrudox (Soil Survey Staff, 2010). The most recent surface, GS III, has a steeper slope (7%) than the other two and Typic Eutrudox soil (Soil