

Evaluation of the roles of metals and humic fractions in the podzolization of soils from the Amazon region using two analytical spectroscopy techniques

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3 **Evaluation of the roles of metals and humic fractions in the podzolization of soils**
4 **from the Amazon region using two analytical spectroscopy techniques**
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62 **ABSTRACT**
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65 Soil organic matter (SOM) plays an important role in environmental
66 sustainability, since it is involved in carbon and nutrient cycling. Consequently, it is a
67 key factor to consider in studies concerning global climate change and agronomy.
68 Among the main components of SOM are humic substances (HS), which are divided,
69 according to their solubility, into humic acid (HA), fulvic acid (FA), and humin (HU)
70 fractions. Study of the chemical properties of this organic matter is important for
71 understanding the biogeochemical processes occurring in the soil. The aim of this work
72 was to determine the metals iron (Fe) and aluminum (Al), using flame atomic
73 absorption spectrometry (FAAS) and laser-induced breakdown spectroscopy (LIBS), in
74 order to elucidate the role of organic matter in the transport of these metals in
75 Amazonian soils. The results showed that FA was important for Al, while the HA
76 fraction was more selective towards Fe. The translocations of these metals to deeper
77 profiles in two different soils involved either young and less humified organic matter, or
78 older organic matter with a low degree of humification. Therefore, these two humic
79 fractions were involved in the process of soil podzolization, with FA having a
80 predominant role in the transport of Al, while HA was mainly responsible for the
81 transport of Fe.
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94 **Keywords:** LIBS, FAAS, Organic matter, Amazon.
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1. Introduction

The Amazon forest provides important services to humanity and the environment, including high biodiversity, climate regulation, carbon sequestration, and regulation of water and nutrient cycles. Soils play crucial roles in most of the processes that occur on the planet, due to their participation in the main biogeochemical cycles [1]. These involve pedogenetic processes transforming rocks and sediments, whose characteristics are influenced by combinations of soil formation factors such as the source material, climate, microorganisms, and time [2].

In the Amazon, Spodosols develop over time from clay soil or sedimentary formations. Organometallic iron (Fe) and aluminum (Al) oxides present in horizons A and E are transported to deeper soil layers, where they accumulate and give rise to horizons rich in organic matter and organometallic species [3]. Hence, organic matter in these soils plays a key role in environmental sustainability, since it is related to carbon and nutrient cycling, and is a crucial factor to consider in studies in the fields of global climate change and agronomy. Humic substances (HS) are among the main components of SOM and can be classified, according to their solubility, into humic acid (HA), fulvic acid (FA), and humin (HU) fractions [4].

Determination of the chemical properties of the organic matter, as well as its interaction with metallic species, is essential for understanding the main processes that occur in the soil. The techniques that have been described for this purpose include flame atomic absorption spectrometry (FAAS) and, more recently, laser-induced breakdown spectroscopy (LIBS). The latter is an attractive technique due to its high sensitivity and precision, as well as the requirement for only minimal sample preparation, making it attractive for use in applications that comply with the concepts of Green Chemistry [5]. This technique is a type of atomic emission spectrometry that uses the generation of plasma by means of high power pulses, resulting in ablation of a small portion of the sample. This material dissociates into ions and excited atoms, emitting a continuum of radiation that enables the measurement of atomic/ionic emission lines and identification of the main elements present in the sample [6].

The main advantages of LIBS are the potential for simultaneous multi-element soil analysis with minimal sample preparation, high processing speed, and low cost of analysis, compared to traditional methods. The LIBS technique has been evaluated as an alternative method for the quantification of contaminants, macro/micronutrients, and carbon (C) in soils [7-9]. It has been used in investigations of texture, pH, and macro-

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180 and micronutrients in fertilizers and soil organominerals [10-12]. However, although
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182 LIBS has been used for soil analysis, it has not previously been employed to investigate
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184 the chemical fractions present in the soil.

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186 The aim of this study was to use the FAAS and LIBS techniques to quantify the
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188 metals Fe and Al in Amazonian Spodosols. The metals were quantified in whole soil
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190 samples and in the different humic fractions (HA, FA, and HU), in order to understand
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192 the role of the SOM in the transport of these metals during the podzolization process.

193 **2. Materials and Methods**

194 *2.1. Study area*

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197 The soil samples (two Spodosols, denoted P1 and P4) were obtained from a site
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199 located in the north of the municipality of Barcelos, near the Demeni River
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201 (0°15'18''N; 62°46'36''W) in the middle watershed of the Negro River region in the
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203 Amazon plains of Brazil. The regional geology is characterized by sediments of the Içá
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205 formation. Sample P1 was from a permanently waterlogged podzol covered by
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207 herbaceous meadow of scrubs and grass, locally known as “campina”. Sample P4 was
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209 from a well-drained podzol under rainforest vegetation, with no influence of
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211 groundwater. Further details of the study area can be found in Tadini et al. [13].

212 *2.2. Preparation of the samples for analysis*

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214 The procedures adopted for sampling, preservation, and preparation of the soils
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216 followed the recommendations of official methods [14-16]. Extraction and purification
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218 of the humic acid (HA), fulvic acid (FA), and humin (HU) fractions followed the
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220 procedures proposed by the International Humic Substances Society (IHSS), as used by
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222 Rice and MacCarthy [17], and Swift [18].

223 *2.3. Flame atomic absorption spectrometry (FAAS)*

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225 Sample decomposition was performed using 100 mg portions of the soils and the
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227 humic fractions (HA, FA, and HU), following the recommendations of the United States
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229 Environmental Protection Agency (Method 3052) [19]. Quantification of Fe and Al was
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231 performed using a PerkinElmer PinAAcle 900T flame atomic absorption spectrometer.
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233 Calibration curves were constructed using metal standard solutions and a blank (water)
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235 prepared in 1.0 mol⁻¹ HCl (comparable to the sample preparation).
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2.4. Laser-induced breakdown spectroscopy (LIBS)

The LIBS system employed a Nd:YAG laser operating at 532 nm in the visible (VIS) region. The VIS pulse had a maximum energy of 180 mJ, a width of 4 ns, and was generated by a QuantaL Brilliant Q-Switched Nd:YAG laser coupled to a second harmonic generator module. An ARYELLE 400-Butterfly system was used to detect and select the wavelengths. The spectrometer was operated in the spectral range 175-330 nm, with resolution of 13-24 pm, and was equipped with an intensified charge-coupled device (ICCD) camera (1024 × 1024 pixels). The beam from the lasers was directed and focused on the sample by means of dichroic mirrors at appropriate wavelength. Two lenses were placed between the sample and the tip of the fiber, for efficient collection of the emitted plasma. The sample support was placed in a micro-controlled x-y stage to enable easy and fast scanning by the laser beam impinging on it. An eight-channel pulse generator (Model 9618, Quantum Composers) was used to synchronize the delay time between pulse and the detection acquisition during the experiments.

Acquisition of the LIBS spectra was performed using a 532 nm visible laser beam with energy of 30 mJ and accumulation of 5 laser shots. The beam was focused and aligned to hit the sample in overlapping laser shots mode. The gate width was set at 1.5 μs and the gate time at 1.0 μs. Each whole soil and humic fraction sample was submitted to 30 measurements performed in different positions.

The outlier spectra were excluded using a technique called Spectral Angle Mapper (SAM) [20], involving calculation of a normalized scalar product between the individual spectrum and the average spectrum, returning a value between -1 and 1. The closer the value is to 1, the greater the similarity between the spectra. The imposition of a limit below 1 enables the exclusion of spectra that differ from the average. The use of this procedure resulted in elimination of only around 2% of the spectra, indicative of good stability of the experimental system. Finally, an average spectrum was calculated for each sample.

2.4. Transitions identification

Identification of the Fe and Al transitions was performed using pixel correlation [11] and the NIST database [21]. Briefly, calculation was made of the linear Pearson correlation between the intensity of a specific pixel and the variation of the concentration. This process was repeated for all pixels in the spectrum. The reference

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298 elemental concentration value was measured by FAAS. In this way, the pixels with
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300 higher correlation values were more likely to be representative of a transition line. This
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302 analysis assisted in eliminating saturated transitions and those with interference. As a
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304 result, three transition lines were selected for each metal: Al I (237.20 nm), Al II
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306 (265.25 nm), Al (281.62 nm), Fe I (248.33 nm), Fe II (273.95 nm), and Fe (302.05 and
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308 302.06 nm). The last Fe transition is a superposition of two Fe lines, so the integrated
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310 area of the entire region was used as a single intensity value.

311 *2.5. Multivariate calibration*

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313 The LIBS intensity was linearly correlated with the Al and Fe concentrations of
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315 the samples, resulting in a calibration curve. The LIBS intensity was obtained by means
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317 of a multivariate calculation involving the areas for each transition and the area for the
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319 background, as shown in Equation 1:

$$320 \quad I = \alpha_1 * A_1 + \alpha_2 * A_2 + \alpha_3 * A_3 - \beta * C \quad (1)$$

321 where A_i is the area of each atomic transition, C is the background area, and α_i and β are
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323 positive parameters fitted to the best linear correlation. The A_i values were calculated by
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325 summing the intensities of pixels inside a transition. The value of C was obtained as the
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327 sum of the intensities in a region with no apparent transitions.

328 **3. Results and Discussion**

329
330 Table 1 shows the values for carbon, Fe, and Al in the whole soil samples and
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332 in the humic fractions extracted from the Amazonian Spodosols, obtained using FAAS.
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Table 1. Concentrations of carbon (%) and the metals Fe and Al (g/kg) in the whole soil samples and in the humic fractions (HA, FA, and HU) extracted from the Amazonian Spodosols.

Metals	Samples			Carbon (%)				Concentration of metals (g/kg)			
	Area	Horizon	Depth (cm)	Soils	HA	FA	HU	Soils	HA	FA	HU
Fe	P1	A	0-15	22.5 ± 0.9	45 ± 3	18.2 ± 0.5	52.03 ± 0.08	1.20 ± 0.01	0.4 ± 0.2	0.07 ± 0.01	0.3 ± 0.1
		A-E	15-30	1.01 ± 0.09	51 ± 1	26.9 ± 0.2	24.38 ± 0.01	0.95 ± 0.01	0.3 ± 0.1	*	0.2 ± 0.1
		Bh	40-50	2.1 ± 0.2	56.2 ± 0.2	36.8 ± 0.8	36.67 ± 0.03	0.77 ± 0.01	0.3 ± 0.1	0.12 ± 0.01	0.2 ± 0.1
		Bh-C	240	3.2 ± 0.2	46 ± 2	47.9 ± 0.1	*	6.44 ± 0.01	0.6 ± 0.2	*	0.4 ± 0.1
		C	350	1.2 ± 0.2	51 ± 3	38.7 ± 0.9	5.17 ± 0.00	2.13 ± 0.01	0.2 ± 0.1	0.07 ± 0.01	1.0 ± 0.2
	P4	A	0-20	3.9 ± 0.2	45.2 ± 0.3	34 ± 3	41.43 ± 0.07	2.29 ± 0.01	1.8 ± 0.5	0.2 ± 0.1	0.2 ± 0.1
		A	20-30	3.5 ± 0.2	49.4 ± 0.01	21.6 ± 0.2	*	2.28 ± 0.01	1.9 ± 0.4	*	0.2 ± 0.1
		A	30-40	0.89 ± 0.01	50 ± 2	10.8 ± 0.1	5.76 ± 0.02	2.60 ± 0.01	2.3 ± 0.3	*	0.3 ± 0.1
		Bh	110-120	0.42 ± 0.02	50.0 ± 0.1	39.8 ± 0.6	*	1.81 ± 0.01	1.1 ± 0.2	*	0.4 ± 0.1
		Bh	170-180	0.38 ± 0.01	52 ± 6	3.1 ± 0.0	5.33 ± 0.02	1.72 ± 0.01	1.4 ± 0.2	*	0.3 ± 0.1
Al	P1	Bh	370-380	0.48 ± 0.01	52.8 ± 0.3	32.8 ± 0.2	2.26 ± 0.01	2.49 ± 0.01	1.2 ± 0.6	*	0.4 ± 0.1
		Bh	380-390	0.78 ± 0.01	54.5 ± 0.5	34.5 ± 0.3	*	1.66 ± 0.01	1.3 ± 0.2	*	0.3 ± 0.1
		A	0-15	22.5 ± 0.9	45 ± 3	18.2 ± 0.5	52.03 ± 0.08	43 ± 1	*	16.8 ± 0.2	*
		A-E	15-30	1.01 ± 0.09	51 ± 1	26.9 ± 0.2	24.38 ± 0.01	39 ± 1	*	13.8 ± 0.5	*
		Bh	40-50	2.1 ± 0.2	56.2 ± 0.2	36.8 ± 0.8	36.67 ± 0.03	57 ± 1	*	8.8 ± 0.3	*
	P4	Bh-C	240	3.2 ± 0.2	46 ± 2	47.9 ± 0.1	*	92 ± 1	*	*	*
		C	350	1.2 ± 0.2	51 ± 3	38.7 ± 0.9	5.17 ± 0.00	52 ± 1	*	20.0 ± 0.1	5.0 ± 0.1
		A	0-20	3.9 ± 0.2	45.2 ± 0.3	34 ± 3	41.43 ± 0.07	48 ± 1	6.4 ± 0.4	9.5 ± 0.1	*
		A	20-30	3.5 ± 0.2	49.4 ± 0.01	21.6 ± 0.2	*	47 ± 1	*	27.2 ± 0.2	*
		A	30-40	0.89 ± 0.01	50 ± 2	10.8 ± 0.1	5.76 ± 0.02	46 ± 1	*	17.5 ± 0.1	*
P4	Bh	110-120	0.42 ± 0.02	50.0 ± 0.1	39.8 ± 0.6	*	39 ± 1	*	13.7 ± 0.4	*	
	Bh	170-180	0.38 ± 0.01	52 ± 6	3.1 ± 0.0	5.33 ± 0.02	49 ± 1	*	16.5 ± 0.3	*	
	Bh	370-380	0.48 ± 0.01	52.8 ± 0.3	32.8 ± 0.2	2.26 ± 0.01	41 ± 1	*	20.5 ± 0.2	*	
	Bh	380-390	0.78 ± 0.01	54.5 ± 0.5	34.5 ± 0.3	*	51 ± 1	*	21 ± 1	*	

P1: hydromorphic spodosol; P4: well drained spodosol; * below the detection limit of the calibration curve (%C = 0.04; Fe: 0.10 mg/kg and Al: 2.5 mg/kg).

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The Al concentration profile showed an increase with greater depth in the horizons of soils P1 and P4 (Table 1). In the case of Fe, the highest values were found for the subsurface horizons (A and A-E) and the deep Bh horizons: Bh-C 240 (P1) and Bh 370-380 (P4). A possible explanation for this behavior was that in the case of the hydromorphic Spodosol (P1), there was mobilization of suspended organometallic complexes and metal oxides, controlled by the oscillating groundwater level. In flooded soils, anaerobic environments are created, with the organic matter acting as an electron receptor and enabling reduction of the macro- and micronutrients present [23, 24]. Hence, the results suggested that there was greater mobilization of the organometallic complexes and the reduced iron in soil P1, compared to the well-drained Spodosol (P4), with the precipitation of Fe and decreasing mobilization of the organometallic complexes along the profile. Consequently, there was the accumulation of Fe in horizons with greater amounts of organic matter, resulting in spodic Bh horizons in this system.

The results obtained in this study were in agreement with the findings of Ishida [25] and Santos [22] for a Latosol-Spodosol system in the Amazon region. It was reported that there was accumulation of Al and Fe in the Bh horizons, with the highest value obtained for Al. This accumulation was suggested to be due to translocation of the metals, especially Al, to the spodic Bh horizons in the form of organic complexes.

In previous work by Tadini et al. [13], involving the dating of these Amazonian Spodosols and determination of the humification indices, it was observed that soil P1 presented an accumulation of young organic material with a low degree of humification, which was displaced with depth, due to physical and chemical processes. The highest values for humification of the whole soil and for the humic acid fraction were obtained for the Bh-C horizon, at 240 cm. The data obtained in the present study (Table 1) showed that this horizon presented the highest concentrations of Fe and Al in the whole soil and the humic fractions (HA, FA, and HU).

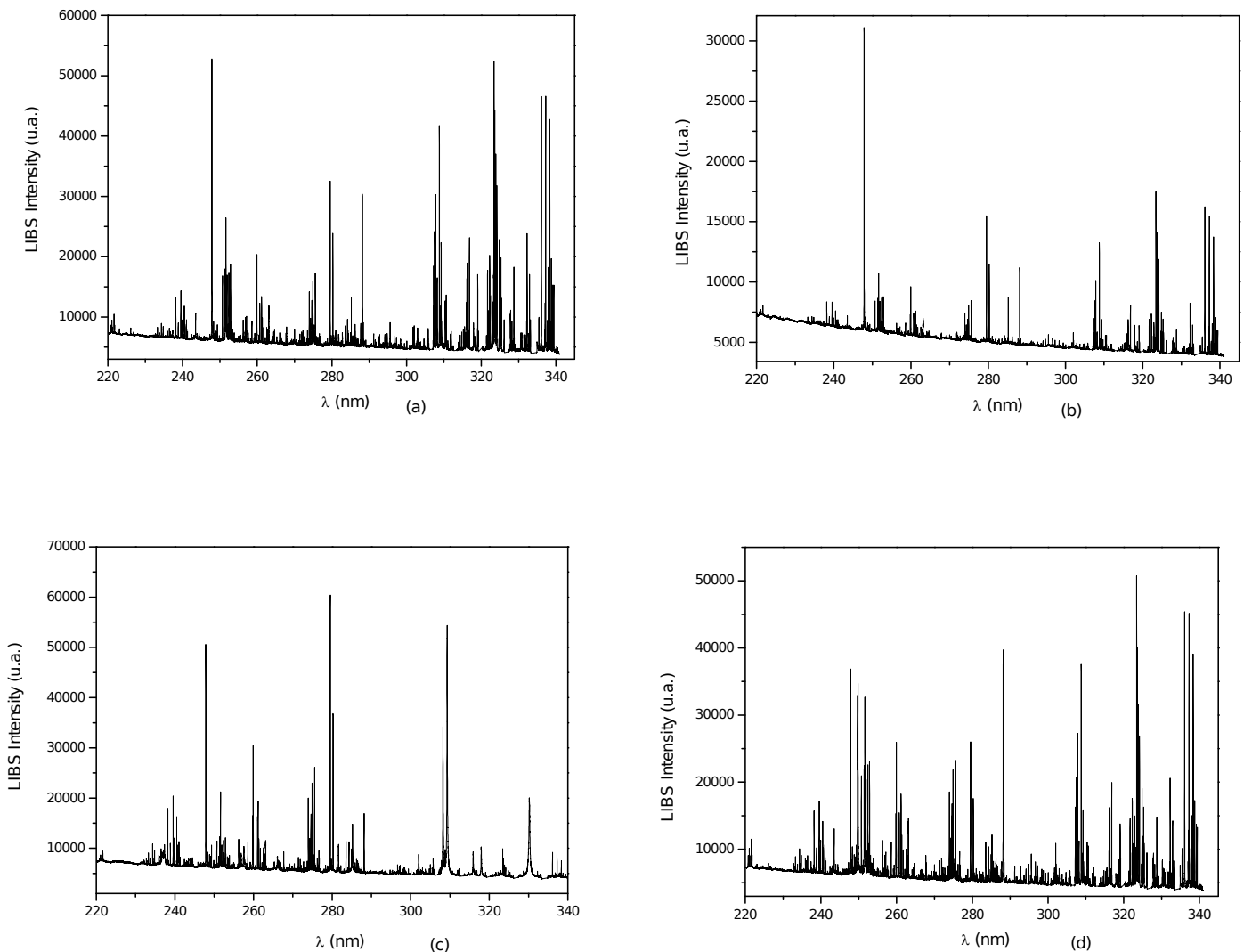
The well-drained Spodosol (soil P4) showed the contribution of old and poorly humified organic matter in horizons Bh 170-180 and Bh 370-380. Therefore, the results indicated that the transfer of iron and aluminum to deeper profiles of soil P1 involved the participation of young and less humified organic matter. Transfer of the metals in soil P4 involved older organic matter with a low degree of humification, which could be attributed to the presence of more recalcitrant compounds derived from lignin [13].

These results indicated that the three humic fractions were involved in the

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457 process of podzolization of the Amazonian Spodosols. The FA fraction played a
458 predominant role in the transport of Al (8.8 to 27.2 g/kg), since this fraction had the
459 highest amount of this metal in its structure, while the HA fraction was responsible for
460 the transport of Fe (0.2 to 2.3 g/kg).
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464 The LIBS technique was also used for analysis of the whole soil samples and the
465 humic fractions extracted from the Amazonian Spodosols. Figure 1 shows typical LIBS
466 spectra obtained for horizon A of the hydromorphic Spodosol (P1).
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470 Figure 1. Typical LIBS spectra for the hydromorphic spodosol (P1 A 0-15 cm): (a) whole soil, (b) humic
471 acids, (c) fulvic acids, and (d) humin.
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After obtaining the LIBS spectra, the data for specific lines were treated in order to determine the concentrations of Fe and Al present in the whole soil and in the humic fractions. The lines selected were as follows: 248.32708 nm (Fe I), 273.95474 nm (Fe II), 302.04907 nm (Fe II), 265.2484 nm (Al I), 281.6185 nm (Al II), and 237.2070 nm (Al I). Three transitions were used for each metal, together with the background. A simple multivariate background analysis was used to obtain the LIBS intensity and correlate it with the concentration of Fe or Al.

Figure 2 shows the graphs for the correlations between the LIBS intensities and the Fe concentrations (g/kg) obtained by FAAS analysis of the whole soil samples and the humic fractions. Very strong Pearson correlations were obtained for the humic acid and humin fractions, with R values of 0.95 and 0.97, respectively (Figures 2(a) and 2(b)), while weaker correlations were found for the whole soils and the fulvic acid fractions. This suggested that the former two fractions, especially the humic acids, strongly participated in the transport of Fe to other horizons of the Amazonian Spodosols.

Figure 2. Correlations between the LIBS intensities and the Fe concentrations (g/kg) in the Amazonian Spodosol samples: (a) humic acids; (b) humin.

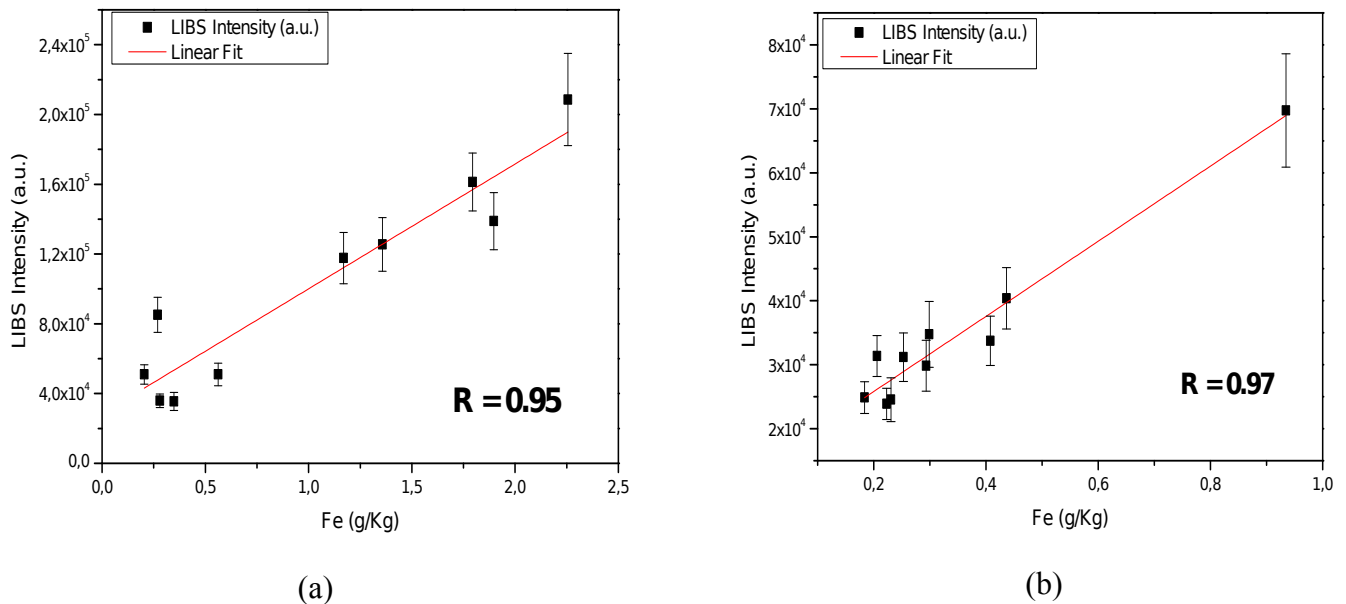
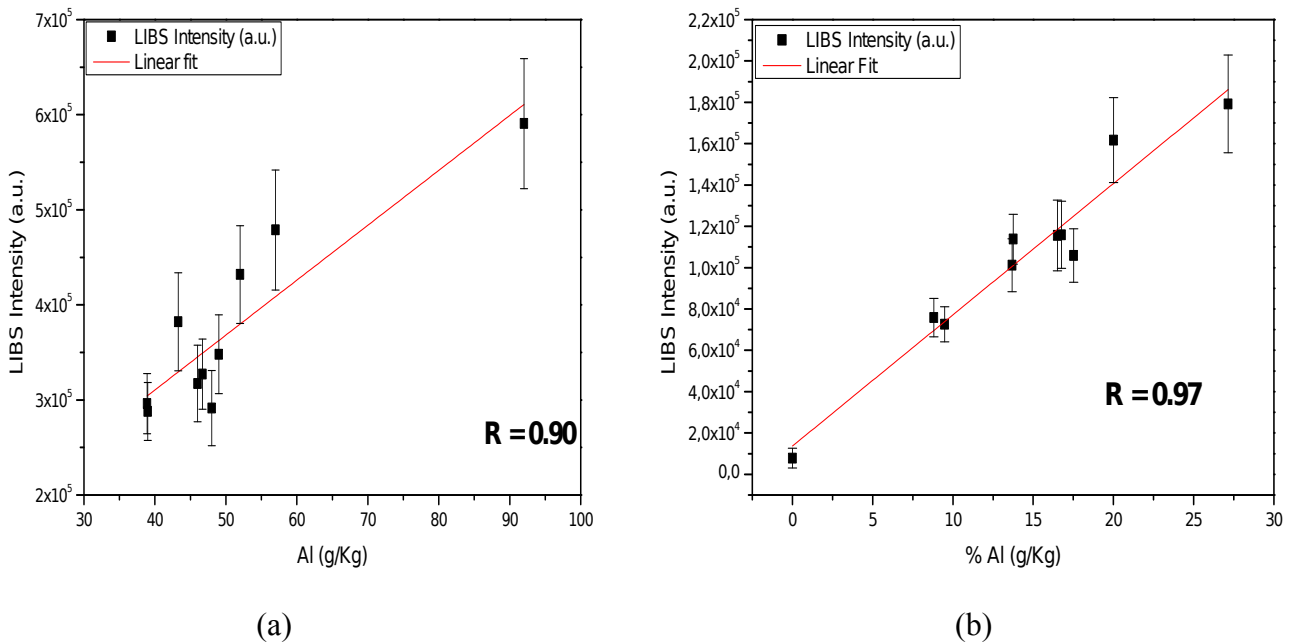


Figure 3 shows the correlation graphs for the LIBS intensity and [Al] (g/kg) determined by FAAS, for the whole soil samples and the fulvic acid fractions. Strong

Pearson correlations were obtained for both the whole soil ($R = 0.90$) (Figure 3(a)) and the fulvic acid fraction ($R = 0.97$) (Figure 3(b)), indicating that the simplest fraction of the organic matter of these Amazonian Spodosols (the fulvic acids) was most important for the transport of Al. The results shown in Figures 2 and 3 were in agreement with those presented in Figure 1. Consequently, in the case of the hydromorphic Spodosol (P1), the presence of groundwater outcrops favored the movement of this metal towards the deeper horizons, as observed by the high amounts of this metal in the whole soil (Table 1), compared to the well-drained Spodosol (P4).

Figure 3. Correlations between the LIBS intensities and the Al concentrations (g/kg) in the Amazonian Spodosol samples: (a) whole soil; (b) fulvic acids.



The results demonstrated that use of the LIBS technique enabled acquisition of important information concerning the humic fractions of the soil organic matter. In particular, it was possible to quantify the contributions of the different humic fractions to the processes of podzolization in these soils. The LIBS technique is faster than conventional techniques and was able to provide important information about key elements present in the humic fractions of organic matter in Amazonian soils.

4. Conclusions

The results showed that the fulvic acid fraction was associated with high

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634 amounts of Al, while the humic acid fraction was more selective towards Fe. The
635 transfer of Fe and Al to deeper profiles involved young and less humified organic
636 matter (soil P1), or older organic matter with a low degree of humification (soil P4). It
637 could therefore be concluded that the three humic fractions (HA, FA, and HU) were
638 involved in the soil podzolization process, with the FA and HA fractions playing
639 predominant roles in the transport of Al and Fe, respectively.
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644 The potential of LIBS as a technique capable of assisting in investigation of the
645 processes of formation of Amazonian Spodosols was also evaluated. The data obtained
646 showed strong correlations with the results of analyses using the reference method
647 (FAAS), for Fe in the humic acid and humin fractions ($R = 0.95$ and 0.97 , respectively),
648 and for Al in the fulvic acid fraction ($R = 0.97$). This is the first study using LIBS
649 applied to samples of environmental humic fractions. In combination with FAAS, it
650 enabled understanding of the roles of the humic fractions in the transport of nutrients
651 and in the process of formation of Amazonian Spodosols.
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657 658 **5. Acknowledgments**

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Figure 1. Typical LIBS spectra for the hydromorphic spodosol (P1 A 0-15 cm): (a) whole soil, (b) humic acids, (c) fulvic acids, and (d) humin.

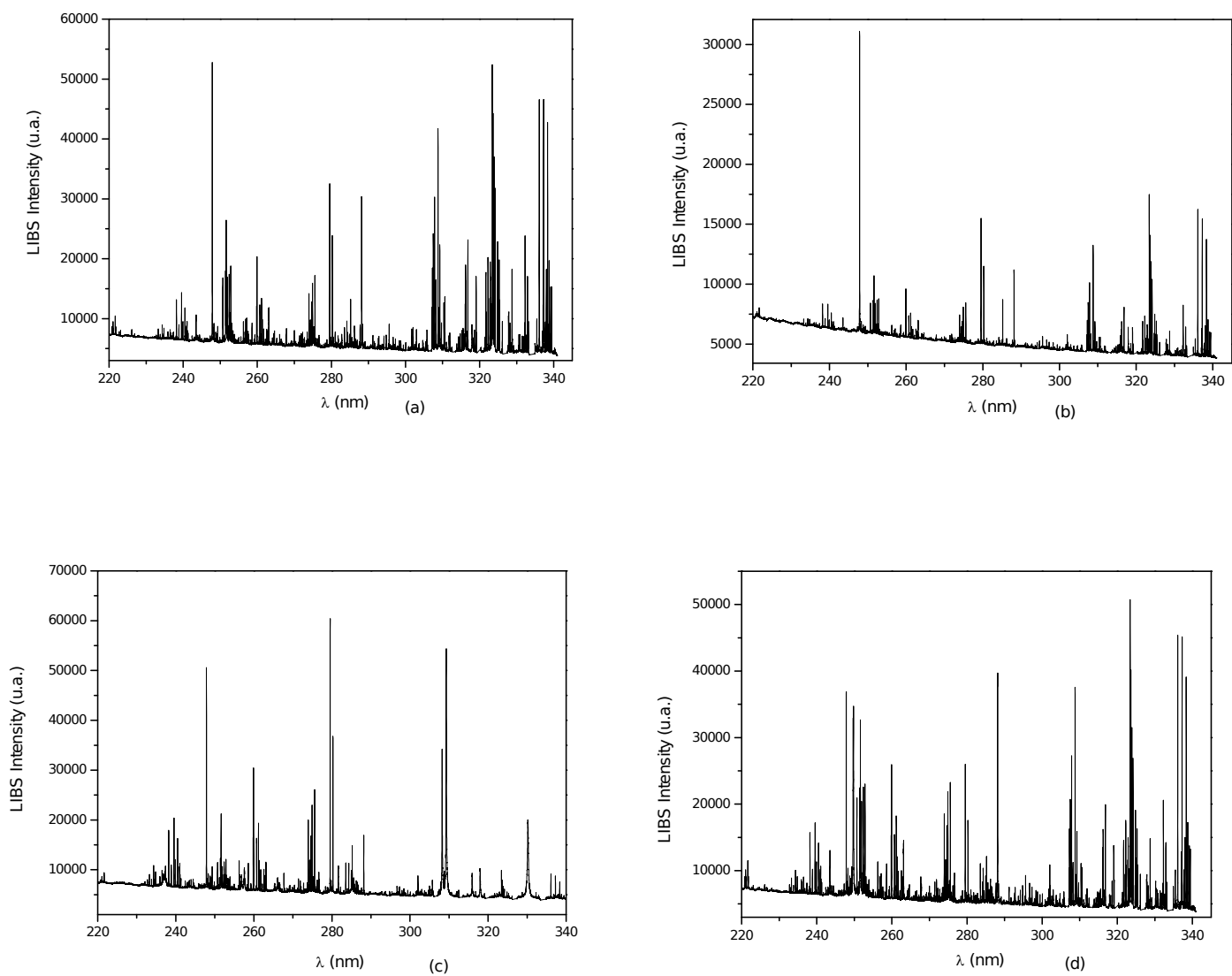
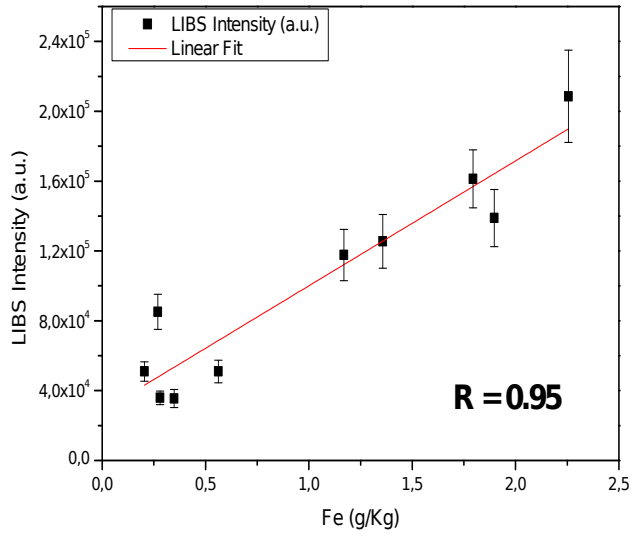
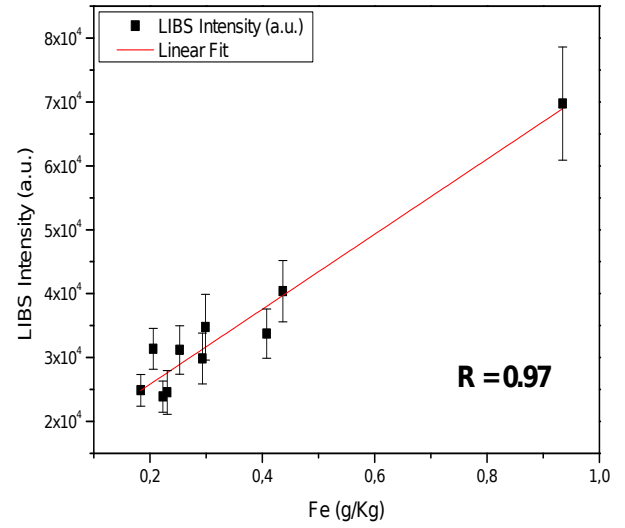


Figure 2. Correlations between the LIBS intensities and the Fe concentrations (g/kg) in the Amazonian Spodosol samples: (a) humic acids; (b) humin.

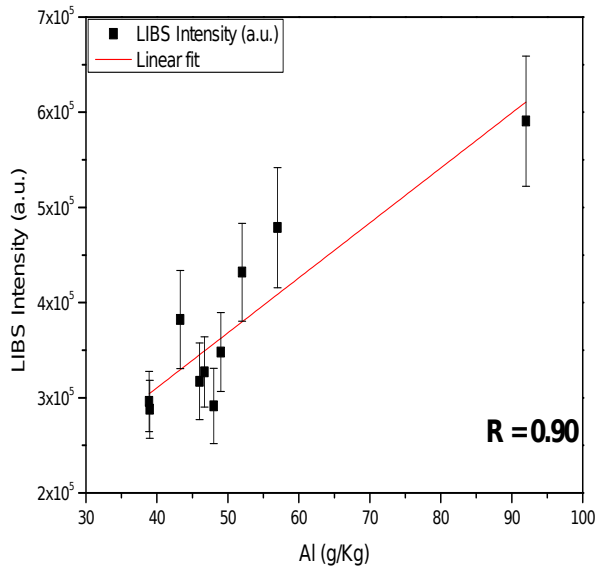


(a)

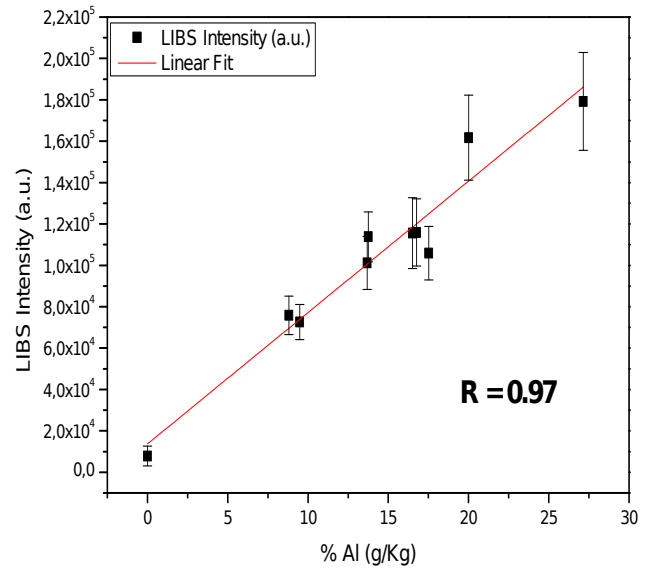


(b)

Figure 3. Correlations between the LIBS intensities and the Al concentrations (g/kg) in the Amazonian Spodosol samples: (a) whole soil; (b) fulvic acids.



(a)



(b)

Table 1. Concentrations of carbon (%) and the metals Fe and Al (g/kg) in the whole soil samples and in the humic fractions (HA, FA, and HU) extracted from the Amazonian Spodosols.

Metals	Samples			Carbon (%)				Concentration of metals (g/kg)				
	Area	Horizon	Depth (cm)	Soils	HA	FA	HU	Soils	HA	FA	HU	
Fe	P1	A	0-15	22.5 ± 0.9	45 ± 3	18.2 ± 0.5	52.03 ± 0.08	1.20 ± 0.01	0.4 ± 0.2	0.07 ± 0.01	0.3 ± 0.1	
		A-E	15-30	1.01 ± 0.09	51 ± 1	26.9 ± 0.2	24.38 ± 0.01	0.95 ± 0.01	0.3 ± 0.1	*	0.2 ± 0.1	
		Bh	40-50	2.1 ± 0.2	56.2 ± 0.2	36.8 ± 0.8	36.67 ± 0.03	0.77 ± 0.01	0.3 ± 0.1	0.12 ± 0.01	0.2 ± 0.1	
		Bh-C	240	3.2 ± 0.2	46 ± 2	47.9 ± 0.1	*	6.44 ± 0.01	0.6 ± 0.2	*	0.4 ± 0.1	
		C	350	1.2 ± 0.2	51 ± 3	38.7 ± 0.9	5.17 ± 0.00	2.13 ± 0.01	0.2 ± 0.1	0.07 ± 0.01	1.0 ± 0.2	
	P4	A	0-20	3.9 ± 0.2	45.2 ± 0.3	34 ± 3	41.43 ± 0.07	2.29 ± 0.01	1.8 ± 0.5	0.2 ± 0.1	0.2 ± 0.1	
		A	20-30	3.5 ± 0.2	49.4 ± 0.01	21.6 ± 0.2	*	2.28 ± 0.01	1.9 ± 0.4	*	0.2 ± 0.1	
		A	30-40	0.89 ± 0.01	50 ± 2	10.8 ± 0.1	5.76 ± 0.02	2.60 ± 0.01	2.3 ± 0.3	*	0.3 ± 0.1	
		Bh	110-120	0.42 ± 0.02	50.0 ± 0.1	39.8 ± 0.6	*	1.81 ± 0.01	1.1 ± 0.2	*	0.4 ± 0.1	
		Bh	170-180	0.38 ± 0.01	52 ± 6	3.1 ± 0.0	5.33 ± 0.02	1.72 ± 0.01	1.4 ± 0.2	*	0.3 ± 0.1	
		Bh	370-380	0.48 ± 0.01	52.8 ± 0.3	32.8 ± 0.2	2.26 ± 0.01	2.49 ± 0.01	1.2 ± 0.6	*	0.4 ± 0.1	
		Bh	380-390	0.78 ± 0.01	54.5 ± 0.5	34.5 ± 0.3	*	1.66 ± 0.01	1.3 ± 0.2	*	0.3 ± 0.1	
	Al	P1	A	0-15	22.5 ± 0.9	45 ± 3	18.2 ± 0.5	52.03 ± 0.08	43 ± 1	*	16.8 ± 0.2	*
			A-E	15-30	1.01 ± 0.09	51 ± 1	26.9 ± 0.2	24.38 ± 0.01	39 ± 1	*	13.8 ± 0.5	*
			Bh	40-50	2.1 ± 0.2	56.2 ± 0.2	36.8 ± 0.8	36.67 ± 0.03	57 ± 1	*	8.8 ± 0.3	*
Bh-C			240	3.2 ± 0.2	46 ± 2	47.9 ± 0.1	*	92 ± 1	*	*	*	
C			350	1.2 ± 0.2	51 ± 3	38.7 ± 0.9	5.17 ± 0.00	52 ± 1	*	20.0 ± 0.1	5.0 ± 0.1	
P4		A	0-20	3.9 ± 0.2	45.2 ± 0.3	34 ± 3	41.43 ± 0.07	48 ± 1	6.4 ± 0.4	9.5 ± 0.1	*	
		A	20-30	3.5 ± 0.2	49.4 ± 0.01	21.6 ± 0.2	*	47 ± 1	*	27.2 ± 0.2	*	
		A	30-40	0.89 ± 0.01	50 ± 2	10.8 ± 0.1	5.76 ± 0.02	46 ± 1	*	17.5 ± 0.1	*	
		Bh	110-120	0.42 ± 0.02	50.0 ± 0.1	39.8 ± 0.6	*	39 ± 1	*	13.7 ± 0.4	*	
		Bh	170-180	0.38 ± 0.01	52 ± 6	3.1 ± 0.0	5.33 ± 0.02	49 ± 1	*	16.5 ± 0.3	*	
		Bh	370-380	0.48 ± 0.01	52.8 ± 0.3	32.8 ± 0.2	2.26 ± 0.01	41 ± 1	*	20.5 ± 0.2	*	
		Bh	380-390	0.78 ± 0.01	54.5 ± 0.5	34.5 ± 0.3	*	51 ± 1	*	21 ± 1	*	

P1: hydromorphic spodosol; P4: well drained spodosol; * below the detection limit of the calibration curve (%C = 0.04; Fe: 0.10 mg/kg and Al: 2.5 mg/kg).