

Division - Soil Processes and Properties | Commission - Soil Chemistry

Geochemical Signature of Amazon Tropical Rainforest Soils

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ABSTRACT: Evaluating soil geochemical diversity in the Amazon Basin has been a challenge largely because most study sites have been at the edge of the basin and it is difficult to get samples in such a region. Here we show that even among the most weathered soils, physicochemical soil properties express lithology. Our results are based on topsoil samples collected from different locations in minimally disturbed areas in the state of Amazonas, Brazil. Soil properties were measured using methods which are suitable for highly developed soils. The Chemical Index Alteration and Weathering Index of Parker was calculated based on the content of metal(loid)s in soils determined by X-ray fluorescence. Descriptive statistics, Pearson correlation, and Principal Component Analysis (PCA) were performed on data. In general, Amazon rainforest soils are more deeply weathered than soils in other Brazilian biomes and tropical rainforests in Asia and Africa. The high coefficient of variation of metal(loid) contents express pedogenesis and parent material diversity. Correlation analysis indicated that the tri-pentavalent elements are strongly associated with Al and Fe contents in the topsoil. In contrast, mono-divalent elements are correlated with sand and silt fractions. According to PCA, five soil groups with defined geochemical compositions and degrees of weathering could be identified: i) acidic sandy podzolized soils; ii) acidic loamy ferralitic soils with the highest content of tri-pentavalent ions; iii) acidic clayey kaolinitic soils with low metal(loid) contents; iv) acidic loamy kaolinitic soils with low metal(loid) contents; and v) silty neutral 2:1 clay soils. This study is the first effort to analyze the geochemical diversity in Amazon rainforest soils. These data are extremely valuable in determining the geochemical background for these soil types and this region. Geochemical variability can be predicted to some extent by lithology and pedogenesis, which can be applied to define the sampling required in future studies.

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INTRODUCTION

Rainforests are very fragile habitats, generally growing on acidic and nutrient-depleted soils in which natural fertility is maintained by biological cycling and mineral weathering. The Amazon tropical rainforest occupies parts of nine countries (Bolivia, Brazil, Colombia, Ecuador, French Guiana, Guyana, Peru, Suriname, and Venezuela) and is considered to be the most species-rich terrestrial ecosystem in the world (Puig, 2001). Within the Amazon rainforest, several phytoecological units occur but are relatively poorly defined (Kricher, 1999). Amazon speciation, with large floristic diversity and areas of endemism, may be a consequence of the variety and distribution of soils (Sombroek, 2000; Ruokolainen et al., 2007; ter Steege, 2010; Guimarães et al., 2013), climatic variables (Clarke and Gaston, 2006), geographical barriers (Hunter Jr, 1999), and periodical disturbances that reduce dominance by species and induce competition (Collins et al., 1998). But in Brazil, these forests are home to 897 thousand native (indigenous) people who sustain themselves through subsistence agriculture, hunting, and fishing, and they are directly affected by contamination (IBGE, 2013).

Rainforests are the only extensively preserved ecosystem in the world. However, contamination of soil and water has been reported from “hidden” land degradation associated with grazing, mining, and industrial activities (Hacon et al., 2008; Aniceto and Horbe, 2012; Grimaldi et al., 2015). Knowledge of the variability of soil geochemistry is needed to understand the background variability in soil composition and to detect contamination of natural systems.

Studies in tropical wetland areas, xeric shrubland, savanna-like vegetation, and Atlantic forest in Brazil have shown metal(loid) contents associated with parent material (Licht et al., 2006; Coringa et al., 2014; Souza et al., 2015; Almeida Júnior et al., 2016). The highest contents of Ti are observed in mafic rocks. Aluminum, Th, and Zr are most abundant in felsic igneous rocks. All these elements are poorly soluble and have very low mobilities in the soil environment, while weathering and anthropic addition is virtually absent, so their contents in the soil reflect the parent material (Fritsch et al., 2002; Wilford, 2012). Banded iron formation and mafic rocks have the highest contents of Fe. Its content in metamorphic and sedimentary rocks depends on abundance of mafic minerals. Under oxidizing conditions, Fe is concentrated during weathering as oxyhydroxides, which can co-precipitate trace elements, such as As, Cd, Co, Cu, and Pb (Hamon et al., 2004; Burak et al., 2010). Calcium and Mg occur in minerals such as plagioclases, olivine, calcite, and dolomite. They are most abundant in mafic igneous and calcareous rocks. Potassium- and Na-rich minerals include feldspars, biotite, muscovite, and some amphiboles. These minerals are commonly found in felsic igneous rocks. The influence of lithology on alkali and alkaline contents decreases with increasing weathering by dissolution of mafic and felsic minerals and leaching of these elements. Consequently, the content of Ca, K, Mg, and Na in weathered soils is controlled by soil organic matter, clay minerals, and biochemical cycles (Martz and de Jong, 1990; Brantley and White, 2009).

Despite environmental policies, gold has been mined within the main river channels and on the floodplains of Amazonia for half a century. The Hg used in gold extraction is volatilized and contaminates the air or is dumped in rivers, with an impact on permanent conservation areas and indigenous reservations (Malm, 1998). To successfully ensure rainforest conservation, it is important to study the soil geochemical background. However, geochemical studies in Amazon soils are few because access to undisturbed areas is difficult. Most roads are concentrated in the east and were constructed in the 1960s and 1970s. Transportation essentially occurs through rivers and by airplane. Studies on Amazonia have been restricted to the exchangeable fraction of metal(loid)s (Wasserman et al., 2007; Birani, 2010). However, metal(loid)s associated with soil organic matter, Fe and Mn oxides, and silicates represent more than 80 % of the total content in tropical soils (Silveira et al., 2006). Thus, these fractions are more important in retaining metal(loid)s and can be used to define the geochemical background.

The hypothesis of the study is that even in the deep weathering of the tropical rainforest, parent material is determinant to metal(loid)s contents. Therefore, the objective of this study was to evaluate the contents of Al, Ca, Co, Cr, Fe, K, Hg, Mg, Mn, Na, Ni, P, Pb, Si, Sr, Ti, Th, V, Zn, and Zr in diverse Amazon soils from a variety of widespread locations in the state of Amazonas.

MATERIALS AND METHODS

Study area

The study area encompasses the state of Amazonas (Brazil) (Figure 1), which constitutes approximately 29 % of the Amazon rainforest. Ninety-eight percent of the total area of the state is primary forest (IBGE, 2012). An east-west precipitation gradient (from 1,700 to more than 4,000 mm yr⁻¹) exists in Amazonas. The air temperature ranges from 18 to 42 °C, with a mean annual temperature of 28 °C (Marengo and Nobre, 2009).

In the state of Amazonas, a Proterozoic craton is partially covered by east-west oriented intracratonic sedimentary basins (Tapajós, Solimões, and Amazonas). At the northern and southern limits there are outcrops formed by syenite, granite, gneiss, and andesite, corresponding to the Guiana (north) and Tapajós (south) shields (Santos et al., 2000). These rocks are essentially composed of quartz, labradorite, andesine, augite, pigeonite, and micas. Olivine, apatite, magnetite, zircon, and ilmenite are accessory minerals (Schobbenhaus and Coelho, 1988; Dardenne and Schobbenhaus, 2001; Angelim, 2006). The Tapajós Basin contains Silurian-Devonian sandstones and gravels deposited in a fluvial system. Sediments of the Amazonas Basin include Paleo-Mesozoic quartz-sandstone beds in an alluvial-fluvial system. In Cenozoic times, the uplift of the Andes created a very extensive marsh and lake region in the upper basin, with deposition of argillaceous rocks (Miocene Solimões Basin) and beds of clay, sand, coquina, and lignite (Pleistocene Solimões Basin). Andean silty particles cover the Quaternary floodplains of the main rivers (Santos et al., 2000).

Due to strong weathering conditions typical of humid tropical regions (Fontes, 2012), highly developed soils originating from deeply weathered saprolites are widespread (Table 1). The spatial distribution of soil groups is highly associated with topography and parent material (Bravard and Righi, 1989; Dubroeuq and Volkoff, 1998). Ferralsols (Oxisols) cover convex hills on Paleo-Mesozoic sandstones (the Amazon Basin) and cover uplands on crystalline shields. Acrisols (Alfisols and Ultisols) occur on low elevation plateaus developed on claystones (Miocene Solimões Basin) and on sandy and clayey unconsolidated sediments (Pleistocene Solimões Basin). Podzols (Spodosols) occur on plains between ferrallitic hills in the sedimentary basins and crystalline shields, being formed by downward movement of organic-mineral complexes influenced by upwelling of groundwater to the soil surface. Fluvisols (Entisols) and Gleysols (great groups of Inceptisols, Entisols, and Ultisols) occur along floodplains of the main rivers, which are occupied by Holocene Andean sediments.

Vegetation in the study area is marked by great contrast from one geomorphic location to another (Cordeiro and Rossetti, 2015): a) dense rainforest (Terra Firme Forest) covers 65 % of the Amazon rainforest over Ferralsols, Acrisols, and Cambisols on remnants of ferrallitic plateaus and convex hills which are not flooded; b) submontane rainforest over Ferralsols on uplands supported by crystalline rocks; c) low sclerophyllous bush as open savannah (Campinarana) occurs on Plinthosols in inter hill valley and on Podzols in plains; and d) the lowest areas, which can be split into i) seasonally flooded fluvial terraces with Fluvisols and open rain forest (Restinga Forest) that have fast growing trees with mesic leaves that can be submerged for up to six months of the year, and ii) constantly flooded fluvial plains with Gleysols that have shorter and more sparse trees of slow growth and sclerophyllous leaves (Igapó Forest).

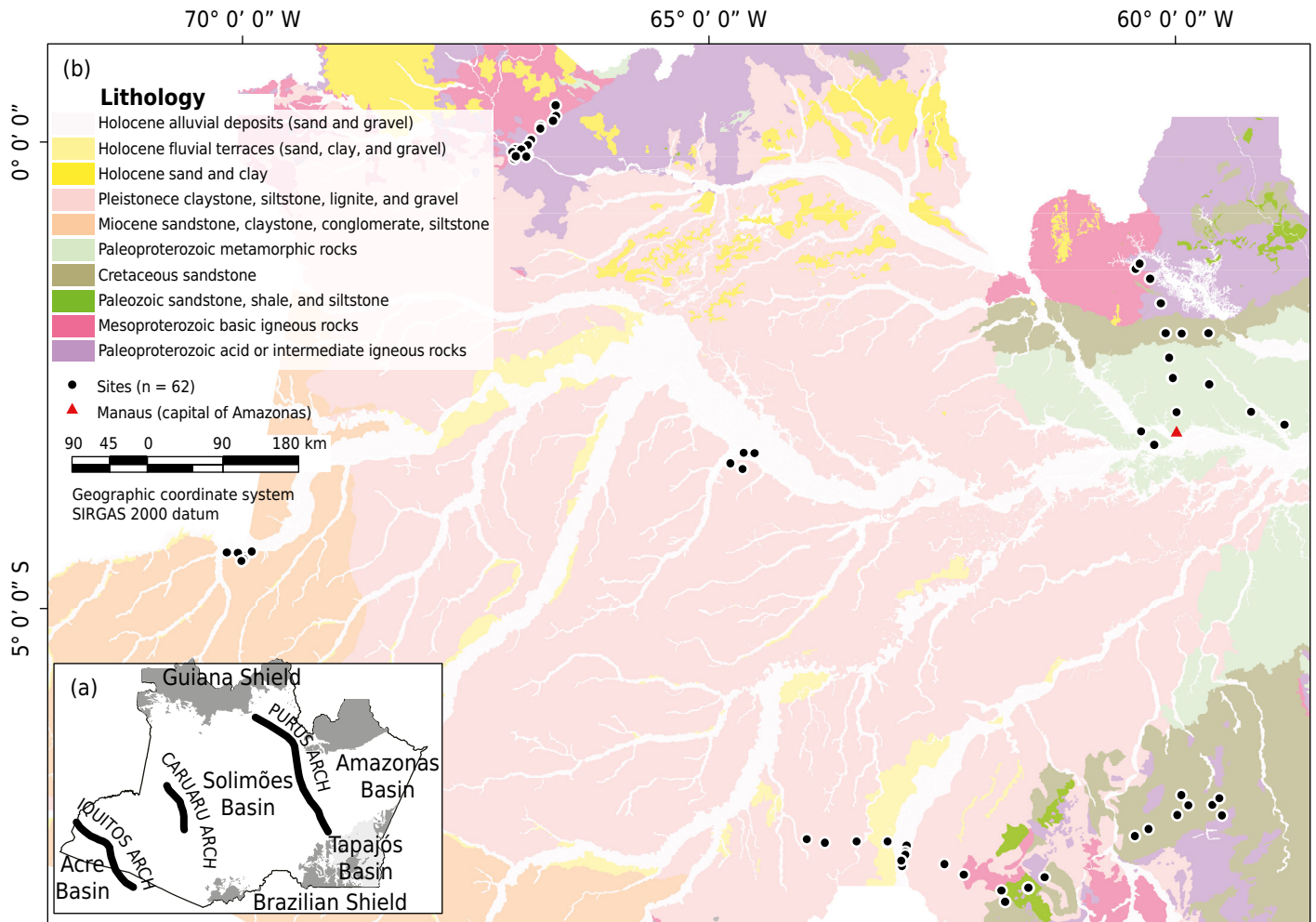


Figure 1. Geologic provinces of the state of Amazonas (a) and sites sampled in the study area based on the lithology (b).

Table 1. Soil type occurrences in the study area

WRB ⁽¹⁾	Soil Taxonomy ⁽²⁾	Area ⁽³⁾ %	Sites Sampled	Lithology ⁽⁴⁾
'Yellow' Acrisol Alumatic (AC-au 'a')	Udults	3	9	Paleo-Mesozoic quartz-sandstone, diamicite, siltite, and shale
'Yellow' Acrisol Alumatic (AC-au 'b')	Udults	30	8	Pleistocene claystone, siltstone, lignite, and gravel
'Yellow' Haplic Acrisol (AC-ha 'c')	Udults	15	5	Miocene sandstone, claystone, conglomerate, and siltstone
Subquatic Arenosol (AR-sq)	Quartzipsamments	1	-	Holocene sand, clay, and gravel
Haplic Cambisol (CM-ha)	Udepts	1	-	Pleistocene claystone, siltstone, lignite, and gravel
Eutric Fluvisol (FL-eu)	Fluvents	2	5	Holocene sand, clay, and gravel
'Yellow' Haplic Ferralsol (FR-ha 'a')	Udox	19	17	Proterozoic sandstone and Mesozoic quartz-sandstone
'Red-Yellow' Haplic Ferralsol (FR-ha 'b')	Perox	8	8	Paleoproterozoic metamorphic rocks, Proterozoic acid or intermediate igneous rocks
Dystric Gleysol (GL-dy 'a')	Aquepts	4	5	Holocene sand, clay, and gravel
Eutric Gleysol (GL-eu 'b')	Aquepts	6	2	Holocene sand, clay, and gravel
Haplic Plinthosol (PT-ha)	Aquox	4	-	Pleistocene claystone, siltstone, lignite, and gravel
Albic Podzol (PZ-ab)	Orthods	7	3	Holocene sand and clay

⁽¹⁾ WRB (2014). ⁽²⁾ Soil Survey Staff (2010). ⁽³⁾ Maia and Marmos (2010). ⁽⁴⁾ Reis et al. (2006).

Sampling and chemical analysis

Sixty-two geo-referenced sites were sampled at the 0.00-0.20 m depth representing regional dominance of topography, geology, and pedology in the state of Amazonas (Figure 1). At each site, ten samples were collected and were maintained apart. Sampling occurred 5.5 to 120 km from potential sources of contaminants (roads, railroads, mining areas). Stainless steel equipment was used for collecting soils and for sample preparation. The World Reference Base for soil resources (Soil Survey Staff, 2010) and Soil Taxonomy (WRB, 2014) were utilized for soil classification.

Samples were oven dried at 40 °C, crushed, and sieved to 2 mm prior to analysis. Soil pH was measured with a glass electrode in a 1:2.5 suspension (v/v soil and deionized water). Potential acidity (H+Al) was extracted by 1 mol L⁻¹ ammonium acetate solution at pH 7. Exchangeable Ca²⁺, Mg²⁺, and Al³⁺ contents were determined in 1 mol L⁻¹ KCl extract. Exchangeable K⁺ and Na⁺ were determined through Mellich-1 extraction (Claessen, 1997). From these results, the sum of bases (SB), base saturation (V%), and cation exchange capacity (CEC) were calculated for each sample. Extractable phosphorus (P_M) was determined in a Mehlich-1 solution. Soil organic carbon was determined by the Walkley-Black method and converted to soil organic matter (SOM) by a factor of 1.724. Sand, silt, and clay fractions were determined by the sieve-pipette method, after dispersion with 0.1 mol L⁻¹ NaOH.

X-ray Fluorescence Spectrometry (XRF) measurements were taken in pressed powder pellets for Al, Ca, Co, Cr, Fe, K, Hg, Mg, Mn, Na, Ni, P, Pb, Sr, Ti, Th, V, Zn, and Zr (Shimadzu μ EDX-1300). The data for each metal(loid) were obtained from 4,000 points, with an incident beam diameter of 50 μ m. A fundamental parameter method was used to correct for the variable matrix effect and to quantify metal(loid) contents using standards and reference materials. This technique has a 2σ of $\pm 1\%$ relative standard deviation for major elements and $\pm 5\%$ for trace elements, when these elements are in concentrations well above their detection limits (typically ± 0.01 wt % for major elements and ± 1 -2 mg kg⁻¹ for trace elements). Accuracy was calibrated using a Montana II Soil Standard Reference Material (SRM 2711a).

Two weathering indices were calculated based on geochemical analysis - the chemical index of alteration (CIA) (Nesbitt and Young, 1982) and the weathering index of Parker (WIP) (Parker, 1970). Both were calculated based on the equations 1 and 2, respectively:

$$\text{CIA} = \{ \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \} \times 100 \quad \text{Eq. 1}$$

$$\text{WIP} = \{ (2\text{Na}_2\text{O} / 0.35) + (\text{MgO} / 0.9) + (2\text{K}_2\text{O} / 0.25) + (\text{CaO}^* / 0.7) \} \times 100 \quad \text{Eq. 2}$$

in which oxides are expressed as molar proportions and CaO* is the calcium content of silicates and excludes CaO combined in carbonate and phosphate minerals. They assume that the dominant process during chemical weathering is the degradation of feldspars, formation of clay minerals, and leaching of bases (Nesbitt and Young, 1982).

Statistical procedures

The ten samples collected from each site were analyzed, and the mean value was calculated and utilized in statistical analysis. Descriptive statistical analyses of data were computed for all 62 sites combined, as well as in accordance with soil classification. Use of the T-test for independent samples enabled us to detect significant differences in the mean values of soil properties between soil groups. Kurtosis and the skewness coefficient showed that the parameters did not follow a normal distribution. Consequently, Pearson's correlation coefficient was calculated for relationships between soil properties and metal(loid) contents after data was log (ln) transformed.

Principal Component Analysis (PCA) was performed to clarify the relationship between variables. The PCA is a multivariate technique that transforms correlated variables into non-correlated

variables, called principal components (PCs). The PCs are ordered in decreasing eigenvalues, which express the majority of data variability. Considering only the PCs of highest eigenvalues, the number of variables is reduced, without losing descriptive power. Prior to PCA, analytical data were logarithm transformed and standardized to provide a normal distribution.

RESULTS

Descriptive statistics of soil properties

The topsoil samples from the state of Amazonas showed, with some exceptions, acidic pH levels and low CEC values, reflecting the high weathering rates prevailing in Amazon soils (Table 2). Eutric Gleysols and Eutric Fluvisols showed pH values close to 6.0, and extractable P from Mehlich-1 (P_M) and base saturation (V%) up to 1,258 and 25 times higher, respectively, than other soil groups. 'Yellow' Acrisols 'c' in the Miocene Solimões Sedimentary Basin had higher SB, CEC, and V% values than other Acrisols.

The median values of SOM for all soil groups are close to 3 %, except for Albic Podzols (PZ-ab, 5.1 %) and 'Yellow' Haplic Ferralsols (FR-ha 'a', 4.0 %). On the basis of texture, the soils can be defined as clayey (AC-au 'c', FR-ha 'a'), silty (GL-dy, GL-eu, FL-eu), loamy (AC-au 'a', AC-au 'b', FR-ha 'b'), and sandy (PZ-ab). The T-test detected statistical SB, CEC, and silt content differences between three groups: (a) non-flooded upland soils derived from sedimentary or crystalline rocks (FR 'a', FR 'b', AC 'a'); (b) flooded soil derived from Andean sediments and non-flooded soil derived from Miocene sediments (FL, GL 'a', GL 'b'); and (c) sandy soils (PZ).

Table 2. Descriptive statistics (median - coefficient of variation %)⁽¹⁾ for topsoil properties for soil groups and data from literature

Soil group (No. of samples)	pH(H ₂ O)	P_M	SB	CEC	V	SOM	Clay	Silt	Sand
		mg kg ⁻¹	cmol _c kg ⁻¹		%		g kg ⁻¹		
AC 'a' (9)	4.2-8 ^a	1.6-71 ^a	0.3-72 ^a	7.5-38 ^a	4-56 ^a	29-33 ^a	410-36 ^a	80-135 ^a	510-54 ^a
AC 'b' (8)	4.4-17 ^a	1.7-186 ^a	0.4-229 ^a	7.1-51 ^a	4-173 ^a	34-53 ^a	360-39 ^a	180-79 ^b	345-43 ^a
AC 'c' (5)	4.8-9 ^a	3.4-31 ^a	2.5-84 ^b	15.4-26 ^b	17-80 ^b	27-16 ^a	350-25 ^a	430-42 ^c	150-89 ^b
FL (5)	5.8-14 ^b	48.3-86 ^b	4.9-73 ^b	8.7-41 ^a	76-36 ^c	20-34 ^b	200-60 ^b	510-34 ^c	290-87 ^a
FR 'a' (18)	4.1-7 ^a	1.6-43 ^a	0.3-113 ^a	9.0-22 ^a	3-110 ^a	40-34 ^c	610-48 ^a	70-120 ^a	240-73 ^a
FR 'b' (8)	4.1-13 ^a	1.9-44 ^a	0.3-74 ^a	7.8-35 ^a	4-36 ^a	33-43 ^a	350-59 ^a	70-79 ^a	155-23 ^b
GL 'a' (4)	4.4-7 ^a	3.5-119 ^a	2.7-117 ^b	10.4-50 ^a	26-84 ^b	26-49 ^a	390-41 ^a	450-50 ^c	162-179 ^b
GL 'b' (2)	5.9-25 ^b	62.9-342 ^b	16.6-88 ^c	21.5-26 ^b	75-45 ^c	30-33 ^a	450-26 ^a	560-31 ^c	150-71 ^c
PZ (3)	4.3-8 ^a	0.5-107 ^a	0.4-112 ^a	6.5-46 ^a	6-73 ^a	51-57 ^d	50-43 ^c	90-52 ^a	860-6 ^b
All sites (62)	4.3-15	2.0-232	0.4-203	8.9-44	4-153	32-44	400-56	220-99	380-71
Comparison data									
PL (4)	5.2-5	2.0-56	2.5-69	16.4-51	18-20	46-23	470-43	270-59	260-43
IN (7)	5.3-11	n.d.	7.1-91	n.d.	n.d.	31-73	200-77	390-45	320-87
PA (3)	5.6-17	n.d.	5.6-92	11.9-36	41-79	10-77	330-55	320-21	350-41
MG (697)	5.3-14	1.7-226	1.1-142	7.9-53	14-37	33-112	340-56	n.d.	n.d.
PE (34)	5.5-17	7.0-241	3.1-479	n.d.	n.d.	27-196	180-69	170-65	640-38
SA (19)	4.4-20	2.1-167	0.5-138	5.5-52	11-112	22-53	250-57	320-55	716-29

AC 'a' = 'Yellow' Acrisol Aluic derived from Paleo-Mesozoic rocks; AC 'b' = 'Yellow' Haplic Acrisol derived from Pleistocene Solimões rocks; AC 'c' = 'Yellow' Haplic Acrisol derived from Miocene Solimões rocks; FL = Eutric Fluvisol; FR 'a' = 'Yellow' Haplic Ferralsol; FR 'b' = 'Red-Yellow' Haplic Ferralsol; GL 'a' = Dystric Gleysol; GL 'b' = Eutric Gleysol; PZ = Albic Podzol; PL = Philippine rainforest soils (n = 4) (Navarrete et al., 2009); IN = Indonesian rainforest soils (n = 7) (Anda, 2012); PA = Tropical wetland of Pantanal soils (n = 3) (Coringa et al., 2012); AF = Atlantic Forest subtropical forest soils (n = 307) (Licht et al., 2006); PE = Xeric shrubland soils (Biondi et al., 2011); SA = Southwestern Amazon soils (dos Santos and Alleoni, 2013). ⁽¹⁾ Different letters indicate difference from means for soil groups according to the T-test for independent samples at p=0.05. pH(H₂O): glass electrode in a 1:2.5 suspension (v/v soil and deionized water). P_M = Mehlich-1 extraction. SB = Ca²⁺, Mg²⁺, Al³⁺ (1 mol L⁻¹ KCl extraction) + K⁺ and Na⁺ (Mehlich-1 extraction); CEC = SB + (H+Al) (extracted by 1 mol L⁻¹ ammonium acetate solution at pH 7); V% = (SB/CEC) × 100; SOM: Walkley-Black method; Sand, silt, and clay fractions = sieve-pipette method.

Metal(loid) contents

Acrisols and Ferralsols had the highest median contents of Al, Co, Cr, Fe, Hg, Pb, Ti, V, and Zr (Table 3 and Table 4). Fluvisols and Gleysols had the highest contents of Ca, K, Mg, Mn, Na, Ni, P, Sr, and Zn. Furthermore, the coefficient of variation for metal(loid) contents indicates that Acrisols and Ferralsols are more heterogeneous than Fluvisols, Gleysols, and Podzols.

Carbonates are virtually absent in the sites sampled, so all the CaO values are attributed to silicate minerals. The CIA and WIP have variations of up to three times among soil groups (Table 3), indicating different degrees of weathering. Alkali and alkaline earths showed a high and positive correlation with silt and sand contents (Figure 2). Trivalent and pentavalent elements registered high correlations with Al and Fe contents. The TiO₂, ThO₂, and ZrO₂ contents were poorly correlated. In general, the metal(loid) contents did not show significant correlations with clay and SOM.

The first two principal components (PCs) explain 74 % of the variance in data. Principal components with eigenvalues below 1.0 did not adequately represent the geochemical variability of the data and explained no additional variance than the original variables taken alone (1/20 original variables = 5 %), so they were excluded from further interpretation (Wackernagel, 2003). The first component (PC1) explained 41.6 % of total variance of the data. The PC1 had large negative loadings from total contents of Al, Co, Fe, and Ti. The second component (PC2) explained 32.3 % of the total variance and is dominated by original variables that express the differences of parent material and the stage of weathering, namely Ca, K, Si, Sr, and Zr contents (Figure 3). The antagonism between Zr and Ca contents shown by PC2 expresses the difference between highly and moderately weathered soils.

The PC1 × PC2 diagram indicates that there are five distinct soil groups (Figure 3): i) siltic seasonally inundated soils (Fluvisols and Gleysols); ii) loamy soils in non-inundated areas developed over Solimões Sediments (Acrisols); iii) clayey soils in non-inundated areas developed over crystalline shields ('Red-Yellow' Haplic Ferralsol 'b'); iv) clayey soils in non-inundated areas developed over Amazonas sediments ('Yellow' Haplic Ferralsols 'a'); and v) sandy soils in seasonally inundated areas (Albic Podzols).

DISCUSSION

The median values of pH, CEC, and V% in Amazonian rainforest were lower than the mean values for other Brazilian biomes (Marques et al., 2004a; Oliveira and Costa, 2004; Dalmolin et al., 2006; Maia et al., 2015; Souza et al., 2015), for rainforest in Ghana (Bowell, 1993), and for rainforest in southeastern Asia (Richter and Babbar, 1991). In Amazonia, median values were up to 17 % lower in pH, 50 % in CEC, and 78 % in V% (Table 2). Similar results for these properties were observed in southwestern Amazon soils (Santos and Alleoni, 2013). The lower fertility in Amazon topsoil compared to other Brazilian biomes (Table 2) suggests that biogeochemical cycles do not compensate deep weathering, and litter is probably the most important pool of nutrients in non-inundated soils.

The median values of metal(loid) contents in the Amazon rainforest topsoil are 0.5 to 300 % lower than the values previously observed in Brazil for Atlantic Forest, xeric shrubland, savanna, and Pantanal soils (Table 4). These results can be attributed to the low content of many elements in parent materials (Dardenne and Schobbenhaus, 2001; Reis et al., 2006; Quesada et al., 2010; Xavier, 2013) and kaolinite dominance in the clay fraction (Fritsch et al., 2002, 2005). In addition, the wet tropical climate over the past 45 ky (Lima, 2001; Wang et al., 2017) conduces intense leaching of elements from topsoil.

In tropical environments, the persistence of organic carbon in soils is fairly low, due to high temperatures and associated high organic matter mineralization rates. The higher

Table 3. Descriptive statistics (median – coefficient of variation %)* for major elements determined by X-ray Fluorescence Spectrometry in topsoils for soil groups and data from the literature

Soil group (No. of samples)	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	SiO ₂	TiO ₂	ThO ₂	ZrO ₂	CIA	WIP
	%						mg kg ⁻¹					
AC 'a' (9)	15.60-22 ^a	0.02-33 ^a	0.90-88 ^a	0.51-24 ^a	0.76-10 ^a	1.20-10 ^a	76.24-11 ^a	1.40-34 ^a	9.80-33 ^a	746.8-21 ^a	90.1	1181
AC 'b' (8)	11.16-32 ^b	0.06-5 ^a	6.34-57 ^b	0.81-13 ^a	1.41-17 ^a	1.97-10 ^a	71.54-5 ^a	1.09-60 ^a	14.32-39 ^a	736.4-10 ^a	79.8	1939
AC 'c' (5)	13.46-6 ^c	0.19-23 ^b	3.74-13 ^c	0.85-3 ^a	1.48-4 ^a	1.93-10 ^a	75.10-4 ^a	0.90-7 ^b	12.10-30 ^a	412.7-10 ^b	82.0	1974
FL (5)	14.34-9 ^a	1.00-59 ^c	5.31-27 ^b	2.28-13 ^b	1.75-8 ^a	1.44-21 ^a	62.80-13 ^b	0.80-6 ^b	15.39-23 ^a	327.9-23 ^b	74.9	2984
FR 'a' (18)	16.75-50 ^a	0.02-45 ^a	1.24-101 ^a	0.03-36 ^c	1.38-8 ^a	1.77-12 ^a	72.64-30 ^a	1.39-54 ^a	12.43-38 ^a	898.2-30 ^a	90.2	1192
FR 'b' (8)	21.56-6 ^a	0.01-30 ^a	10.98-12 ^d	0.03-23 ^c	1.02-18 ^a	1.50-46 ^a	45.60-15 ^c	2.03-9 ^c	20.05-57 ^b	2133.0-20 ^c	93.3	996
GL 'a' (4)	18.26-5 ^a	0.70-65 ^c	6.33-4 ^b	2.75-22 ^b	1.75-7 ^a	1.44-6 ^a	61.76-3 ^b	0.97-9 ^a	16.36-13 ^a	297.6-14 ^b	78.9	3317
GL 'b' (2)	17.83-4 ^a	0.82-6 ^c	6.42-9 ^b	2.25-6 ^b	1.68-10 ^a	1.29-46 ^a	60.73-6 ^b	0.90-6 ^a	12.02-59 ^a	232.1-13 ^b	80.4	2841
PZ (3)	2.16-6 ^d	0.02-18 ^a	0.12-18 ^d	0.02-31 ^c	1.37-10 ^a	1.67-20 ^a	93.30-4 ^d	0.20-12 ^d	8.90-42 ^a	351.6-11 ^b	51.1	1125
All sites (62)	15.60-16	0.06-32 ^a	5.31-37	0.81-19 ^a	1.41-10 ^a	1.52-20 ^a	71.50-10	1.0-22	12.43-37 ^a	412.7-18 ^b	80.4	1682

AC 'a' = 'Yellow' Acrisol Aluminic derived from Paleo-Mesozoic rocks; AC 'b' = 'Yellow' Haplic Acrisol derived from Pleistocene Solimões rocks; AC 'c' = 'Yellow' Haplic Acrisol derived from Miocene Solimões rocks; FL = Eutric Fluvisol; FR 'a' = 'Yellow' Haplic Ferralsol; FR 'b' = 'Red-Yellow' Haplic Ferralsol; GL 'a' = Dystric Gleysol; GL 'b' = Eutric Gleysol; PZ = Albic Podzol; * = different letters indicate significant difference from means for soil groups according to the T-test for independent samples at $p = 0.05$.

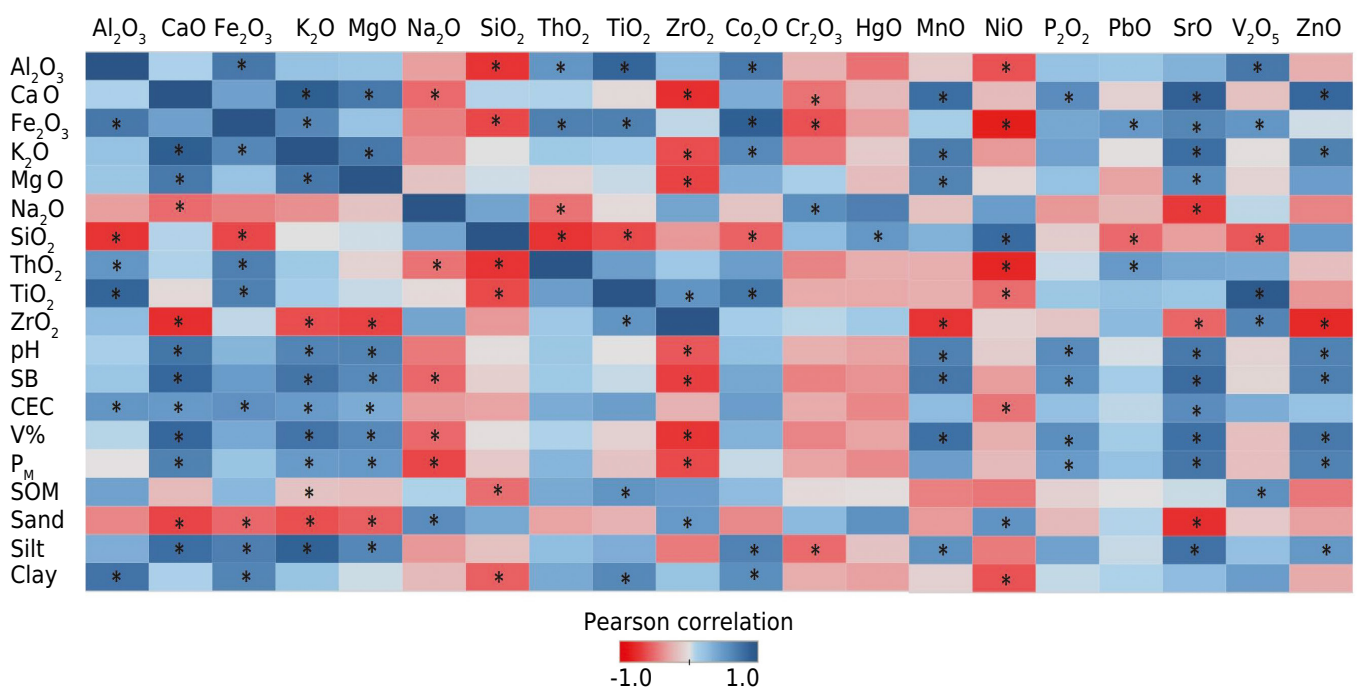

Figure 2. Pearson correlation between metal(loid) contents and soil properties. * = significant correlation at $\alpha = 0.05$.

Table 4. Descriptive statistics [median - coefficient of variation (%)] for minor elements in topsoils for soil groups (mg kg⁻¹)

Element ⁽¹⁾	Amazon soil in this study										Comparison data ⁽²⁾					
	AC 'a'	AC 'b'	AC 'c'	FL	FR 'a'	FR 'b'	GL 'a'	GL 'b'	PZ	All sites	RC	GH	AF	SA	NE	WS
Co	5.0-56	20.0-18	18.5-26	14.9-44	5.9-101	21.7-11	22.2-62	14.5-40	0.9-23	14.9-58	1.4-23	19.6-31.2	3.9-61.9	0.5-20	n.d.	6.9
Cr	164-21	141-30	124-5	204-30	171-17	89-13	121-15	133-31	204-19	141-26	3.4-150	27-91.3	43-230	20-500	<5-47	42
Hg	5.3-10	8.1-4	7.8-6	5.4-31	5.7-17	5.2-39	5.6-7	2.2-59	9.3-28	5.6-34	n.d.	n.d.	13.4-160.7	n.d.	n.d.	0.1
Mn	124-50	166-78	981-60	629-49	113-40	20-49	374-9	521-10	155-11	166-92	8-20	330-890	135-1980	7-309	<5-1180	418
Ni	21.1-22	19.0-36	20.2-21	19.6-10	35.2-47	10.5-28	14.4-33	16.3-13	46.6-18	19.6-50	2.0-67.0	1.9-21.8	8-87	0.5-20	n.d.	18
P	155-23	156-17	302-42	322-47	159-35	562-38	356-9	235-38	131-18	235-53	8.7-91.6	8.7-83	266-1179	0.02-0.08	10-30	n.d.
Pb	106-15	123-45	114-8	102-18	104-18	189-29	117-24	129-26	105-29	114-22	9.7-45	15.4-83.4	15-45	5-90	<5-60	25
Sr	46-10	60-3	83-6	173-32	48-13	86-18	135-28	154-9	45-18	83-54	2-150	23.5-251	12-126	3-350	5-1370	n.d.
V	150-54	139-45	121-6	116-6	154-36	230-9	130-4	121-6	66-11	130-32	9.8-228	287-473	81-856	10-400	<5-524	60
Zn	81-21	77-10	103-10	136-20	78-44	59-25	150-11	145-10	104-8	103-32	n.d.	46.5-157	24-124	40-120	5-102	62

⁽¹⁾ Determined by X-ray Fluorescence Spectrometry. ⁽²⁾ Minimum - maximum values; n.d. = no data. AC 'a' = 'Yellow' Acrisol Aluic derived from Paleo-Mesozoic rocks; AC 'b' = 'Yellow' Haplic Acrisol derived from Pleistocene Solimões rocks; AC 'c' = 'Yellow' Haplic Acrisol derived from Miocene Solimões rocks; FL = Eutric Fluvisol; FR 'a' = 'Yellow' Haplic Ferralsol; FR 'b' = 'Red-Yellow' Haplic Ferralsol; GL 'a' = Dystric Gleysol; GL 'b' = Eutric Gleysol; PZ = Albic Podzol; RC = Democratic Republic of Congo soils (n = 14; Ekosse and Ngole 2011); GH = Ghanaian soils (n = 17; Bowell 1993); AF = Atlantic Forest subtropical forest soils (n = 307; Licht et al. 2006); SA = Brazilian Cerrado soils (n = 18; Kronberg et al. 1979); NE = Northeast Brazilian soils (n = 101; Matschullat et al. 2012); WS = world soil average (Kabata-Pendias, 2010).

median SOM content in 'Red' Haplic Ferralsols 'a' can be attributed to higher clay content. Quality of organic matter, soil composition, and climatic conditions influence SOM decomposition. In addition, humus is not readily decomposed in clayey soils because it is either physically protected inside soil aggregates or it is chemically too complex to be used by most organisms (Carter, 2000; Šimanský and Bajčan, 2014). In contrast, the high SOM content in Podzols is associated with groundwater fluctuations which generate waterlogging, reducing conditions in the topsoil.

The high contents of tri-pentavalent elements in Acrisols and Ferralsols reflect strong acid weathering under the tropical rainforest climate. High temperatures and rainfall result in rapid weathering of minerals. Intense leaching of alkaline (earth) metals, partial leaching of Si, and relative accumulation of Al, Fe, Ti, Th, and Zr in tropical soils result in accumulation of kaolinite, Fe and Al-oxyhydroxides in the clay fraction (Fontes and Weed, 1991; Juo and Franzluebbers, 2003). The high CEC and content of alkali and alkaline earths in silty Fluvisols and Gleysols are associated with incipient pedogenesis in alluvial sediments predominantly derived from the Andes Mountains (McClain and Naiman, 2008). Seasonal flooding and deposit of sediments seems to attenuate weathering of minerals and leaching of bases.

The range of the CIA is from 1, for unweathered rocks, increasing towards infinity for completely weathered rocks composed of kaolinite and gibbsite (Nesbitt and Young, 1982). According to the CIA, tropical conditions lead to a similar weathering pathway in all parent materials, resulting in soil chemical homogeneity. Amazon soils registered mean CIA values similar to clayey soils in rainforest soils in Southwestern Brazil, Ghana,

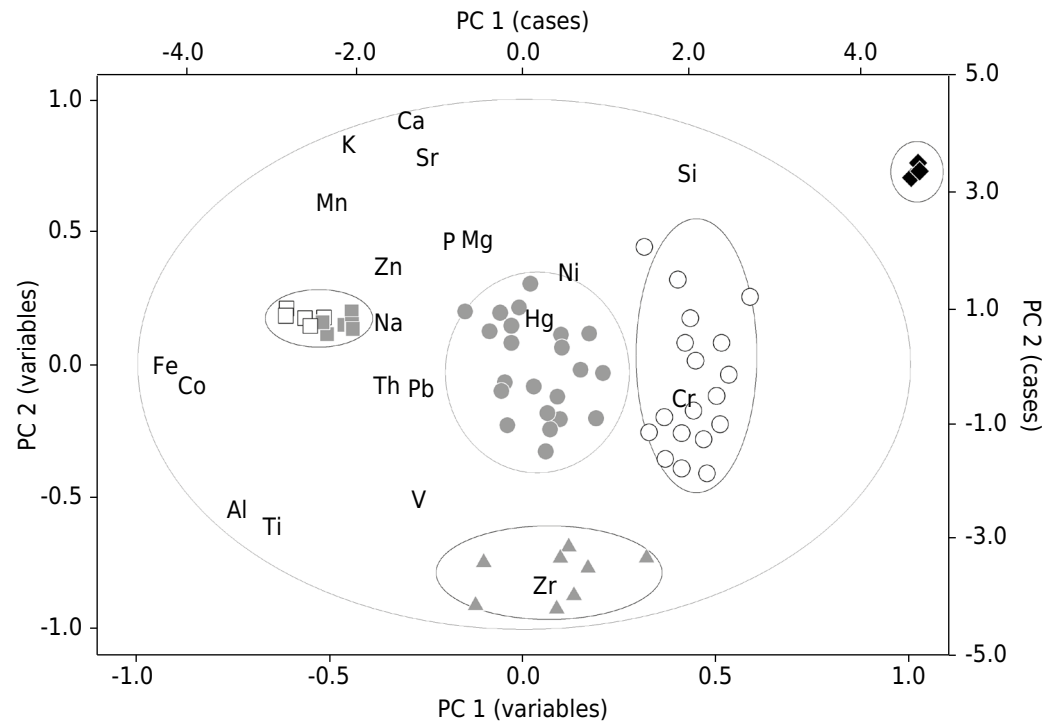


Figure 3. Projection of variables and cases on the PC1 × PC2 factor plane. Legend: black diamonds = Albic Podzols, gray triangles = ‘Red-Yellow’ Haplic Ferralsols ‘b’, open circles = ‘Yellow’ Haplic Ferralsols ‘a’, gray circles = Acrisols, gray squares = Gleysols, open squares = Fluvisols.

the Democratic Republic of Congo, and the Philippines (Table 3). In contrast, the WIP indicates differences among rainforest sites. Amazon soils registered WIP values as low as 34 % of the values in other sites (Bowell, 1993; Navarrete et al., 2009), suggesting a deeper leaching of alkali and alkaline earth elements (Table 3).

The low CIA value indicated that Podzols have an incipient weathering stage (Table 3). However, Podzols can be formed by intense hydrolysis, oxide removal, and clay eluviation from Ferralsols and Acrisols in Amazonia (Dubroeuq and Volkoff, 1998). Thus, Al and Fe are depleted by downward migration with organic matter, from topsoil to deeper horizons (Horbe et al., 2004; Nascimento et al., 2004). Aluminum is considerably immobile during weathering by the CIA, and its downward movement during the podsolization process explains an incipient stage of chemical weathering, as erroneously indicated to Podzols (Table 3). This study supports that the WIP is a more reliable weathering index because it is based on the proportions of only alkali and alkaline earths.

The high values of the coefficient of variation of soil properties and metal(loid) contents show the influence of parent material and pedogenesis. Amazon soils, even highly weathered ones, usually retain some geochemical signature of the parent material (Tables 2 and 3, Figure 3). This result may be generalized for all tropical rainforest soils, as supported by results from Southeast Asia and West-Central Africa (Matheis, 1981; Anda, 2012). Furthermore, pedogenetic processes contribute to the enrichment, depletion, and mobilization of elements in the soil profile, and consequently to soil diversity (Schaeztl and Anderson, 2005; Vodyanitskii et al., 2011). In this study, the persistence of Ca and Zr in the topsoil results in higher values of the coefficient of variation among the elements analyzed. Strong correlation between silt/sand fraction and mono-divalent elements is attributed to the influence of parent material. Chlorite, feldspar, smectite, vermiculite, and illite dominate the sand and silt fractions of the soils derived from Holocene Andean sediments (Marques et al., 2002). The weathering of these minerals ensures high alkali and alkaline earth element contents in the soil. In contrast, quartz dominance in the sand fraction of non-inundated soils (Kitagawa and Moller, 1979; Xavier, 2013; Mendonça et al.,

2014) is related to deep weathering and intense leaching of mono-divalent elements. The Zr content of soil is generally inherited from parent rocks since it displays very low mobility under most environmental conditions, mainly due to the stability of the principal host mineral zircon and the low solubility of the hydroxide $Zr(OH)_4$ (Faure, 1991; Lentz, 2003; Kabata-Pendias, 2010). Biogeochemical cycles induced by trees also influence metal(loid) contents in the surface layers of soil according to the importance of different elements to the plant, and trees increase soil diversity (Lucas, 2001; Jobbágy and Jackson, 2004).

Titanium, Th, and Zr are very persistent in soils and, therefore, their ratios should reflect their original ratios in the parent material. The poor correlations among Ti, Th, and Zr (r from 0.18 to 0.53, Figure 2) indicate that soils are derived from different parent materials. Amazon soils have been formed from both ancient and recent parent materials under one of the most severe weathering conditions in the world. Amazon soils in floodplains have higher alkali and alkaline earth metal contents due to Holocene Andean alluvial sediments (Table 3). Conversely, higher Ti, Zr, and Th contents in the Ferralsols of Amazonia compared to other tropical rainforest areas reflect the higher degree of leaching (Matheis, 1981; Bowell, 1993; Fletcher, 1996; Ekosse et al., 2011; Arafa et al., 2015).

The high correlations between metal(loid) contents and soil properties for soils with different parent materials is attributed to the pedogenic process (Chen et al., 1999; Hamon et al., 2004; Marques et al., 2004b; Oliveira et al., 2014; Souza et al., 2015). The correlation coefficients between Fe, Al, and tri-pentavalent element contents were the strongest among all soil properties. Aluminum and Fe are concentrated as oxides in soil during desilication and ferrallitization. The Fe/Al oxide minerals incorporate and adsorb metal(loid)s during their formation in soils (Perelomov and Kandeler, 2006; Kabata-Pendias, 2010; Alloway, 2013). Under reducing conditions associated with raised water tables, gleyzation leads to Fe oxide dissolution and leaching of incorporated elements. Aluminum also can be depleted due to organo-complexation. Furthermore, the hypothesis that relates metal(loid) contents in soil to parent material is only partially true. Therefore, inheritance of metal(loid) contents derived from parent material can be modified by pedogenesis.

Several studies have shown a positive correlation between clay and metal(loid) contents of soils (Chung and Sa, 2001; Deschamps et al., 2002; Fontes and Gomes, 2003; Kabata-Pendias, 2010). However, the predominance of kaolin minerals with minimal substitution of structural cations (88 to 96 % of the clay fraction) in Amazon 'Yellow' Haplic Ferralsols (Corrêa et al., 2008) would promote a relatively weak and limited pH-independent exchange capacity. So, the correlation between clay content and metal(loid) contents is weakened (Figure 2).

The differences in metal(loid) contents in non-inundated soils on crystalline shields and sedimentary basins are associated with differences in parent material. Higher contents of Co, Cr, Ni, and other metal(loid)s in igneous and metamorphic rocks (Reis et al., 2006) cause higher contents in soils compared to soils developed from non-mineralized clastic rocks. Furthermore, the higher Al and Fe contents in more acidic soils of crystalline shields is associated with the higher level of metal(loid) incorporation in the goethite structure (Fitzpatrick and Schwertmann, 1982).

The low metal(loid) contents in Amazon Podzols are attributed to their low contents of clay and Fe. In Podzols, Fe removal and clay depletions are associated with most elements leaching out from the upper horizons to deeper horizons or from the profile (Vodyanitskii et al., 2011). Dissolution of Mn and Fe oxides under reducing conditions (which often accompanies podzolization) promotes the release and leaching of elements usually coprecipitated with Fe and Mn oxides, including Ni, Co, and Cr (Horváth et al., 2000). Both Zn and Cu form stable complexes with organic ligands, which favors the eluvial-illuvial redistribution of these metal(loid)s by organic matter migration (Kabata-Pendias, 2010).

The floodplain is important to ecosystem services, influencing human occupation and farming activities. This is especially evident in isolated indigenous communities, which derive most of their food from local sources. Amazonas hosts the largest indigenous population in Brazil, which is distributed in 204 reservations (IBGE, 2013). In this study, the low coefficient of variation for metal(loid) contents in Fluvisols and Gleysols suggests that the samples are free of contamination; therefore, these data are extremely valuable in determining the geochemical background of these soil types.

More than 92 % of the state of Amazonas is covered by primarily forest and has one of the lowest population densities in Brazil (2.23 inhabitants per km²). Almost half of the total population is concentrated in the capital, Manaus. Metal(loid) contents in topsoil are influenced by the type, the intensity, and the history of anthropogenic activities and occupation (Matschullat et al., 2000). The contribution of atmospheric deposition in topsoil is traceable to very high values of the coefficient of variation (Hovmand et al., 2008; Thorpe and Harrison, 2008; Saby et al., 2011). The low values of the coefficient of variation of metal(loid) contents in soils of the Manaus region, 'Yellow' Haplic Ferralsols (FR-ha 'a'), 'Yellow' Acrisols Alomic (AC-au 'a'), and Albic Podzols (PZ-ab) (Table 4), suggest that possible atmospheric deposition of pollutants was not detected.

Colluvial material transported in the past can cover weathered rocks and give rise to soils with no relation to the lithology below. In general, allochthonous materials are cited as parental material for tropical soils (Pedro and Melfi, 1983). However, the geochemical evidence in the soils on different lithologies can be interpreted as soils being composed of mostly autochthonous material. Especially in the Amazon Basin, the persistence of a wet climate over the past 45,000 years (Wang et al., 2017) could impede quantification of allochthonous contribution. The presence of allochthonous material is plausible not only on the sites sampled in this study but also on most soils and similarly dissected landscapes. However, from the large differences among the soils investigated, it can be inferred that the possible presence of allochthonous material does not necessarily invalidate the representativeness of this study and the conclusion that mainly lithology controls the metal(loid) content (Kronberg et al., 1979; Marques et al., 2004b; Licht et al., 2006; Souza et al., 2015).

CONCLUSIONS

The distinctive geochemical differences among soil groups demonstrate the influence of parent material and pedogenic processes on metal(loid) contents. Upland Amazon soils mostly reflect a deeply weathered condition, with acidic pH, lower contents of mobile elements, and lower values of cation exchange capacity than for other Brazilian biomes and other tropical rainforest areas around the world.

This study is the first effort to analyze the variability of metal(loid)s in Amazon rainforest soils. The results obtained suggest that the metal(loid) contents in the soil exhibit a close relationship to parent material, even for the most weathered soils, and to pedogenesis. The results of this study can be used as a reference to identify soils contaminated by anthropogenic activities in Amazonia.

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