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Natural contents of heavy metals in soils of the southern Amazonas state, Brazil

Teores naturais de metais pesados em solos da região sul do estado do Amazonas

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Abstract

Heavy metals occur naturally in the soil as a product of rock weathering and, are commonly associated with environmental pollution and toxicity to living beings. This association deserves much attention since some heavy metals, such as Fe, Mn, Cu, Zn, and Ni, are essential to plants. Our attention should thus be drawn not only to the element itself, but also to its contents in the soil. This is because its occurrence and quantities are covariates of the geomorphic, geologic, pedologic, and anthropogenic diversity. In this context, the present study aimed to determine the natural contents of heavy metals in the soils of three physiographic regions of the south of Amazonas state, comparing them to natural contents in some other Brazilian soils. Twenty-four soil samples were collected in three physiographic regions (field/forest, animated relief, and flooded/non-flooded areas), in the superficial and subsurface horizons. The digestion of the samples was based on the EPA-3051A method and the determination by atomic absorption spectrophotometry (AAnalyst 800 Perkin Elmer). The results indicate a low potential of soils from the south of Amazonas in supplying heavy metals, which were found in the following decreasing order: Ba>Fe>Cr>Pb>Zn>Cu>Mn>Co>Cd. The natural heavy metal contents vary depending on the type of soil, weathering level, and physiographic regions, and are similar or inferior to those observed in other regions of the country; with Neosols presenting the highest natural contents; and Cambisols, the lowest, for most of the metals evaluated.
Key words: Amazonas. Natural metal concentration. Micronutrients.

Resumo

Os metais pesados ocorrem naturalmente no solo como produto do intemperismo das rochas e, comumente, são associados com poluição ambiental e toxidade aos seres vivos. Essa relação merece atenção mais cautelosa, uma vez que alguns são essenciais às plantas como Fe, Mn, Cu, Zn e Ni. Assim,

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a preocupação deve estar voltada não apenas ao elemento em si, mas aos teores desses no solo, visto que sua ocorrência e quantidade são covariativas da diversidade geomorfológica, geológica, pedológica e antrópica. Neste sentido, objetivou-se determinar os teores naturais dos metais pesados nos solos de três regiões fisiográficas da região Sul do Amazonas, comparando-os com os teores naturais de alguns solos do país. Foram coletadas 24 amostras de solo em três regiões fisiográficas (Campo/Floresta, Relevo Movimentado e Várzea/Terra Firme), nos horizontes superficiais e subsuperficiais. A digestão das amostras baseou-se no método EPA-3051A, e a determinação com espectrofotometria de absorção atômica (AAnalyst 800 Perkin Elmer). Os resultados indicam baixo potencial dos solos do Sul do Amazonas em suprir metais pesados, sendo os maiores teores encontrados na seguinte ordem decrescente: Ba>Fe>Cr>Pb>Zn>Cu>Mn>Co>Cd. Os teores naturais de metais pesados variam em função da classe de solo, grau de intemperismo e das regiões fisiográficas e são semelhantes ou inferiores aos observados em outras regiões do país; com Neossolos apresentando teores naturais mais elevados e, os Cambissolos, os mais baixos, para a maioria dos metais avaliados.
Palavras-chave: Amazonas. Concentração natural de metais. Micronutrientes.

Introduction

Heavy metals are a group of chemical elements naturally available in the environment as secondary components of rocks. Some of these elements are micronutrients (Fe, Mn, Cu, and Zn) and others are especially beneficial to vegetal metabolism (Co, Ni, and V) (BIONDI et al., 2011; MACEDO et al., 2012). However, the aforementioned elements can be harmful to fauna and flora when at high quantities (MECHI; SANCHES, 2010; KABATA-PENDIAS, 2010), while others are considered by the Agency for Toxic Substances and Disease Registry as extremely hazardous (Cd, Cr, Hg, and Pb). Among them, Cd and Pb can be considered the most potentially dangerous elements, even in low concentrations, because of their carcinogenic or mutagenic characteristics (ATSDR, 2012).

In the absence of anthropogenic interventions, natural contents of heavy metals depend on soil source material, pedogenetic processes, and soil development level (SILVA et al., 2016). In general, under these conditions, these metals neither present a real threat to ecosystems nor to human health, as they occur in low concentrations (ATSDR, 2012). According to Ng et al. (2016), the soil is the main reservoir of Cd, Pb, Mn, Zn, Cu, Ba, Fe, Co and Cr, in which the bioavailability is controlled by biotic and abiotic factors. Thus, the potential of a soil in supplying plants with these elements can help botanical, ecological, and agricultural investigations, since certain species of plants can have a preference and have different tolerance levels for specific elements. (KABATA-PENDIAS, 2010). For this author, the accumulation of some heavy metals in plants occurs in the following sequence: Ni > Zn > Pb > Mn > Cu; thus, being phyto-indicators of alterations in the natural heavy metals content in the soil.

From an ecological standpoint, the metal contents in soil, water and in plants allow us to make considerations as to the quality of the ecosystem (balance/environmental pollution) (MECHI; SANCHES, 2010). Thus, our knowledge regarding the origin and determination of natural metal contents in soil is of extreme importance to the establishment of environmental quality parameters of soils, which can guide the impact evaluation of human activities, since they are the main cause for increasing metal content in ecosystems (CONAMA, 2009).

In compliance with the national legislative organs, determining the natural content of the soil is necessary to frame it in the guiding parameters: Reference Guideline Values of Quality (RVQ), Variation Prevention (VP) and of Investigation (VI) (CONAMA, 2009). Through these numbers, it is possible to elaborate a legislation with monitoring norms and intervention measures, bearing in mind that determining natural concentrations allows us to differentiate the origin of these metals in the soil as natural or anthropic (SILVA et al., 2016; ALMEIDA JÚNIOR et al., 2016). Consequently, public authorities are capable of elaborating a specific legislation for monitoring and for legal interventions in line with the local reality (BAIZE; STERCKEMAN, 2001).

Only a few Brazilian states have had their natural heavy metal content defined, mainly because of their size, soil diversity, financial cost, and lack of professional (professional demand). São Paulo (CETESB, 2001), Espírito Santo (PAYE et al., 2010), Pernambuco (BIONDI et al., 2011a, b), Paraíba (ALMEIDA JÚNIOR et al., 2016), and Rio Grande do Norte (PRESTON et al., 2014) are prominent states compared to the others since they use this information for monitoring and for legal interventions befitting to the local reality. Thus, anthropic, agricultural, and urban actions able to increase heavy metal content levels could be avoided.

The state of Amazonas is still in need of this information, especially because of its global relevance and large territory, in addition to it possessing several types of soil each with peculiar characteristics, originated from different kinds of sediments. In this context, this study aimed to determine the contents of heavy metals in soils of three different physiographic regions of the southern part of Amazonas state, comparing it to the natural metal content of a few of the country's soils.

Material and Methods

This study was conducted in three physiographic regions of the southern Amazonas state: field-forest ecotone (F/F), animated relief (AR), and flooded/non-flooded (F/N). The F/N and F/F areas are located in the city of Humaitá. The flooded areas are susceptible to seasonal floods, which occur near the banks of muddy rivers, and, during these periods, accumulate material from other origins (allochthonous). The non-flooded areas undergo no flooding conditions, so being formed by tertiary sediments. They are transitional areas between current alluvial and Holocene deposits, as well as sediments from the Solimões Formation, Upper Pleistocene, containing material prevenient from continental, fluvial, and lacustrine environmental depositions (BRASIL, 1978).

The sediments of this formation come from two sedimentation cycles: a) bottom sandy banks, which represent the pluvial and fluvial sedimentation; and b) upper clayey sediments, indicating lacustrine sediments. The other regions are located in the city of Manicoré, resting on Rondonianos Granites of Intrusive cratogenic origin (BRASIL, 1978). Their mineralogical composition is characterized by muscovite, biotite, adamellites, and granodiorites (CAMPOS, 2009).

The climate of the region is of the rainy tropical (A) and monsoon (Am) type, with a short dry period (ALVARES et al., 2014). The rainy season starts in October and ends in June and the average annual rainfall ranges from approximately 2,250 to 2,750 mm. Average annual temperatures vary from 25º C to 27º C and average relative humidity of the air varies from 85 to 90%.

From August to December, in the years of 2014 to 2016, twelve representative soil profiles of the southern region of Amazonas were selected, i.e. four in each of the physiographic environments studied (Table 1). In each of these locations, two samples were collected using a steel auger at the 0.0-0.2 m and 0.8-1.00 m layers, totalizing 24 samples.

In the 0.0-0.2 m layer, ten subsamples were taken in a spacing of 3 m (each spaced out 3 m from the other), forming a compound sample, i.e. one subsample at the central point (mark), eight subsamples at the cardinal points (E, W, N, S, NE, NW, SW and SE), and one randomly chosen point. The homogeneity among the subsamples was considered for color, soil texture, topography, drainage, and vegetal cover (vegetation). At the 0.8-1.00 m layer, three simple auger samplings were randomly done for the formation of a compound sample (Table 2). The physical, chemical and Ki and Kr weathering analyses were conducted as described by Embrapa (2011). Grain size was determined by pipette analysis using a 0.1 N NaOH solution as a chemical dispersant and mechanical agitation in a high rotation device for 10 minutes. The fraction of clay was separated by sedimentation, the sand by sieving and silt was calculated by differentiation. The available organic carbon, Ca, Mg, Al, K, P, and potential acidity (H + Al) were determined (identified). Next, base sum (BS), cation exchange capacity (CEC), and base saturation (V %) were calculated. The pH was potentiometrically determined using the 1:2.5 soil ratio in water (Table 2).

Table 1. Classes, location, physiographic regions, municipality and geographic coordinates of the studied soils in Southern Amazonas.

Profile	Soil Classe	Municipality	Location
	Field/Forest		
P1	CAMBISSOLO HÁPLICO Alítico plíntico (Haplic Cambisol)	Humaitá-AM	07º30’22,6”S 63º04’57,3”W
P2	GLEISSOLO HÁPLICO Alítico típico (Haplic Gleysol)	Humaitá-AM	07º30’16,3”S 61º04’57,3”W
P3	CAMBISSOLO HÁPLICO Alítico gleissólico (Haplic Cambisol)	Humaitá-AM	07º29’59,0”S 63º04’50,0”W
P4	ARGISSOLO VERMELHO Alítico plíntico (Red Argisol)	Humaitá-AM	07º29’55,1”S 63º04’51,3”W
	Animated Relief		
P5	LATOSSOLO VERMELHO Distrófico típico (Red Latosol)	Manicoré-AM	07º59’58,8”S 61º34’27,7”W
P6	ARGISSOLO VERMELHO-AMARELO Distrófico abrúptico (Red – Yellow Argisol)	Manicoré-AM	07º59’51,6”S 61º34’36,7”W
P7	LATOSSOLO VERMELHO-AMARELO Eutrófico típico (Red – Yellow Latosol)	Manicoré-AM	07º59’54,8”S 61º34’46,4”W
P8	LATOSSOLO VERMELHO-AMARELO Distrófico típico (Red – Yellow Latosol)	Manicoré-AM	07º59’56,2”S 61º34’51,5”W
	Flooded/Non-Flooded		
P9	LATOSSOLO AMARELO Distrófico plíntico (Yellow Latosol)	Humaitá-AM	7º30’22”S 63º01’15”W
P10	LATOSSOLO AMARELO Distrófico argissólico (Yellow Latosol)	Humaitá-AM	7º30’22”S 63º01’15”W
P11	NEOSSOLO FLÚVICO Ta Eutrófico típico (Fluvisol Neosol)	Humaitá-AM	7º30’22”S 63º01’15”W
P12	NEOSSOLO FLÚVICO Ta Eutrófico gleissólico (Fluvisol Neosol)	Humaitá-AM	7º30’22”S 63º01’15”W

Embrapa (2013).

After naturally drying, the samples were weighed in nylon bags with 2-mm openings. Next, a portion of this material was collected and macerated in an agate mortar, and put through a stainless-steel strainer containing 0.074-mm openings, as in ABNT NBR nº 50, (with a stainless steel mesh), to avoid contaminations. The digestion consisted of transferring 1 g of the samples to Teflon tubes, and adding 9 mL of nitric acid and 3 mL of hydrochloric acid. After verifying the tubes were hermetically sealed, they were kept in a microwave oven (Mars Express) for 13 min, i.e. enough time for the equipment to reach 175º C, as in the EPA 3051A method (USEPA, 1998).

The acids used in the analyses were all of high purity (Merck PA). Dilutions and solutions were prepared with certified balloons and pipettes (NBR ISO/IEC), and in ultrapure water (Direct-Q 3 Millipore System). The extracts were filtered with quantitative paper filters – blue strip, slow filtration (Macherey Nagel®). For glassware cleaning and decontamination, the instruments were maintained in a 5% nitric acid solution for 24 hours, and dried with distilled water. The assessments of heavy metal contents were performed using atomic absorption spectrophotometry, flame photometry (air-acetylene). To evaluate the dependency between variables, principal component analysis was conducted, which is an exploratory multivariate technique to project the original information into a smaller set of latent variables, which are the eigenvectors constructed with the eigenvalues extracted from the covariance matrix, preserving the most relevant original information as possible (HAIR et al., 2005). After the standardization of the variables of the soil (heavy metals, chemical and physical), the number of components with eigenvalues above 1.00 were selected, as proposed by Kaiser (1958). Due to the exploratory character of the data, the descriptive statistics were performed (mean, median and deviation) and Pearson's linear correlations were established between the metals and the main soil attributes. All the statistical analyses were processed in the Statistica® software, version 7.0 (STATSOFT, 2008).

Results and Discussion

The variability of the heavy metal contents in the studied soils reflected the geologic and geomorphologic variations and the degree of pedogenesis of the southern region of Amazonas. The highest contents of heavy metals were observed in the Neosol profiles, situated in the F/N environments; following this order from lowest to highest: Ba > Zn > Fe > Cu > Pb > Co > Cd. While the highest content of Mn and Cr were observed in the Latosol and Argisol profiles of the AR. This is because these elements are concentrated in the form of oxides in more weathered soils (KABATA-PENDIAS, 2010; SILVA et al., 2016) (Table 3, 4, and 5).

The average contents of Cu, Co and Cd were higher in the Fluvisols (profiles 11 and 12) of the C/F physiographic region (Table 3). Although the contents present a wide range of variations of Cu (1.85 – 16.75 mg kg^{-1}) and Co (0.03 – 8.68 mg kg^{-1}), no abrupt variations were observed within a single horizon, which draws attention to Haplic Gleysol (profile 2), because of its Cu contents, nearly five times higher than those from the surface. This indicates a strong influence of materials carried in from other environments, especially during the flooding period.

Table 2. Physical and chemical characterization of soils in different physiographic environments in Southern Amazonas.

Point	Order	depth	pH H_2O	Ca	Mg	K	Al	H+Al	SB	CEC	V	OC	Sand	Silt	Clay	Ki	Kr
		cm	(1:2.5)	------------- cmolc kg^{-1}					------------------		%	g kg^{-1}	--------- g kg^{-1}		---------		
Field/Forest																	
1	Cambisol	0 – 20	4.6	0.1	0.03	0.07	3.1	5.6	0.3	7.2	3.5	26.14	239.8	614.3	145.9	0.91	0.56
		80 – 100	5.2	0.1	0.00	0.04	6.0	8.3	0.2	10.7	2.0	19.34	238.7	479.9	281.4	1.15	0.60
2	Gleysol	0 – 20	4.4	0.2	0.03	0.07	2.7	9.9	0.4	14.9	2.5	36.71	96.2	688.0	215.8	1.06	0.83
		80 – 100	5.1	0.2	0.77	0.04	9.3	10.1	2.8	20.9	13.1	18.45	34.0	529.5	436.5	0.83	0.52
3	Cambisol	0 – 20	3.9	0.2	0.13	0.07	3.1	7.0	0.3	11.7	4.9	24.97	274.8	595.9	129.3	1.12	0.73
		80 – 100	2.4	0.2	0.01	0.04	5.3	7.5	0.2	12.4	2.3	19.40	308.4	200.6	491.0	1.25	0.85
4	Argisol	0 – 20	4.5	0.2	0.14	0.16	4.5	10.9	16.6	16.6	3.2	32.91	66.0	736.7	197.3	1.19	0.70
		80 – 100	4.9	0.1	0.03	0.04	5.4	8.1	19.1	18.9	1.3	19.85	49.4	705.2	245.4	0.86	0.52
Animated Relief																	
5	Latosol	0 – 20	4.0	0.1	0.1	0.1	1.7	13.2	0.3	11.1	14.0	40.0	223.3	478.8	297.9	0.42	0.19
		80 – 100	4.6	0.2	0.0	0.0	0.6	6.4	0.3	4.8	9.0	30.54	184.9	269.6	545.5	0.33	0.15
6	Argisol	0 – 20	4.4	0.2	0.2	0.1	0.6	5.0	1.5	4.6	34.0	28.85	231.0	546.8	222.2	0.79	0.33
		80 – 100	5.2	0.2	0.3	0.0	0.4	1.7	1.0	2.2	44.0	21.25	536.8	0.8	462.4	0.73	0.36
7	Latosol	0 – 20	3.9	0.1	0.1	0.1	1.7	3.3	0.8	2.1	37.0	28.00	598.9	177.7	223.4	0.90	0.43
		80 – 100	4.5	0.2	0.0	0.0	1.7	3.4	1.3	2.5	51.0	19.60	364.9	265.0	370.1	0.87	0.37
8	Latosol	0 – 20	3.7	0.1	0.1	0.1	2.5	8.4	0.8	2.1	37.0	29.40	255.2	120.0	624.8	0.80	0.35
		80 – 100	4.7	0.2	0.0	0.0	0.9	3.3	1.3	2.5	51.0	23.05	174.3	322.0	503.7	0.77	0.38
Flooded/Non-Flooded																	
9	Latosol	0 – 20	3.4	0.5	0.2	0.1	3.4	13.8	1.0	9.5	11.0	89.92	347.4	490.6	162.0	0.71	0.52
		80 – 100	3.9	0.4	0.2	0.0	4.8	8.0	0.8	5.2	17.0	79.68	121.8	784.7	93.5	1.18	0.64
10	Latosol	0 – 20	3.4	0.7	0.5	0.1	4.8	11.2	1.6	9.2	18.0	26.56	499.1	316.8	184.1	0.84	0.57
		80 – 100	3.9	0.4	0.3	0.0	3.3	4.4	0.9	6.8	13.0	19.52	681.6	190.1	128.3	0.87	0.53
11	Neosol	0 – 20	3.8	12.8	2.5	0.2	4.6	12.8	15.9	21.6	74.0	87.04	16.9	472.9	510.2	1.37	0.65
		80 – 100	4.2	11.7	1.2	0.1	3.2	7.7	13.4	19.0	71.0	83.52	6.0	609.8	384.2	1.12	0.64
12	Neosol	0 – 20	4.0	10.2	0.8	0.1	7.1	16.5	11.4	18.3	63.0	86.72	12.3	659.1	328.6	1.26	0.68
		80 – 100	4.5	31.0	1.1	0.1	8.4	16.3	32.4	41.1	79.0	75.20	1.1	859.4	139.5	1.15	0.62

SB= Sum of bases; CEC = Cation exchange capacity; V= Base saturation; CO= Organic carbon; Ki e Kr= Degree of soil weathering.

Table 3. Natural contents of Cu, Co and Cd in the surface (sup.) and subsurface (sub.) horizon of the main classes of soils in Southern Amazonas.

Profile	Cu		Co		Cd	
	Sup	Sub	Sup	Sub	Sup	Sub
	------------------ mg kg^{-1} ------------------					
			Field/Forest			
1	2.43	3.15	0.20	0.50	<Ld	<Ld
2	16.75	3.43	0.28	0.88	<Ld	<Ld
3	1.85	2.43	0.25	0.48	<Ld	<Ld
4	3.00	3.18	0.45	0.48	<Ld	<Ld
Average	6.01	3.05	0.30	0.59	0.00	0.00
			Animated Relief			
5	6.63	8.85	0.10	0.03	<Ld	<Ld
6	3.95	3.93	1.63	0.80	<Ld	<Ld
7	3.78	5.85	1.85	2.03	<Ld	<Ld
8	7.45	8.55	3.38	2.18	<Ld	<Ld
Average	5.45	6.80	1.74	1.26	0.00	0.00
			Flooded/Non-Flooded			
9	3.10	3.48	0.05	0.85	<Ld	<Ld
10	3.63	3.78	0.20	0.35	<Ld	<Ld
11	21.40	19.63	6.48	6.38	0.23	0.05
12	16.25	14.43	8.28	8.68	0.08	0.13
Average	11.10	10.33	3.75	4.07	0.08	0.05
Median	3.86	3.85	0.36	0.83	0.00	0.00
Average	7.52	6.72	1.93	1.97	0.03	0.01
Standart deviation	6.71	5.36	2.76	2.72	0.07	0.04
Asymmetry	1.26	1.65	1.65	1.97	2.90	2.78
Kurtosis	0.12	2.13	1.73	3.02	8.71	7.81

< Ld: Less than the detection limit.

Table 4. Natural contents of Fe, Mn and Zn in the surface (sup.) and subsurface (sub.) horizon of the main classes of soils in Southern Amazonas.

Profile	Fe		Mn		Zn	
	Sup	Sub	Sup	Sub	Sup	Sub
	---------- g kg^{-1} ---------		----------------------- mg kg^{-1} ----------------------			
			Field/Forest			
1	8.24	19.74	0.03	0.12	1.85	1.68
2	3.37	20.45	0.13	0.06	8.05	2.80
3	6.57	22.76	0.26	0.08	1.93	1.00
4	8.62	7.15	0.37	0.04	5.70	2.28
Average	6.70	17.53	0.20	0.08	4.38	1.94
			Animated Relief			
5	23.76	14.32	0.56	0.46	2.63	1.60
6	16.67	12.45	7.20	1.76	1.55	0.35
7	12.24	11.50	6.00	3.79	1.10	2.43
8	16.07	25.96	7.55	6.73	2.95	2.63
Average	17.19	16.06	5.33	3.19	2.06	1.75
			Flooded/Non-Flooded			
9	5.87	14.39	0.01	0.41	1.28	<Ld
10	7.06	14.48	0.19	0.26	0.60	<Ld
11	22.32	28.67	3.07	1.97	46.93	43.53
12	23.80	26.45	5.74	7.45	49.43	24.88
Average	14.76	21.00	2.25	2.52	24.56	17.10
Median	10.43	17.11	0.47	0.44	2.28	1.98
Average	12.88	18.19	2.59	1.93	10.33	6.93
Standart deviation	7.41	6.8	3.12	2.66	17.81	13.38
Asymmetry	0.45	0.10	0.70	1.44	2.00	2.41
Kurtosis	-1.39	-1.14	-1.51	0.79	2.50	5.35

< Ld: Less than the detection limit.

Table 5. Natural contents of Ba, Cr and Pb in the surface (sup.) and subsurface (sub.) horizon of the main classes of soils in Southern Amazonas.

Profile	Ba		Cr		Pb	
	Sup	Sub	Sup	Sub	Sup	Sub
	------------------------------------- mg kg^{-1} –------------------------------------					
	Field/Forest					
1	12.63	17.33	7.58	14.63	6.08	8.78
2	33.78	21.88	8.33	12.35	14.28	12.10
3	10.88	14.23	5.48	16.70	4.20	6.63
4	26.00	22.65	6.60	6.13	6.85	6.60
average	20.07	19.02	7.00	12.45	7.85	8.53
	Animated Relief					
5	3.03	1.68	33.50	24.45	6.95	5.05
6	4.95	8.25	25.85	24.28	9.23	7.35
7	4.03	5.73	9.08	9.23	8.45	9.70
8	6.83	15.23	13.63	19.80	11.43	10.30
Average	4.71	7.72	20.52	19.44	9.02	8.10
	Flooded/Non-Flooded					
9	8.75	8.40	5.20	13.73	2.55	2.68
10	9.95	14.45	7.13	12.03	4.93	4.55
11	150.45	55.48	17.15	19.15	20.18	19.33
12	80.18	98.50	13.90	15.95	12.63	8.48
Average	62.33	44.21	10.85	15.22	10.07	8.76
Median	9.35	14.84	8.7	15.29	7.70	7.91
Average	29.04	23.65	12.78	15.7	8.98	8.46
Standart deviation	43.96	27.27	8.86	5.59	4.96	4.31
Asymmetry	2.36	2.29	1.52	0.1	1.01	1.40
Kurtosis	5.51	5.34	1.69	-0.44	1.00	3.08

In F/F and AR profiles (1, 2, 3, 4, 5, 6, 7 and 8) and in the F/N profiles (9 and 10), concentrations were lower than the detection limit (DL), corresponding to almost 83% of the profiles analyzed. Only in the environments F/F (profile 2) and F/N (profile 11 and 12) was the presence of Cd observed. However, even for these environments, the results were lower than the prevention value (VP = 1.3 mg kg^{-1}) stated by CONAMA (2009), and are similar to the contents found in the States of Espírito Santo (<0.13 mg kg^{-1}) (PAYE et al., 2010), São Paulo (<0.5 mg kg^{-1}) (CETESB, 2001) and Paraíba (0.08 mg kg^{-1}) (ALMEIDA JÚNIOR et al., 2016).

Besides the geomorphologic aspects conditioning the accumulation and maintenance of heavy metals in the F/N environment, the Lithologic composition of the Argisols (Rondonianos Granite) is a determining factor in the elevated levels of Fe found in this environment. These soils, represented by profiles P11 and P12, are pedogenetically less evolved, as shown by the Ki ratio (1.37 and 1.26) (Table 2). Thus, this environment contains higher concentration and maintenance of Fe than the soils from other physiographic regions, because of its richness in Fe minerals, such as smectite, vermiculite, and biotite, which, when broken throughout time, release Fe into the soil.

Contrastingly to the F/N soils, the soils from the AR physiographic region are more weathered because of oxidizing conditions and free drainage (CAMPOS, 2009). In this case, the desilicatization (Ki=0.33 to 0.77) was intense, making residual minerals, such as Fe oxides, predominant (EMBRAPA, 2013); thus, explaining the high levels of Fe in the Latosol profiles 5 and 8. Yet the highest Fe levels, in the subsurface of the transitional F/F regions, are attributed to the ferruginous concretions in the plinthic P1 profile (with plinthic characteristics); while in the P2 profile, to the reducing conditions (Fe^{+2}) of the environment. Still, all the Fe contents were higher in the subsurface, i.e. closer to the rock. The magnitude of the Fe contents in the southern region of Amazonas, found in this study, is in agreement with the results reported by Biondi et al. (2011), but much lower than those observed by Caires (2009).

The major abundance of Mn was found in the soils with elevated Fe content (profiles 11 and 12), especially in more weathered soils (profiles 6, 7 and 8), exhibiting the same geochemical behavior; i.e. they are constituents of ferromagnesian rock, as reported by Biondi et al. (2011). However, Mn contents reported here were much lower than were those of Fe and Mn ones quantified by Caires (2009) and Biondi et al. (2011).

Zinc levels were highest in superficial and subsurface horizons of F/N soils, which presented 46.93 and 43.53 mg kg^{-1}, respectively, for the Fluvisol (profile 11) (Table 4); followed by profile 12, 49.43 and 24.88 mg kg^{-1}. In general, the Zn contents were inferior to other studies (SU; YANG, 2008; BIONDI et al., 2011; PRESTON et al., 2014; ALMEIDA JÚNIOR et al., 2016), confirming the low Zn supplying lithology potential in the southern region of Amazonas, as verified by the low contents in the subsurface horizons.

The highest levels of Ba were recorded in the F/N and F/F soils, possibly because of the incipient weathered soils from the flooded areas and the formation of Mn concretions and Fe oxyhydroxides with plinthic characteristics (KABATA-PENDIAS, 2010) (Table 5). In the AR soils, lower contents of Ba occurred due to the more intense weathering (Latosols and Argisols). In the F/N areas, we noted an increase of Ba contents at the surface of profile 11 (150 mg kg^{-1}), surpassing the results of VP (150 mg kg^{-1}), established by CONAMA (2009) for the subsurface horizon (55.48 mg kg^{-1}). The disparity of results between the two horizons occurred due to surrounding sediment transportation (allochthonous), while the subsurface horizon reflected the material of origin (autochthonous).

The highest contents of Cr were found in the Highland region, Red Latosol (profile 5) and Red-Yellow Argisol (profile 6), having lower levels than most of the reference results from the rest of the Brazilian regions; e.g. São Paulo (40.0 mg kg^{-1}) (CETESB, 2001) and Espírito Santo (54.13 mg kg^{-1}) (PAYE et al., 2010).

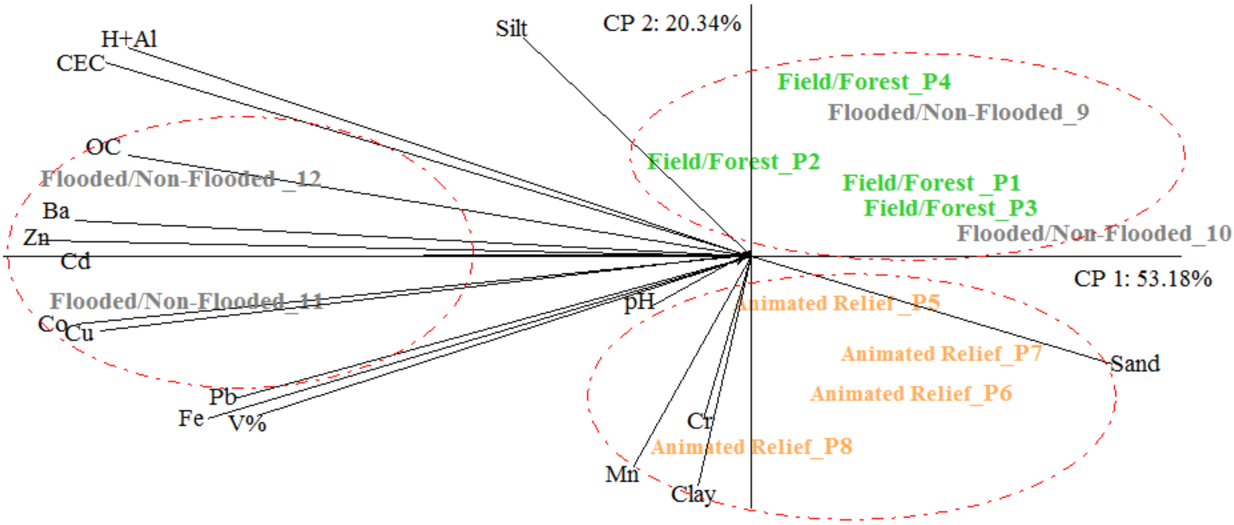
Regarding Pb (Table 5), the highest results were observed in Fluvisols (profiles 11 and 12) and Haplic Gleysol (profile 2), which coincide with the elevated levels of Fe, because of its intense affinity with Fe oxides, forming more stable connections (KABATA-PENDIAS, 2010). In general, the soils presented no environmental contamination risks, since they contained lower Pb contents than the VP (72 mg kg^{-1}), as determined by CONAMA (2009). Comparing the levels of Pb, it is possible to notice the similar averages of Pb content in Gleysol (7.08 mg kg^{-1}), Neosol (14.64 mg kg^{-1}) and in Latosol (10.81 mg kg^{-1}) (PAYE et al., 2010).

The results obtained from the principal component analysis (PCA) showed different patterns in the soils of the physiographic regions (Table 6 and Figure 1). The variance quantity retained in the first two principal components was of 73.52% (53.18% in CA1 and 20.34% in CA2). CA1 was characterized by a process involving the variables: H+Al, CEC**,** V%, OC (organic carbon), sand, Cu, Co, Cd, Fe, Zn, Ba, and Pb. Figure 1 shows that the F/N environment (profiles 11 and 12) was characterized by high values of CEC, V%, CO, Ba, Zn, Cd, Co, Cu, Pb and Fe and low pH, Cr, Mn, clay, silt and sand results, while the information on the silt, clay, Mn and Cr variables were retained in CA2. However, the soils with the highest sand contents were less associated to the heavy metal contents, when the latter presented no geochemical process.

Table 6. Correlation between each principal component, heavy metals and soil attributes in the surface and subsurface horizons of the physiographic regions Field/Forest, Animated Relief and Flooded/Non-Flooded in Southern Amazonas.

Variables	CP1	CP2
pH	-0.029868	-0.073387
H+Al	-0.657594	0.611095
CEC	-0.758349	0.547329
V%	-0.788136	-0.463869
OC	-0.747092	0.277417
Sand	0.707093	-0.336200
Silt	-0.479792	0.810580
Clay	-0.284924	-0.770466
Cu	-0.947069	-0.147928
Co	-0.933165	-0.133600
Cd	-0.967379	0.023406
Fe	-0.818926	-0.424537
Mn	-0.423150	-0.644193
Zn	-0.977102	0.030389
Ba	-0.961349	0.142645
Cr	-0.207811	-0.601706
Pb	-0.752758	-0.322685

Figure 1. Principal component analysis (PCA) based on soil variables in different physiographic of Southern of the state of Amazonas.



In profile 11 (Eutric Fluvisol) and in profile 12 (Fluvi-Eutric Gleysol) (Figure 1), chemically richer soils were observed, which can be confirmed by the CEC and V% attributes. The highest values of organic C are due to the hydromorphic conditions of the soil in the flooded area, which slow down organic matter (OM) decomposition. Thus, organic carboxylic and phenolic radicals release H^+ (RANGEL; SILVA, 2007), which will compose the CEC and complex metals, such as Fe, Cd, Ba, Zn, Co, Cu and Pb (LI et al., 2013).

The contents of Cr and Mn were strongly associated with the soils containing higher levels of clay, i.e. soils in advanced decomposition stages, especially in profile 8, regarding the dystrophic Latosol. Yet, the other profiles (5, 6, and 7) of the AR pedological unit were differentiated because of the sand contents. On the other hand, none of the variables was capable of differentiating the profiles 1, 2, 3, and 4 from the F/F pedological units, and profiles 9 and 10 physiography F/N**.** However, the proximity of these environments suggests transitional environments, possibly because of the seasonal effect, which consists of flooding during the rainy season and drying during the drought periods (CAMPOS, 2009).

Positive correlations (Table 7) were found for Cu, which was the only element to establish correlation ($p<0.01$) with Ba (r-0.85; r=0.70, Cd (r = 0.82; r = 0.72), Zn (r =0.83; r = 0.93), Co (r = 0.72; r = 0.85) and Pb (r = 0.91; r = 0.67) for both horizons. These close relations (r>67%) suggest a common association with Rondonianos Granite. Although the clay content presented no positive correlation in the subsurface horizon, this was the attribute that best correlated ($p<0.01$) in the superficial horizon with Co (r = 0.64), Pb (r = 0.68) and Mn (r = 0.58). As highlighted by Li et al. (2013), higher contents of clay elevate the CEC, and the Fe and Al contents, maximizing adsorption of heavy metals in the sorption complex.

The Fe and clay contents in the superficial horizon (r = 0.62) showed significant correlation, indicating predominance of this metal in soils containing higher clay content. Additionally, they were concentrated especially in the forms of clay minerals and Fe oxides of the most weathered soils (Latosol and Argisol). Fe positively and significantly correlated ($p < 0.01$ and $p < 0.05$) to Cr (r = 0.77) at the surface, while correlating to Ba (r = 0.60), Cu (r = 0.64) and Pb (r = 0.61) at the subsurface, and in both horizons to Co (r = 0.71; r = 0.65) and Zn (r = 0.61; r = 0.64).

Table 7. Pearson correlation coefficients among the metal contents in reference soils of Southern Amazonas.

	Surface									
	Ba	Cd	Co	Zn	Cu	Pb	Cr	Fe	Mn	Al
Cd	0.98**									
Co	0.77**	0.73**								
Zn	0.92**	0.86**	0.91**							
Cu	0.85**	0.82**	0.72**	0.83**						
Pb	0.81**	0.81**	0.72**	0.73**	0.91**					
Cr	0.07^{ns}	0.15^{ns}	0.18^{ns}	0.13^{ns}	0.20^{ns}	0.27^{ns}				
Fe	0.48^{ns}	0.50^{ns}	0.71**	0.61*	0.46^{ns}	0.50^{ns}	0.77**			
Mn	0.10^{ns}	0.12^{ns}	0.59**	0.25^{ns}	0.18^{ns}	0.41^{ns}	0.34^{ns}	0.55^{ns}		
Al	0.10^{ns}	0.16^{ns}	0.04^{ns}	0.13^{ns}	0.30^{ns}	0.25^{ns}	0.85**	0.63*	-0.02^{ns}	
pH	-0.06^{ns}	-0.14^{ns}	-0.16^{ns}	-0.08^{ns}	0.00^{ns}	0.14^{ns}	0.13^{ns}	-0.08^{ns}	-0.04^{ns}	0.11^{ns}
OM	-0.43^{ns}	-0.42^{ns}	-0.51^{ns}	-0.46^{ns}	-0.10^{ns}	-0.06^{ns}	0.42^{ns}	-0.04^{ns}	-0.20^{ns}	0.61*
Clay	0.47^{ns}	0.52^{ns}	0.64*	0.46^{ns}	0.55^{ns}	0.68*	0.35^{ns}	0.62*	0.58*	0.24^{ns}
	Subsurface									
	Ba	Cd	Co	Zn	Cu	Pb	Cr	Fe	Mn	Al
Cd	0.97**									
Co	0.93**	0.94*								
Zn	0.78**	0.74*	0.86**							
Cu	0.70**	0.72*	0.85**	0.93**						
Pb	0.41^{ns}	0.31^{ns}	0.54^{ns}	0.76**	0.67*					
Cr	-0.02^{ns}	0.09^{ns}	0.10^{ns}	0.17^{ns}	0.35^{ns}	0.10^{ns}				
Fe	0.60*	0.55^{ns}	0.65*	0.64*	0.64*	0.61*	0.36^{ns}			
Mn	0.56^{ns}	0.63*	0.70*	0.36^{ns}	0.54^{ns}	0.25^{ns}	0.17^{ns}	0.48^{ns}		
Al	0.04^{ns}	0.19^{ns}	0.20^{ns}	0.25^{ns}	0.53^{ns}	0.09^{ns}	0.81**	0.17^{ns}	0.25^{ns}	
pH	-0.1^{ns}	-0.02^{ns}	-0.02^{ns}	-0.06^{ns}	0.04^{ns}	0.16^{ns}	0.57^{ns}	0.48^{ns}	0.10^{ns}	0.37^{ns}
OM	-0.11^{ns}	-0.08^{ns}	-0.07^{ns}	-0.20^{ns}	-0.17^{ns}	-0.03^{ns}	0.45^{ns}	-0.10^{ns}	0.21^{ns}	0.13^{ns}
Clay	-0.3^{ns}	-0.35^{ns}	-0.22^{ns}	-0.08^{ns}	0.00^{ns}	0.37^{ns}	0.27^{ns}	-0.15^{ns}	0.01^{ns}	0.31^{ns}

** Significant at 1% ($p < 0.01$); * Significant at 5% ($p < 0.05$); ns: not significant.

In compliance with Araújo et al. (2002), this is due to its strong affinity to OH^- radicals, in the surface of the Fe oxides, and, on the other hand, is less correlated to humic substances, as revealed by the negative correlations between OM and Ba, Cd, Co, Zn, Cu, Pb, Cr, and Mn. This behavior shows that the contents of Ba, Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn in soils from the southern Amazonas state are of natural origin, as a large part of these metals is associated with the inorganic fraction of the soil.

Conclusions

The results reported in this study indicate that soils of the southern Amazonas state have a low potential of supplying heavy metals. The contents of these elements found are in the following decreasing order: Ba>Fe>Cr>Pb>Zn>Cu>Mn>Co>Cd.

The natural contents of heavy metals vary depending on the soil type, weathering level and, physiographic regions, being similar or inferior to the contents found in other Brazilian regions. For most of the evaluated metals, Neosols presented the highest natural contents, while Cambisols showed the lowest ones.

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