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Cleide Aparecida de Abreu^a, Gustavo Souza Valladares^b, Otávio Antônio de Camargo^a, Gláucia Cecília Gabrielli dos Santos^a & Jorge Paz-Ferreiro^c

^a Instituto Agronômico, Campinas, São Paulo, Brazil

^b Universidade Federal do Ceará, Ceará, Brazil

^c Facultad de Ciencias, A Coruña, Spain

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Total and Available Copper in Some Soil Profile Samples from the State of São Paulo

CLEIDE APARECIDA DE ABREU,¹
GUSTAVO SOUZA VALLADARES,²
OTÁVIO ANTÔNIO DE CAMARGO,¹
GLÁUCIA CECÍLIA GABRIELLI DOS SANTOS,¹
AND JORGE PAZ-FERREIRO³

¹Instituto Agronômico, Campinas, São Paulo, Brazil

²Universidade Federal do Ceará, Ceará, Brazil

³Facultad de Ciencias, A Coruña, Spain

Chemical information obtained through soil analysis requires overall and simultaneous statistical treatment of variables and samples for better data interpretation. Multivariate analysis is the simultaneous analysis of several samples and variables; it provides complementary information not evidenced by the ordinary univariate statistical analysis. Therefore, the objective of the present work was to evaluate the copper (Cu) concentration in several soil profiles and also to evaluate the influence of some soil properties on Cu concentrations, using different extraction methods. Multivariate main component analysis was performed on the dataset. Available and total Cu concentrations were determined in the A and B horizon samples of 28 soil profiles from representative soil unities of the State of São Paulo, Brazil. The extracting solutions used to determine the available Cu forms were diethylenetriaminepentaacetic acid (DTPA), pH 7.3 (CuDTPA); Mehlich 1 (CuM1); 0.1 mol L⁻¹ hydrochloric acid (HCl) (CuHCl); ethylenediaminetetraacetic acid (EDTA) (CuEDTA); and 1.0 mol L⁻¹ ammonium acetate (NH₄OAc) (CuAc). Most soil samples presented medium to high available Cu concentrations, indicating that such soils are sufficient to supply Cu to plants. All correlations between different Cu forms were positive and significant, indicating that a correspondence exists between the extractive capacities of the methods tested. The most significant correlations were CuDTPA × CuEDTA, CuDTPA × CuHCl, and CuEDTA × CuHCl, at $r = 0.98$. The soil properties that most influenced Cu concentrations were iron oxides ($r = 0.81$), magnesium (Mg) ($r = 0.69$), silt ($r = 0.64$), and pH ($r = 0.63$). The main component analysis revealed an association among the following soil properties: silt, pH, Mg, Cation Exchange Capacity (CEC), silicon (Si), aluminum (Al) and iron (Fe) oxides, total copper (CuT), and CuM1, which presented values greater than 0.64 in F1. In F2, the association among clay, fine sand, and aluminum oxide contents was evidenced. It was concluded that most soil samples presented medium to high Cu concentrations; similar forms of Cu were extracted by DTPA, EDTA, and HCl; and the main component analysis was efficient for grouping the soils from the same parent material.

Keywords Chemical extracting solutions, copper in soils, multivariate analysis

Address correspondence to Cleide Aparecida de Abreu, Instituto Agronômico, Caixa Postal, 13012-979, Campinas, São Paulo, Brazil. E-mail: cleide@iac.sp.gov.br

Introduction

The natural occurrence of copper (Cu) in soils depends mainly on the parent material from which the soil originated, its formation processes, and the composition and proportion of its solid-phase components. Soils originating from basic rocks, naturally richer in metals, have greater Cu contents when compared with those developed over granites, gneisses, sandstones, and siltstones (Tiller 1989; Oliveira 1996). In igneous rocks, such as granite and basalt, total Cu contents varied from 10 to 100 mg kg⁻¹; however, in sedimentary rocks such as limestone, sandstone, and shale, total Cu can be smaller (Krauskopf 1972).

In addition, plant availability of metals appears to be greater in soils from a basaltic origin compared with those that were developed from gneiss and sandstone + sediments from the Tertiary (Luchese and Behnen 1987; Oliveira 1996). In addition to the nature of the parent material, other factors such as content and composition of the soil clay fraction, organic-matter content, and physicochemical conditions may influence Cu concentration (Oliveira 1996). In a study conducted in the State of Paraná involving 22 soil profiles developed from different parent materials, there was a positive correlation between total Cu and clay ($r = 0.70$, $P < 0.01$) and Fe₂O₃ ($r = 0.58$, $P < 0.01$) contents; however, correlations among Cu and organic-matter contents and pH were not significant (Santos Filho and Rocha 1982). Higher total Cu content was obtained in soils that originated from basalt and coincided with the greatest content of iron (Fe) and manganese (Mn) oxides, with which Cu forms strong association (Valadares 1975; Santos Filho and Rocha 1982; Pereira et al. 2001).

Copper availability can be evaluated with the use of chemical extractants. These can be classified as saline, acid, chelating, oxidizing/reducing, or mixed solutions. Caridad Cancela et al. (2001), evaluating the Cu concentration in 61 soil samples from the State of São Paulo, found significant correlations between the concentration Cu in corn plants and soil Cu concentration. These correlations were 0.60, 0.73, 0.72, and 0.36 ($P < 0.01$) using the methods Mehlich 1 (Mehlich 1953), Mehlich 3 (Mehlich 1984), diethylenetriaminepentaacetic acid (DTPA) (Lindsay and Norvell 1978), and ammonium bicarbonate (AB)–DTPA (Soltanpour and Schwab 1977), respectively. In contrast, Abreu, Lopes, and Santos (2007), reviewing methods to analyze Cu available in soils from Brazil, found no significant correlations among Cu concentration in several plants and Cu concentration in soil by extractants: hydrochloric acid (HCl) (Council on Soil Plant Test Analysis 1980), Mehlich 1 (Mehlich 1953), Mehlich 3 (Mehlich 1984), DTPA (Lindsay and Norvell 1978), and ethylenediaminetetraacetic acid (EDTA). Consequently, there are three official methods in Brazil to assess Cu availability, namely, DTPA (pH 7.3), used in the State of São Paulo; HCL, used in Rio Grande do Sul and Santa Catarina; and Mehlich 1, adopted in several other states, such as Minas Gerais, Espírito Santo, and Goiás.

Principal component analysis (PCA) is an important tool to assess the influence of soil properties on the availability of Cu as determined by a given extractant. Multivariate statistical methods consider samples and variables as a whole, allowing the extraction of supplementary information that univariate analysis cannot provide (Moura et al. 2006). Principal component analysis is a multivariate analysis technique based on linear combinations of the original variables. The first principal components explain most of total variance contained in the entire data set and can be used to represent it (Moura et al. 2006). The method provides suitable tools to identify the most important variables in the principal components space (Moita Neto and Moita 1998). Several studies have used PCA analysis to identify heavy-metal sources in soils and to discriminate between natural and anthropogenic contributions (Facchinelli, Sacchi, and Mallen 2001; Fadigas et al. 2002; Boruvka, Vacek, and Jehlicka 2005; Moura et al. 2006).

The objective of this work was to quantify Cu in several soil profiles from the State of São Paulo and to evaluate the influence of some soil properties on Cu extracted by different methods using PCA.

Material and Methods

Fifty-seven soil samples from both surface and subsurface horizons from 28 profiles representative of soils from the State of São Paulo (Valadares 1972) were assayed for total and available Cu. Among those, eight profiles originated from basic rocks (two Litholic Neosols, two Red Nitols, and four Red Ferric Latosols); eight profiles originated from modern sediments (six Red Latosols and two Red-Yellow Argisols); four profiles originated from sediments of Bauru sandstones (Red-Yellow Argisol); two profiles originated from alluvial and colluvial sediments (Gleisols); and six profiles originated from sediments of the Botucatu sandstones (two Red-Yellow Latosols, two Dark Red Latosols, and two Regolith Neosols).

All samples were assayed for pH, carbon (C), calcium (Ca), Mg, potassium (K), CEC, SiO₂, Al₂O₃, Fe₂O₃, Ki (weathering index), clay, silt, fine sand, and sand according to Camargo et al. (1986).

Soil samples from surface and/or subsurface layers were assayed for Cu using the methods described in Table 1.

Results were submitted to Pearson's correlation analysis, and ratios were determined between Cu concentration (CuT, CuDTPA, CuM1, CuHCl, CuEDTA, and CuAc) and a number of soil properties (clay, silt, fine sand, coarse sand, pH, Ca, Mg, K, CEC, SiO₂, Al₂O₃, Fe₂O₃, C, and Ki).

Comparisons between extractable levels by the various methods utilized in this study were made through linear regression analysis ($Y = b_0 + b_1X$) (Miller and Miller 1993). The null hypothesis was that the slope coefficient (b_1) was not different from one (1) and the intercept coefficient or intercept (b_0) was not different from zero (0). Both hypotheses were tested using 95% confidence intervals. Analyses of variance (F tests) were carried out.

The data were also submitted to PCA considering the following soil properties: clay, silt, fine sand, coarse sand, pH, Ca, Mg, K, CEC, iron oxide, aluminum oxide, Si, C, Ki, CuT, CuDTPA, CuM1, CuHCl, CuEDTA, and CuAc. The data were standardized for mean 0 and variance 1, and analyses were performed in the data matrix.

Results and Discussion

Among the methods employed to evaluate soil Cu content, total Cu (CuT) had the broadest amplitude of variation, followed by extractable Cu (CuEDTA, CuHCl, CuDTPA, and CuM1), which exhibited similar amplitudes (Table 2). This can be attributed to a number of factors, such as the interaction between Cu and solid-phase soil components, the chemical nature of the extractors, and the complexing order of the elements with chelating agents. Only a small percentage of total soil Cu is in the "available pool" that is represented by the water-soluble, exchangeable, and organic-matter-linked forms (Abreu, Abreu, and Berton 2002).

Considering only total Cu contents in the surface layer of the 28 soil profiles, 64.2% of the samples showed Cu concentrations (CuT) within background concentration (35 mg kg⁻¹), 7.2% were between quality reference (35 mg kg⁻¹) and prevention values (65 mg kg⁻¹), and 28.6% were within the prevention range (CETESB 2005). All soil samples with Cu contents in the prevention range came from soils derived from basic rocks.

Table 1
Methods used to extract Cu from soils

Method	Description	Reference	Depth analyzed
CuT	Five g air-dried soil + 6 ml concentrated HF + 1 ml concentrated HClO ₄ + 5 ml 5 mol L ⁻¹ HCl; sand bath at 200 °C	Valadares (1972)	Surface and Subsurface
CuDTPA	Ten cm ³ air-dried soil + 20 ml of the extracting solution (0.005M diethylenetriaminepentaacetic acid + 0.1 mol L ⁻¹ triethanolamine + 0.01 mol L ⁻¹ calcium chloride at pH 7.3); agitation for 2 h	Lindsay and Norvell (1978)	Surface and Subsurface
CuM1 (Mehlich-1)	Five cm ³ air-dried soil + 20 ml of the extracting solution (0.05 mol L ⁻¹ HCl + 0.0125 mol L ⁻¹ H ₂ SO ₄); agitation for 15 min	Mehlich (1953)	Surface and Subsurface
CuHCl	Five cm ³ air-dried soil + 20 ml 0.1 mol L ⁻¹ HCl solution; agitation for 30 min	Wear and Sommer (1948)	Surface only
CuEDTA	Five cm ³ air-dried soil + 50 ml 0.05 mol L ⁻¹ ethylenediamineacetic acid solution; agitation for 30 min	Viro (1955)	Surface only
CuAc	Five cm ³ air-dried soil + 50 ml 0.1 mol L ⁻¹ NH ₄ OAc solution; agitation for 30 min	Adams (1965)	Surface only

Note. Cu in the extracts was determined by atomic absorption spectrometry.

Although chemical extraction methods and the criteria for partitioning Cu analysis results in different content classes, plant-available Cu ranges will vary from region to region. Interpretation tables for soil analysis results are already available, as defined by official institutions, such as the States of Rio Grande do Sul and Santa Catarina, Paraná, Espírito Santo, São Paulo, Minas Gerais, and the Cerrado region (Abreu, Lopes, and Santos 2007).

For the State of São Paulo, the following interpretation values are available using DTPA (pH 7.3, in mg dm⁻³): low (0–0.2), medium (0.3–0.8), high (0.9–1.5), and very high (1.6–15) (Abreu et al. 2005). Based on these values, 17.9% of the samples from the A horizon had low values, 35.7% of the values were considered medium, 11% were considered high, and 35.7% were considered very high. In the latter class, the soil samples had their origins in basic rocks (Table 2). A predominance of soils with high Cu contents as extracted by DTPA were found in soils samples from the Jundiá region, originated from schists, and in soil samples from the State of Rio de Janeiro (Galvão 2002).

In soils from the Cerrado region, the Mehlich 1 solution was adopted for Cu extraction, with the following interpretation values (in mg dm⁻³): low (0–0.4), medium (0.1–0.8), high (>0.8) (Galvão 2002). Among the 28 samples from the A horizon, 32.1% had low values, 35.8% of the values were considered medium, and 32.1% were considered high; in the latter class most soil samples had their origins in basic rocks (Table 2).

Table 2

Means, standard deviations (SD), minimum, and maximum of Cu contents (mg kg⁻¹) extracted from different soil profiles from the State of São Paulo using several chemical extractors

Profile/horizon	Extractants					
	CuT	CuAc	CuDTPA	CuM1	CuHCl	CuEDTA
Soils originated from basic rocks						
Litholic Neosols						
P1 / A	156.90	0.30	3.60	0.80	5.20	11.00
P1 / AC I	109.10		2.90	14.30		
P2 / A	251.70	0.80	11.40	14.90	21.50	35.00
Red Nitosols						
P3 / A1.1	340.60	0.50	25.80	12.10	34.00	72.00
P3 / B23	358.60		4.00	21.90		
P4 / Ap	161.20	0.50	4.10	2.50	5.00	13.00
P4 / B22	173.00		1.10	4.50		
Red Ferric Latosols						
P5 / A1	219.70	0.50	7.00	6.10	10.00	15.00
P5 / B22'	213.70		1.40	6.70		
P6 / A1	203.90	0.50	6.80	5.90	9.00	11.50
P6 / B22	203.50		2.70	7.70		
P7 / Ap'	95.40	0.30	3.80	2.60	4.00	4.60
P7 / B22	94.90		1.30	2.50		
P8 / A1	88.10	0.50	3.70	2.60	4.40	4.80
P8 / B22'	94.30		1.60	2.90		
Soils originated from modern sediments						
Red Latosols						
P9 / A1	36.80	0.30	1.20	0.70	2.00	1.80
P9 / B22	38.20		0.20	0.50		
P10 / A1	17.90	0.30	0.50	0.60	1.60	1.40
P10 / B21	20.10		0.20	0.40		
P11 / A11	20.60	0.30	0.60	0.50	1.60	1.20
P11 / B22	20.30		0.10	0.40		
P12 / A11	16.90	0.30	0.70	0.40	1.30	1.20
P12 / B22	16.00		0.10	0.30		
P13 / Ap	11.20	0.30	0.30	0.20	1.00	0.60
P13 / B2	14.00		0.10	0.40		
P14 / A11	6.00	0.30	0.10	0.40	1.00	0.30
P14 / B22	7.60		0.10	0.30		
Red-Yellow Argisols						
P15 / A1	20.30	0.30	2.70	2.70	4.20	3.70
P15 / B22	20.70		0.20	0.90		
P16 / Ap	52.50	0.30	7.00	7.10	11.00	13.00
P16 / B22	45.30		1.00	2.20		
P16 / B3	45.90		0.40	1.40		

(Continued)

Table 2
(Continued)

Profile/horizon	Extractants					
	CuT	CuAc	CuDTPA	CuM1	CuHCl	CuEDTA
Soils originated from sediments of the Bauru sandstones						
Red-Yellow Argisols						
P17 / Ap	4.90	0.30	0.20	0.50	1.20	0.30
P17 / B22	7.30		0.30	0.40		
P18 / A1	6.40	0.30	0.30	0.40	1.20	0.30
P18 / B22	9.50		0.10	0.60		
P19 / Ap	4.10	0.30	0.50	0.30	1.20	0.50
P19 / B21	6.60		0.10	0.20		
P20 / A11	6.20	0.30	0.30	0.20	1.20	0.90
P20 / E3	7.30		0.20	0.20		0.30
Soils originated from alluvial and colluvial sediments						
Gleisols						
P21 / Ap	28.80	0.30	1.00	0.60	2.60	4.30
P21 / C2g	34.20		1.10	1.00		
P22 / A1	26.10	0.30	2.10	2.20	5.20	4.80
P22 / C1g	26.60		1.00	1.50		
P22 / C3g	33.20		0.90	1.00		
Soils originated from sediments of the Botucatu sandstones						
Red-Yellow Latosols						
P23 / A1	11.00	0.30	0.50	0.70	1.50	0.70
P23 / B22	11.90		0.10	0.40		
P24 / A1	2.80	0.30	0.10	0.30	0.80	0.10
P24 / B22	3.80		0.10	0.30		
Dark Red Latosols						
P25 / Ap	8.80	0.30	0.50	0.60	1.00	0.70
P25 / B22	15.10		0.20	0.40		
P26 / A1	10.80	0.30	0.40	0.60	1.10	0.70
P26 / B22	16.30		0.20	0.40		
Regolith Neosols						
P27 / Ap	1.80	0.30	0.10	0.20	0.30	0.20
P27 / A14	1.00		0.10	0.20		
P28 / A11	1.90	0.30	0.10	0.40	0.30	0.30
P28 / C3	2.50		0.30	0.60		
Mean	60.8	0.4	1.9	2.5	4.8	7.3
Minimum	1.0	0.3	0.1	0.2	0.3	0.1
Maximum	358.6	0.8	25.8	21.9	34.0	72.0
SD	86.7	0.1	3.9	4.3	7.3	14.7
N	57	28	57	57	28	28

The States of Santa Catarina and Rio Grande do Sul chose to establish Cu interpretation limits using HCl (in mg dm⁻³) as follows: low (<0.15), medium (0.15–0.4), and high (>0.4) (CFS-RSSC 1994). Of the samples, 92.9% had high contents, while 7.1% had medium contents. None of the soil samples from the surface layer had low Cu contents.

Table 3

Confidence interval of slope coefficients and intercept values for the linear regression estimated between Cu contents extracted by DTPA (X) and those extracted by strong acid (CuT), Mehlich 1 (CuM1), HCl (CuHCl), EDTA (CuEDTA), and ammonium acetate (CuAc) (Y) in different soil profiles from the State of São Paulo (n = 57)

Y	X	Angular coefficient			Linear coefficient			R ²	F
		Minimum	Mean	Maximum	Minimum	Mean	Maximum		
CuT	CuDTPA	12.07	16.17	20.27	12.61	30.28	47.94	0.53*	62.5*
CuM1	CuDTPA	0.44	0.67	0.90	0.22	1.21	2.21	0.38*	34.0*
CuHCl	CuDTPA	1.26	1.36	1.46	0.07	0.65	1.24	0.96*	823.7*
CuEDTA ^a	CuDTPA	2.55	2.74	2.94	-2.26	-1.08	0.10	0.97*	824.3*
CuAc ^a	CuDTPA	0.007	0.014	0.021	0.27	0.31	0.35	0.40*	17.6*

* $P < 0.05$.

^an = 28.

Comparison of the distribution of extractable Cu levels by the three analytical methods described previously into availability classes suggests similar distribution when DTPA and Mehlich 1 were used but dramatically different results with HCl extraction, which resulted in the majority of samples (92.9%) aggregated in the high content class. These results indicate that most soils in the State of São Paulo would contain sufficient levels of available Cu to supply plant needs.

The slope coefficient of regression equation estimated (Table 3) gives an idea of the Cu amount extracted by each method. The Cu amounts extracted by the various methods (CuT, CuHCl, CuM1, CuEDTA, and CuAc) in relation to DTPA were as follows: CuT, CuEDTA, and CuHCl had slope coefficients greater than 1.0, indicating greater extraction; and CuM1 and CuAc had slope coefficients smaller than 1.0, showing lower extraction (Table 3).

The diluted strong acid solutions remove metals from the soil solution, exchange sites, and part of those that are complexed or adsorbed; chelating solutions extract labile metals without dissolving nonlabile forms; while saline solutions preferentially extract metals from the soil ion exchange sites (Abreu, Lopes, and Santos 2007). Therefore, the greater extraction provided by HCl was probably due to solubilization of part of the Cu adsorbed to oxides.

The greater Cu extraction by EDTA cannot be explained by the stability constant of complex formation. The formation constant (log k) for CuEDTA is 18.8, while for CuDTPA it is 21.5, with higher complex formation power (Tandy et al. 2004). This is probably due to the pH value of the DTPA extracting solution buffered at pH 7.3, which may have made extraction more difficult. Because the EDTA solution is not buffered and is more acidic than the DTPA solution, greater extraction was facilitated. Further, the results from this study are in agreement with those by Shuman (1991), who reported that no Cu was found in exchangeable form.

All correlations between different Cu forms were positive and significant, indicating that a correspondence exists between the extractive capacities of the methods tested (Table 4). The greatest significant correlations were CuDTPA × CuEDTA, CuDTPA × CuHCl, and CuEDTA × CuHCl, at $r = 0.98$ (Table 4). The high correlations among the DTPA, EDTA, and HCl extractants indicate similarities in the Cu forms they extract. Among all forms, CuAc, which represents exchangeable Cu, had the lowest correlation with extraction by the other methods, ranging from $r = 0.64$ (CuDTPA

Table 4

Correlation coefficients between Cu extracted by different methods, considering all soil samples ($n = 57$) and some properties of soils from the State of São Paulo

	CuT	CuDTPA	CuM1	CuHCl	CuEDTA ^a	CuAc ^a
Clay	0.33*	0.09	0.20	0.18	0.13	0.21
Silt	0.64*	0.54*	0.49*	0.69*	0.68*	0.55*
Sandy fine	-0.38*	-0.21	-0.26	-0.29	-0.25	-0.23
Sandy coarse	-0.49*	-0.27*	-0.34*	-0.37	-0.35	-0.42*
pH	0.63*	0.38*	0.56*	0.46*	0.46*	0.52*
C	0.11	0.27*	0.02	0.18	0.20	0.01
Ca	0.49*	0.44*	0.57*	0.57*	0.62*	0.37
Mg	0.69*	0.64*	0.58*	0.69*	0.70*	0.65*
K	0.36*	0.36*	0.30*	0.36	0.36	0.43*
CEC	0.27*	0.28*	0.25	0.25	0.28	0.12
SiO ₂	0.33*	0.19	0.34*	0.32	0.28	0.21
Al ₂ O ₃	0.34*	0.14	0.22	0.26	0.21	0.27
Fe ₂ O ₃	0.81*	0.46*	0.55*	0.52*	0.51*	0.68*
Ki	0.04	0.10	0.25	0.16	0.18	-0.01
CuT		0.73*	0.84*	0.88*	0.87*	0.80*
CuDTPA			0.61*	0.98*	0.98*	0.64*
CuM1				0.93*	0.85*	0.83*
CuHCl					0.98*	0.70*
CuEDTA						0.64*

* $P < 0.05$.

^a $n = 28$.

and CuEDTA) to $r = 0.83$ (CuM1). The low correlation observed between CuDTPA and CuM1 (Table 4) is worth noting, since the minimum, maximum, and medium values for those extractors were very close (Table 3).

The soil properties with the greatest influence on soil Cu contents extracted by the various methods were iron oxide content followed by Mg, silt content, and pH (Table 4). With the exception of Mg, the influence of those properties on Cu content extracted from the soil has been previously reported (Luchese and Behnen 1987). The relationship between Cu and organic C has been extensively described in the literature (Shuman 1991); however, only CuDTPA had a significant correlation with C (Table 4).

Total Cu content (CuT) was more influenced by the oxide ($r = 0.81$), magnesium ($r = 0.69$), and silt content ($r = 0.64$). Furthermore, there was a close relationship between what are considered to be bioavailable Cu forms (CuDTPA, CuM1, CuHCl, CuEDTA, and CuAc) and pH values, magnesium, silt, and iron oxide content (Table 4). Hence, CuDTPA extractable levels were best correlated with magnesium ($r = 0.64$) and silt content ($r = 0.54$), whereas CuM1 extractable levels were correlated with magnesium ($r = 0.58$), calcium ($r = 0.57$), and pH ($r = 0.56$). CuHCl and CuEDTA extractable levels were best correlated with silt content ($r = 0.69$ and $r = 0.68$, respectively), and CuAc extractable levels were correlated with Fe₂O₃ ($r = 0.68$).

The PCA analysis revealed that the first two principal components (represented by F1 and F2) explained 62.7% of variation (Table 5). According to Boruvka, Vacek, and

Table 5
Eigenvalue and variance (%) by principal components analysis

Parameter	F1	F2	F3
Eigenvalue	7.372	3.282	2.153
Variance (%)	43.366	19.306	12.666
Acumulated (%)	43.366	62.672	75.338

Jehlicka (2005) and Facchinelli, Sacchi, and Mallen (2001), only the first three principal components can be taken into consideration. In the present work, these components explained 75.3% of total variation.

Preliminary results showed associations between the following soil properties: silt content, pH, Mg, CEC, SiO₂, Al₂O₃, Fe₂O₃, CuT, CuDTPA, and CuM1, with values higher than 0.61 (Table 6) in F1. Fine sand and coarse sand contents indicated a negative association in F1. In F2, an association was demonstrated among the contents of clay, aluminum oxide, Ki, and calcium. Ambiguity was observed in F1 and F3 for clay and aluminum oxide, as well as in F1 and F2 for CEC. Organic C had greater values in the third-order factor (Table 6).

Based on the clusters of soil samples, the values for F1 and F2 in the third quadrant were negative, and soil samples from the Bauru and Botucatu sandstones are positioned in that quadrant, with a clear separation between both parent materials (Figure 1). These soil samples are characterized by sandy or loamy texture with predominance of a fine sand fraction, lower organic C contents, pH values ranging from acidic to neutral (Bauru

Table 6
Factors calculated by principal components analysis for the samples studied (n = 57) based on content matrices for the elements under study

Parameter	F1	F2	F3
Clay	0.636	0.691	-0.017
Silt	0.851	0.066	0.004
Sand fine	-0.684	-0.594	-0.018
Sand coarse	-0.724	-0.303	0.039
pH	0.711	-0.367	-0.169
C	0.475	0.172	0.637
Ca	0.573	-0.663	0.188
Mg	0.684	-0.311	-0.179
K	0.472	-0.575	0.267
CEC	0.681	-0.033	0.663
SiO ₂	0.756	0.307	0.412
Al ₂ O ₃	0.681	0.680	0.007
Fe ₂ O ₃	0.712	0.024	-0.507
Ki	0.177	-0.674	0.544
CuT	0.795	-0.240	-0.471
Cu DTPA	0.612	-0.349	-0.266
Cu M1	0.676	-0.362	-0.352

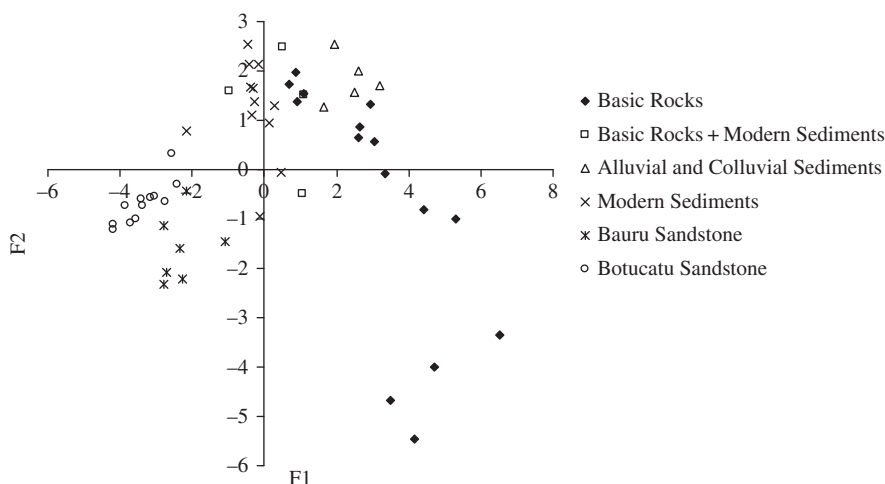


Figure 1. Clusters in the principal components analysis of soil samples studied in the State of São Paulo ($n = 58$).

Sandstone) and from strongly acidic to acidic (Botucatu Sandstone), low Fe_2O_3 contents, and low Zn contents when compared with soils developed from the other parent materials.

The soil samples developed from modern sediments were clearly clustered and were mainly positioned in the second quadrant, with negative F1 and positive F2 values in most samples (Figure 1). These samples had textures between loamy and clayey, pH ranging from 4.4 to 5.5, low and medium Fe_2O_3 contents, and medium to high SiO_2 and Cu contents.

Samples from alluvial sediments were positioned in the first quadrant (Figure 1), with good clustering. These samples have a clayey texture, pH between 4.4 and 5.5, low and medium Fe_2O_3 contents, and high contents of Cu forms, but lower than the values observed in basalt soils.

Of the 15 samples from basic rocks, 10 fell within the first quadrant, with a more clayey texture and heavily weathered soils, while 5 fell in the fourth quadrant with a loamy texture and incipiently weathered soils (Figure 1). The first quadrant samples were partially clustered with soil samples from alluvial sediments, because of similarities in the properties studied. As to other properties, these soils showed the highest pH values (above 5.5), as well as high Fe_2O_3 and SiO_2 contents. The greatest contents of Cu forms were observed in these soils.

Soils originated from basic rocks with influence from sediments had the poorest clustering between one another. One sample was located in the fourth quadrant, clustered with soil samples from basic rocks with similar properties. Two other samples fell into the second quadrant, near samples from modern sediments. A fourth sample was clustered with other basalt soil samples, with properties similar to those soils. Such clustering makes sense because one half of the samples were closer to basalts while the other half were close to modern sediments, and all showed similarities with both of these groups.

Conclusions

Extractable Cu levels in the majority of soils representative of the State of São Paulo, Brazil, that were assayed by a multitude of availability indices were classified in the

sufficiency range. The high correlations among DTPA, EDTA, and HCl extractors indicate similarities in the Cu forms they extract. Principal component analysis proved effective in clustering soils from the same parent material and indicated that the Cu forms analyzed are positively influenced by Fe_2O_3 , pH, silt, Mg content, CEC, and Si.

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