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Integrated Geochemical Assessment of Soils and Stream Sediments to Evaluate Source-Sink Relationships and Background Variations in the Parauapebas River Basin, Eastern Amazon

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Abstract: This study aims to handle an integrated evaluation of soil and stream sediment geochemical data to evaluate source apportionment and to establish geochemical threshold variations for Fe, Al, and 20 selected Potentially Toxic Elements (PTE) in the Parauapebas River Basin (PB), Eastern Amazon. The data set used in this study is from the Itacaiúnas Geochemical Mapping and Background Project (ItacGMBP), which collected 364 surface soil (0–10 cm) samples and 189 stream sediments samples in the entire PB. The <0.177 mm fraction of these samples were analyzed for 51 elements by ICP-MS and ICP-AES, following an aqua regia digestion. The geochemical maps of many elements revealed substantial differences between the north (NPB) and the south (SPB) of PB, mainly due to the geological setting. The new statistically derived threshold values of the NPB and SPB regions were compared to the threshold of the whole PB, reported in previous studies, and to quality guidelines proposed by Brazilian environmental agencies. The natural variation of geochemical background in soils and stream sediments of PB should be considered prior to defining new guideline values. At the regional scale, the local anomalies are mostly influenced by the predominant lithology rather than any anthropogenic impact.

Keywords: surface geochemistry; geoprocessing; geogenic enrichment; Itacaiúnas river watershed; Carajás mineral province

1. Introduction

Multi-element geochemical mapping is useful for both, mineral exploration surveys and environmental studies as previously demonstrated [1–4]. For both applications, the unusually high concentrations (also known as anomalies) are strong pieces of evidence of a potential mineral deposit or a possible anthropogenic impact. Evaluating the spatial distribution of an element, in a given sampling medium (e.g., soils, sediments, water, and rocks), along with different geographic information (land cover and land use, hydrology, geomorphology, geology, and mineralized zones) may assist in accurately identifying the source of enrichment (for some authors, contamination), whether anthropic or not [5–7].

Traditional studies in environmental geochemistry usually carry out impact assessments separately for each sampling medium [8–10]. Taking this into consideration, an integrated assessment, using geochemical data from different sampling mediums, might be

a powerful strategy for identifying source apportionment and evaluating the geochemical variability in terrestrial environments. In relation to the large geochemical data set, this strategy became more affordable due to recent advances in data analysis using a robust programming language in addition to geoprocessing techniques. Similar approaches have been conducted elsewhere [11–13].

Prior to conducting an integrated assessment methodology, it is indispensable to understand the limitations in terms of physicochemical properties and representativeness, regarding the medium of sampling [14]. For instance, soil samples have local representativeness and medium (A horizon) to low (B horizon) susceptibility in terms of changes in local conditions. In general, soils have a strong correlation to the parent geological material. In contrast, stream sediment samples have a wider representativeness, restricted to the whole upstream catchment area of the sampling point, and high susceptibility, not only due to the different lithologies occurring in the catchment area, but also due to changes in the hydrosedimentological dynamics, influenced by local seasonal variations, and changes in land cover and land use [15,16].

In addition, the determination of geochemical background is a mandatory approach for this assessment. The background concept has not been clearly established [17–19], but the term is often used as a naturally occurring concentration range of an element or chemical compound [20], determined by a given analytical method [21], which can be established by direct, indirect and integrated methods [6]. Some authors consider that the upper limit of the geochemical background, also known as the threshold value, can be used to distinguish between natural and anthropogenic influences [17]. The threshold concentration value is regularly used as a reference to define action levels in environmental legislation [22,23], whereas, the lower background limit has not been widely discussed, perhaps due to its low relevance for exploration and environmental purposes.

The Parauapebas River Basin (PB) is particularly relevant for geochemical studies because: (i) The basin is located in the Carajás Mineral Province, the largest mineral province of Brazil, and large open pit Fe (N4, N5 and S11D), Cu (Sossego) and Cu-Au (Antas North) mines, besides other mineral deposits, are situated on it (Figure 1d); (ii) The PB has protected areas that are covered by preserved tropical forest but most of it was deforested. Hence, the study area has strong contrasts of land use and cover; (iii) The possible impact in the environment related to mining activities and the effects of deforestation and increase of human occupation, with agricultural development and livestock production, should be evaluated. All these aspects can be evaluated by studying the spatial distribution of chemical elements particularly those of iron, the most voluminous mineral resource produced in the region, and Potentially Toxic Elements (PTE).

This study is associated with the Itacaiúnas Geochemical Mapping and Background Project (ItacGMBP), a large geochemical mapping project carried out by the Instituto Tecnológico Vale (ITV) in the entire Itacaiúnas River Watershed (IRW; Figure 1b). In the PB area (Figure 1c), a previous study about the soil [24] geochemistry has been conducted. However, an integrated and refined interpretation using soil and stream sediment geochemical data sets of the PB is presented here for the first time. To address the source apportionment and establishing geochemical threshold variations, a series of advanced data analyses were implemented, mainly by using geoprocessing techniques and traditional statistical methods. This integrated assessment of geochemical data is of great importance to fill the knowledge gaps identified in previous studies.

This study aims to handle an integrated evaluation of soil and stream sediment geochemical data to evaluate source apportionment and to establish geochemical threshold variations for Fe, Al, and 20 selected PTE (Ag, B, As, Ba, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, U, V, and Zn) in the PB. The study was designed to answer several questions:

- How is the spatial distribution of the PTE in soils and stream sediments of the PB? Are they similar or not?
- Are the soil and stream sediment samples correlated? Do they share the same source apportionment?

- How do the geological domains affect the variations of the geochemical background and distribution of anomalies in the PB and what is their relevance for the definition of environmental guidelines?
- Is there any evidence of anthropogenic impact in the area?

2. Study Area and Geological Setting

The study area of the present research is the Parauapebas River Basin (PB), situated in the eastern Amazon Rainforest (Figure 1a). The PB is classified as one of the eight sub-basins of the IRW (Figure 1b), which covers an area of approximately 9600 km², encompassing two main urban areas (Parauapebas and Canaã dos Carajás; Figure 1c), parts of conservation areas, represented mainly by the remaining preserved forest in the Center-West of the PB (Figure 1b), and active open-pit Fe (N4, N5, and S11D), Cu (Sossego) and Cu-Au (Antas North) mines (Figure 1d).

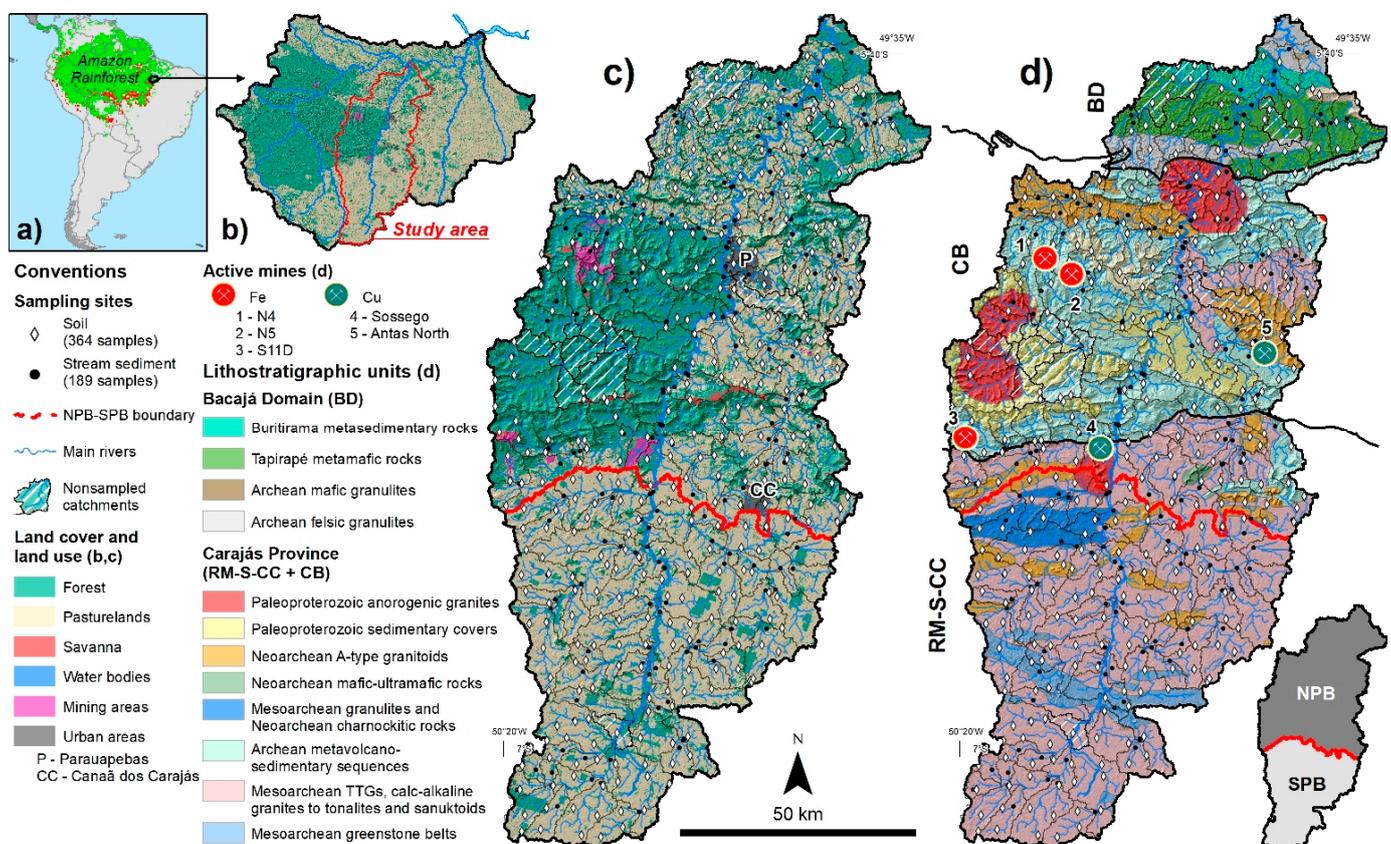


Figure 1. Location of the Parauapebas River Basin (PB) in the eastern Amazon region (a), situated in the Itacaiúnas River watershed (b). The land cover and land use map (c) and the geological map (d) are presented along with the sampling sites for soil and stream sediments. These two maps are overlaid on a shaded-relief digital elevation model (DEM). Inset shows the Northern (NPB) and Southern (SPB) PB. Map coordinates are in degrees (WGS84). Source: modified from [24].

For the purpose of the present study, the geology of the PB can be simplified into three different domains (Figure 1d):

- Rio Maria—Sapucaia—Canaã dos Carajás domains (RM-S-CC): It is restricted to the south of PB (Figure 1d), and is composed essentially of Mesoarchean tonalite—trondhjemite—granodiorite (TTG) series associated with greenstone belt sequences and calc-alkaline granites to tonalites and sanukitoids [25–28]. Neoproterozoic A-type like granitoids, charnockitic rocks, mafic-ultramafic bodies, and Paleoproterozoic anorogenic granites crosscut the Mesoarchean units [25,29–33].

- Carajás Basin (CB): It is restricted to the center of PB (Figure 1d), and is composed dominantly of Neoproterozoic mafic to felsic metavolcanic rocks and banded-iron formations (BIF), which hold the world-class Fe deposits of Carajás [34,35]. Neoproterozoic A-type like granite plutons [29,36] and mafic-ultramafic stratified bodies [31,37], as well as Paleoproterozoic anorogenic granites [38–40] also occur.
- Bacajá Domain (BD): It is restricted to the north of PB (Figure 1d), and is mainly composed of high-grade charnockitic rocks, with subordinate mafic orthogneisses and para-derived granulites [41], supracrustal mafic metamorphic rocks of the Tapirapé Formation, and metasedimentary lithologies of the Buritirama Formation [42].

3. Materials and Methods

3.1. Sampling Procedure

The sampling strategies, data storage, screening, and validation of the ItacGMBP were entirely assisted by a computer-based framework associated with a geographic information system environment. Firstly, a sampling protocol was structured to guide the field teams in storing all field data using tablets in a geochemical database. Further information can be accessed elsewhere [43].

The soil survey was designed on a nominal scale of 1:250,000, with a sampling density of 1 sample/25 km², using grids of 5 km × 5 km, homogeneously distributed along the whole IRW (Figure 1b). The surface soil samples were collected at a constant depth of 10 cm. Each surface soil sample was collected and then bulked to provide one composite sample (approximately 5 kg).

The stream sediment survey was designed on a nominal scale of 1:1,000,000, with a sampling density of 1 sample/100 km², using 2nd–3rd order drainage microcatchments along the entire IRW (Figure 1b). The collection of stream sediment samples (approximately 3 kg) was carried out in active sedimentation areas at the catchment outlet, preferably in the middle of the channel to minimize contamination occurring at the margins.

For the quality control procedure, a duplicate sample was collected for every 20 samples collected. Samples were collected as close as possible to the location defined in the planning field map. Most of the unsampled sites are located in remote areas with severe access limitations. The detailed sampling procedure and description of different sampling media used in the ItacGMBP can be found elsewhere [24,43–46].

In the PB, 364 samples of surface soil and 189 samples of stream sediment were collected. The sampling sites are plotted over the land use and land cover (Figure 1c) and geological layers (Figure 1d) for further inspections.

3.2. Sample Preparation and Chemical Analyses

The ItacGMBP's analytical program was extensive, but only the relevant analyses for the present study are described. For more information, refer to previous studies [24,43–46]. Both soil and stream sediment samples were submitted to the same preparation and analytical protocols. The samples were oven-dried at 70 °C, disaggregated, homogenized, and sieved through a <0.177 mm (80 mesh) sieve. Approximately 50 g of the samples were grounded, sieved through a <75 µm (200 mesh) sieve, and submitted to aqua regia (1:3 M HNO₃:HCl) digestion. The aqua regia soluble concentrations of 51 elements (the most relevant for the present study are Fe, Al, Ag, B, As, Ba, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, U, V, and Zn) were determined via Inductively Coupled Plasma—Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma—Mass Spectrometry (ICP-MS). All samples were prepared and analyzed in laboratories of ALS Brasil Ltda (Belo Horizonte, Brazil), a certified/accredited laboratory.

3.3. Data Processing and Statistical Analysis

Firstly, the censored data (values below the lower limit of detection—LLD), commonly observed in the geochemical data set, was replaced by $LLD/2$ indicated for each element, according to the analytical method. This procedure is widely used in the literature [22,23,45,46]. It is important to highlight that, eventually, two sets of data were used in this study, one for the NPB (soils = 223 samples; stream sediments = 122 samples) and another one for the SPB (soils = 141 samples; stream sediments = 67 samples) (cf. Figure 1). Standard statistical procedures [22,23,47] were undertaken in this research, which involves calculating several descriptive statistics parameters (amount of data below LLD, arithmetic mean, standard deviation—SD, minimum—Min, median—Med, and maximum—Max), constructing graphs based on the exploratory data analysis (e.g., box plots, scatter plot and quantile-quantile plot) and conducting hypothesis test (e.g., Mann–Whitney–Wilcoxon test). Data analysis was performed using the R programming language in RStudio.

3.4. The Determination of Geochemical Background Values

A variety of statistical methods was used for the calculation of geochemical threshold values, which is highly recommended by experts in the field. These methods are described elsewhere [19,20,22,23,48], and the general steps are highlighted herein.

Median + 2 * Median Absolute Deviation (M_{MAD}): The M_{MAD} is considered one of the most prestigious methods for deriving geochemical threshold values [19]. Firstly, a requirement for using the M_{MAD} method is that the raw data should be prior transformed to a common logarithm (\log_{10}) scale to get close to a normal distribution, unusually seen in geochemical data set [23]. In this approach, the median absolute deviation (MAD; Equation (1)), leads to a robust estimation of the variability of univariate geochemical data [23].

$$MAD_{(y)} = 1.48 * median_i | y_i - median_j(y_j) | \quad (1)$$

Afterward, the MAD value should be multiplied by two and added to the median. At this stage, the result should be back-transformed, from logarithmic scale to natural scale, to derive the M_{MAD} threshold value (Equation (2)):

$$M_{MAD(y)} = 10^{(median(y) + 2 * MAD(y))} \quad (2)$$

Tukey's Inner Fence (TIF): The TIF method depends solely on the data distribution. In addition, background values can be calculated even if no outliers are present in the data set (threshold value greater than the maximum value). Moreover, the threshold value obtained from this approach is most informative if the true number of outliers is below 10% of the data [19,23]. Firstly, the \log_{10} transformation is required prior to using this approach [19]. The TIF method consists of determining the upper ($Q3 = 75$ th percentile) and lower ($Q1 = 25$ th percentile) quartiles of the boxplot. Then, the inner fence is determined as the interquartile range ($IQR = Q3 - Q1$) extended by 1.5 times. The threshold value based on the TIF method is calculated following Equation (3):

$$TIF = 10^{(Q3 + 1.5 * IQR(y))} \quad (3)$$

Percentile-based approaches: These approaches are considered as the most straightforward methods for deriving threshold values [48,49], widely used by many environmental agencies from different countries (e.g., Brazil [50], Australia [51], and Finland [52]). The 98th percentile (P98) has become widespread as a 2% outliers (1 in 50 rate) is deemed acceptable, and it distances the method from the 97.5 percentile, 2.5% 1 in 40 rate, which delivers similar results to the "Mean + 2 * Standard Deviation" (outdated method) when a normal distribution of a given element is satisfied [19]. The 95th percentile (P95) corresponds to a more restricted value, as it considers 5% of all samples as outliers. Other percentile values are also used (e.g., 90th, 85th, and 75th), however, they are not going to be considered as threshold values in the present study.

3.5. Geoprocessing and Spatial Representation of Soil and Stream Sediment Geochemical Data

Spatial analyses were processed using the software ArcGIS 10.4.1, under the World Geodetic System 1984 (WGS84) datum. The construction of integrated stream sediment and soil geochemical maps was based on two techniques: (i) Catchment-based representation (polygon) for stream sediment data [53–55] which, simply involves attributing the element concentrations to their respective catchment watershed, with the sample collected at the outlet; (ii) Geochemical dot representation (point) for surface soil data, attributing the uni-element concentration to the sampling site [55,56]. The class intervals were defined according to the quantile method, usually applied to right-skewed distribution, commonly seen in geochemical data [57]. For the correct construction of integrated geochemical maps, the same class interval was used for the representation of the concentration (usually in mg kg^{-1} , except for Fe and Al in wt.%) of a given element in soil and in stream sediment. Finally, spatial analyses using geoprocessing techniques (e.g., buffer, clip, intersect and merge) were eventually used for further interpretation.

4. Results

In this study, integrated soil and stream sediments geochemical maps are presented for selected elements (Fe, Al, Cu, Mo, As, and Hg in Figure 2; Ni, Cr, Co, V, Mn, and Zn in Figure 3). Additional geochemical maps for the remaining PTE (Ag, B, Ba, Bi, Cd, Pb, Sb, Se, Sn, and U) are provided in the supplementary material (Figure S1). In these maps, the catchment-based representation (polygons) was used to display the distribution of elements in stream sediment samples, whereas the point representation was used for soil samples.

The spatial distribution of each element (cf. Figures 2 and 3, Figures S1 and S2) revealed a clear difference between the Northern PB (NPB) and Southern PB (SPB). The NPB region corresponds almost exactly to the BD and CB and the SPB to the RM-S-CC. The chemical compositions of soils and stream sediments from those regions are strongly influenced by the dominant lithologies occurring in their respective geological domains (Figure 1d). Boxplots for Fe, Al, and selected PTE (Figure 4) were constructed by taking into account the compositions of soil and stream sediment samples from the three different geological domains distinguished in the PB. Additional boxplots are provided in the supplementary material (Figure S3). It is apparent that the distributions of some elements (e.g., Al, As, Bi, and Cr; Figure 4) are similar in both BD and CB, representing the NPB, and contrast with that observed in the RM-S-CC domains that occupy the SPB. On the contrary, Cu spatial distribution exhibit remarkable differences among all geological domains (Figure 4).

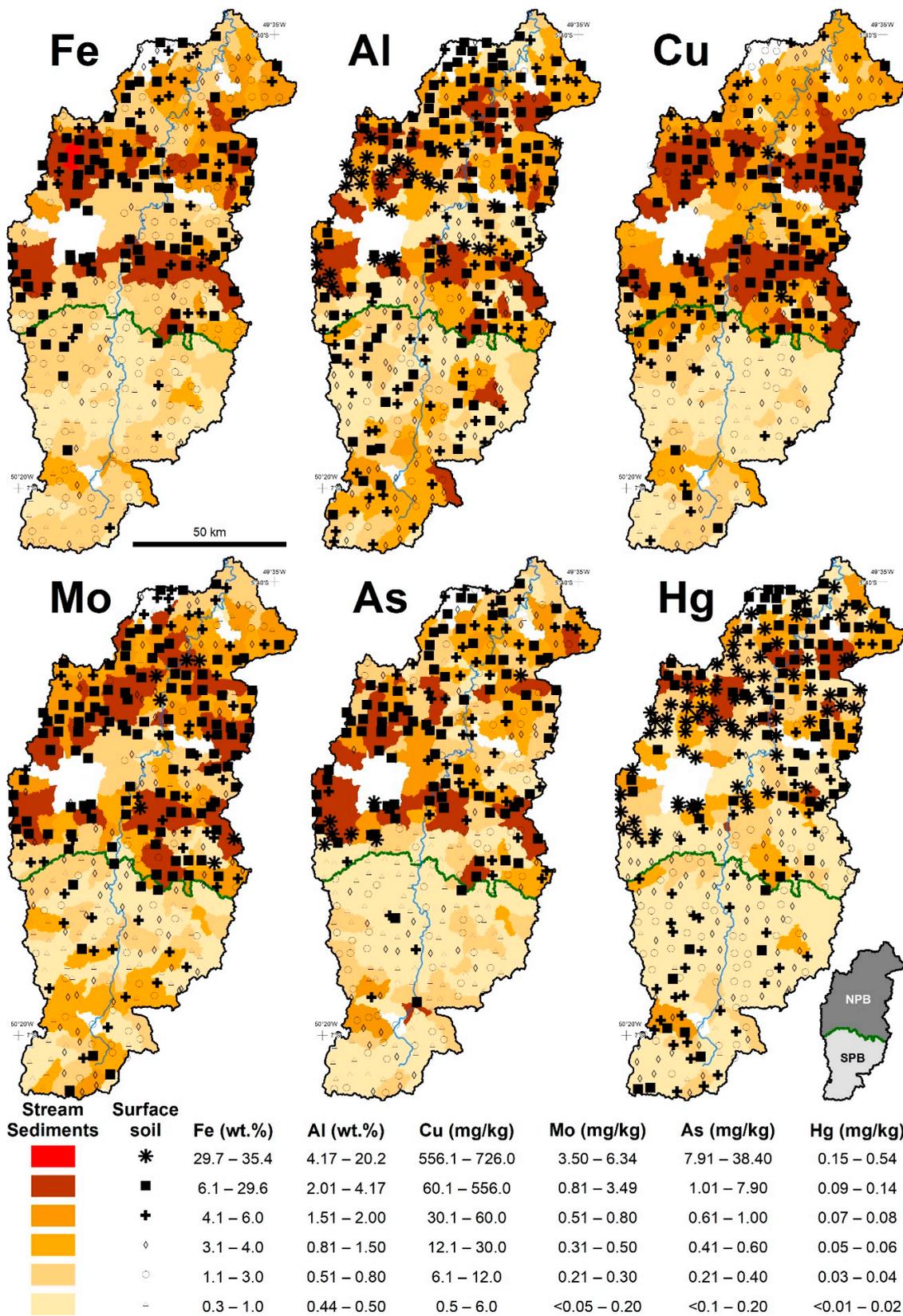


Figure 2. Geochemical maps for Fe, Al, Cu, Mo, As, and Hg in stream sediments (catchment area—polygon) and surface soil (in-situ sampling site—point) in the Parauapebas River Basin (PB). Note that the same concentration range for each element is used for the map representation on both sampling media. Inset shows the Northern (NPB) and Southern (SPB) PB. Refer to Figures S1 and S2 for the geochemical maps of the remaining PTE.

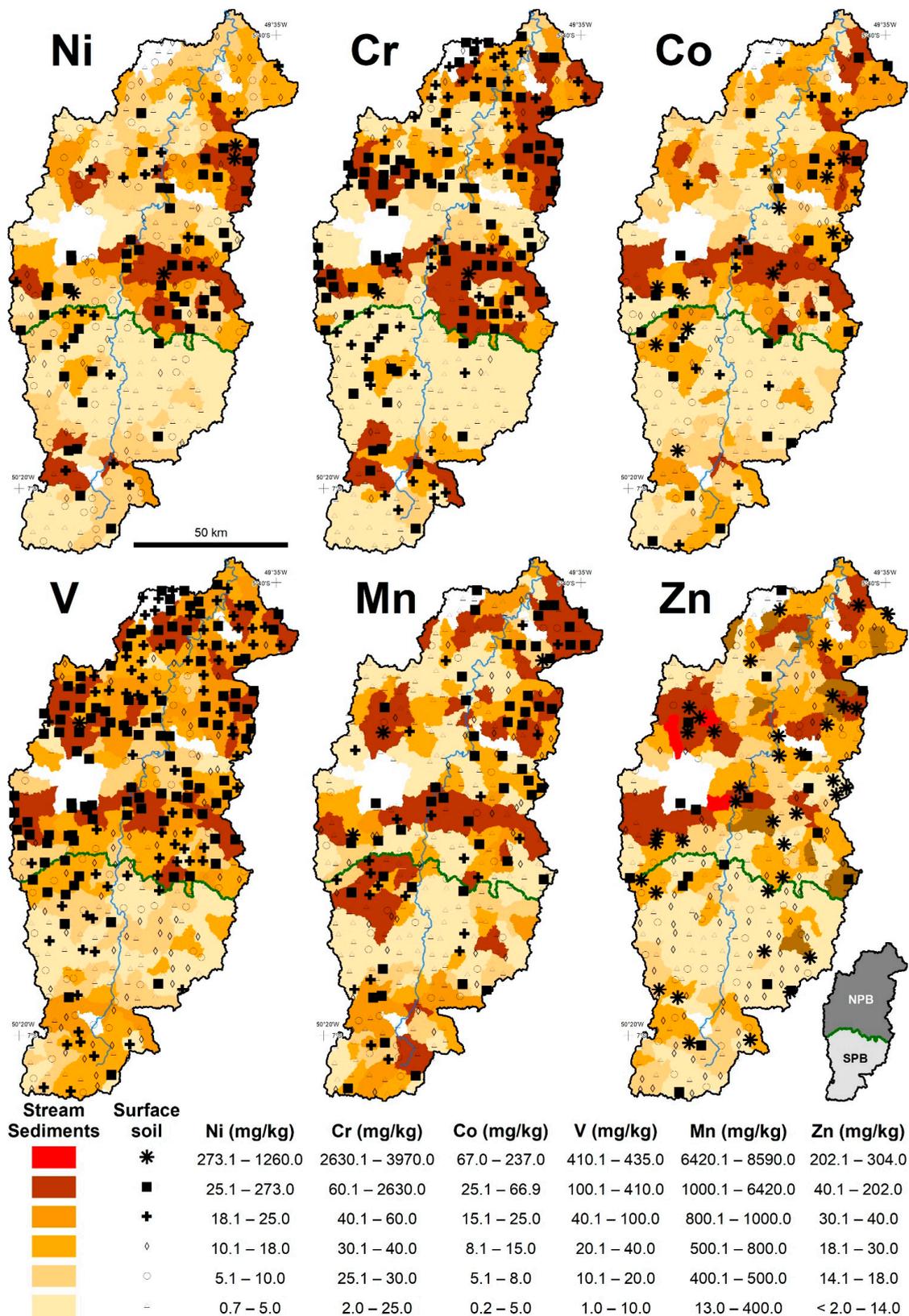


Figure 3. Geochemical maps for Ni, Cr, Co, V, Mn, and Zn in stream sediments (catchment area—polygon) and surface soil (in-situ sampling site—point) in the Parauapebas River Basin (PB). Note that the same concentration range for each element is used for the map representation on both sampling media. Inset shows the Northern (NPB) and Southern (SPB) PB. Refer to Figures S1 and S2 for the geochemical maps of the remaining PTE.

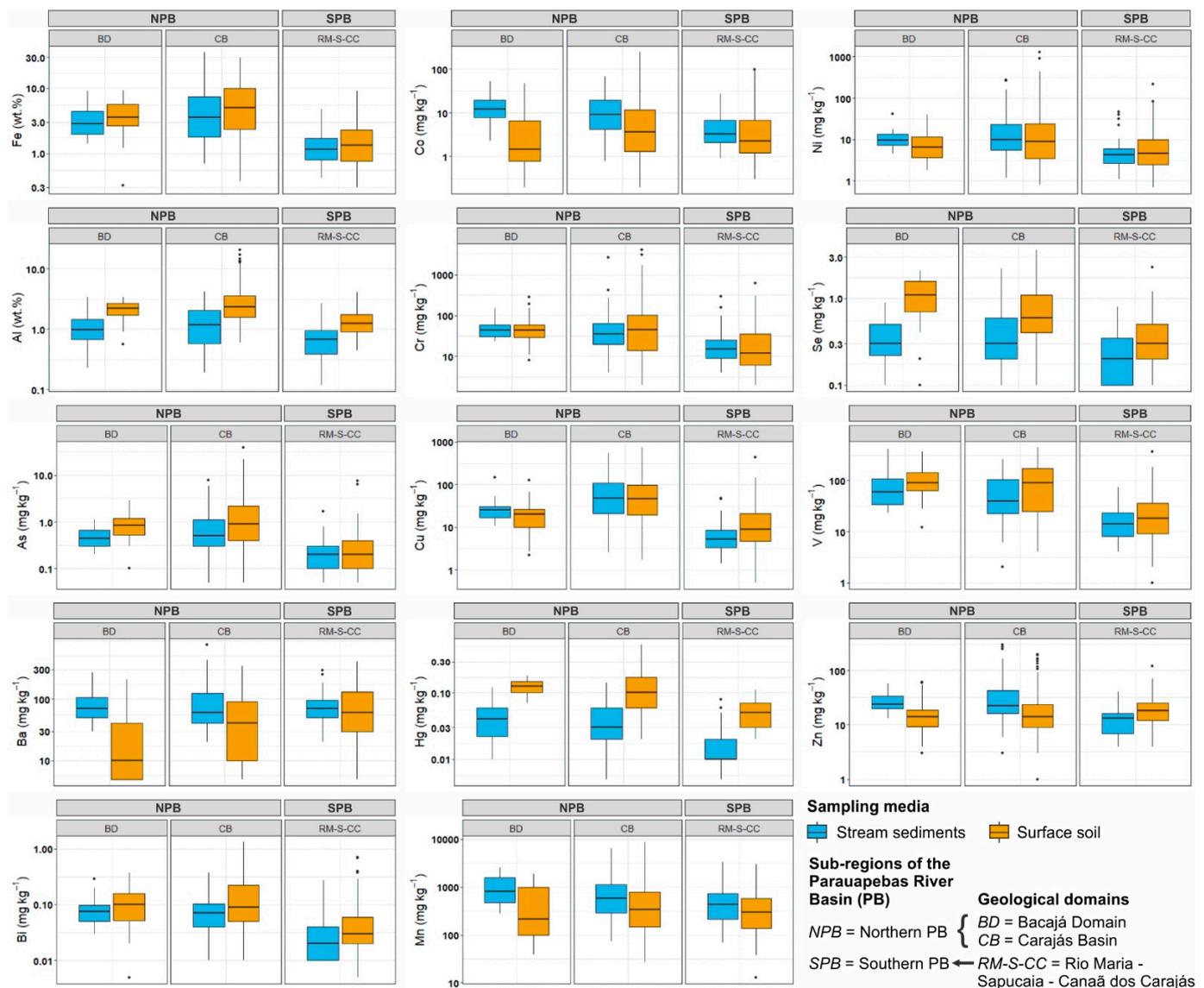


Figure 4. Boxplots for Fe, Al, and 12 potentially toxic elements (PTE; As, Ba, Bi, Co, Cr, Cu, Hg, Mn, Ni, Se, V, and Zn) in surface soils and stream sediments samples of the Parauapebas River Basin (PB), according to the major geological domains of the study area: BD = Bacajá Domain and CB = Carajás Basin, both domains comprised at the Northern PB (NPB); and RM-S-CC = Rio Maria—Sapucaia—Canaã dos Carajás domains, comprised at the Southern PB. Refer to Figure 1 for the geological setting of the study area. Refer to Figure S3 for the boxplot of the remaining PTE.

In addition, the MWW test was carried to devaluate if the composition of soil and stream sediment samples from BD and CB are statistically similar. Table 1 summarizes the p -values of the MWW calculated for each element in surface soils and stream sediments separately. In these results, the null hypothesis states that there is no difference between the distribution of a given element in a given sampling media in BD and CB. By assuming a significance level (σ) of 0.05, the p -values below σ imply rejecting the null hypothesis and inform that the distributions of the respective element in BD and CB are statistically different. In summary, Al, Ag, As, Bi, Cr, Hg, Ni, Sn, V, and Zn presented similar distribution in both sampling medium; Fe, B, Ba, Cd, Co, Mo, Pb, Sb, Se, and U presented similar distribution only in stream sediments; Mn presented similar distribution only in soils, and Cu presented different distribution in both sampling medium.

The integrated evaluation of the data (geochemical maps, Figures 2 and 3, Figures S1 and S2; boxplots, Figure 4 and Figure S3; and, MWW results, Table 1) highly indicates that the study area can be divided into two separate geochemical regions, the NPB and SPB.

For this reason, the original data set was split into two subsets for further investigation. Table 2 summarizes the descriptive statistics (mean, SD, Min, Med, and Max) of the studied elements in surface soils and stream sediments in the entire PB (soils = 364 samples; stream sediments = 189 samples), which was retrieved from previous studies [24,58] using the same data set, and for each subregion, NPB (soils = 223 samples; stream sediments = 122 samples) and SPB (soils = 141 samples; stream sediments = 67 samples).

Table 1. Summary of the *p*-values obtained from Mann–Whitney–Wilcoxon (MWW) Test used to verify the similarities in the distribution of the studied elements in a sampling medium (Surface soils and stream sediments) from two different geological domains (BD = Bacajá Domain and CB = Carajás Basin). Refer to Figure 1d for the location of the geological domains.

Element	Do the Samples from BD and CB Have Similar Distribution? (<i>p</i> -Values of the MWW Test)		Element	Do the Samples from BD and CB Have Similar Distribution? (<i>p</i> -Values of the MWW Test)	
	Surface Soils	Stream Sediments		Surface Soils	Stream Sediments
Fe		0.40	Hg	0.22	0.21
Al	0.13	0.46	Mn	0.12	
Ag	0.18	0.37	Mo		0.29
As	0.37	0.43	Ni	0.09	0.90
B		0.12	Pb		0.09
Ba		0.93	Sb		0.50
Bi	0.75	0.50	Se		0.92
Cd		0.59	Sn	0.43	0.74
Co		0.20	U		0.29
Cr	0.88	0.13	V	0.30	0.07
Cu			Zn	0.80	0.86

Note: Blank entries indicate *p*-value < 0.05.

Table 2. Descriptive statistics for Fe, Al, and 10 potentially toxic elements (PTE; As, Co, Cr, Cu, Hg, Mn, Mo, Ni, V, and Zn) in surface soils and stream sediments. Values were calculated for the entire Parauapebas River Basin (PB; soils = 364 samples; stream sediments = 189 samples) and for the northern (NPB; soils = 223 samples; stream sediments = 122 samples) and southern (SPB; soils = 141 samples; stream sediments = 67 samples) regions separately. Refer to Table S1 for the descriptive statistics of the remaining elements.

Element	Region	Surface Soil						Stream Sediments					
		LLD (% < LLD)	Mean	SD	Min	Med	Max	LLD (% < LLD)	Mean	SD	Min	Med	Max
Fe	PB *	0.01 (0)	4.96	5.82	0.3	2.71	29.6	0.01 (0)	4.01	5.17	0.42	1.98	35.4
	NPB	0.01 (0)	6.95	6.60	0.32	4.75	29.6	0.01 (0)	5.48	5.92	0.68	3.5	35.4
	SPB	0.01 (0)	1.84	1.63	0.3	1.34	9.04	0.01 (0)	1.34	0.81	0.42	1.16	4.79
Al	PB *	0.01 (0)	2.48	2.51	0.44	1.80	20.2	0.01 (0)	1.14	0.84	0.12	0.87	4.17
	NPB	0.01 (0)	3.17	2.96	0.57	2.29	20.2	0.01 (0)	1.37	0.91	0.19	1.11	4.17
	SPB	0.01 (0)	1.40	0.66	0.44	1.26	4.06	0.01 (0)	0.74	0.48	0.12	0.67	2.69
As	PB *	0.1 (5.2)	1.24	2.9	<0.1	0.5	38.4	0.1 (10.1)	0.66	1.00	<0.1	0.3	7.9
	NPB	0.1 (1.8)	1.79	3.50	<0.1	0.9	38.4	0.1 (3.3)	0.90	1.17	<0.1	0.5	7.9
	SPB	0.1 (10.6)	0.37	0.82	<0.1	0.2	7.5	0.1 (22.4)	0.22	0.24	<0.1	0.2	1.7
Co	PB *	0.01 (0)	10.71	22.6	0.2	2.9	237	0.01 (0)	11.60	12.88	0.8	6.8	66.9
	NPB	0.01 (0)	12.24	25.98	0.2	3.3	237	0.01 (0)	14.96	14.52	0.8	9.7	66.9
	SPB	0.01 (0)	8.27	15.69	0.3	2.3	97.5	0.01 (0)	5.49	5.21	0.9	3.3	26.8
Cr	PB *	1 (0)	82.34	296.3	2	31	3970	1 (0)	58.38	196.57	4	30	2630
	NPB	1 (0)	114.35	371.76	2	44	3970	1 (0)	75.83	241.32	4	37.5	2630
	SPB	1 (0)	32.63	65.82	2	12	612	1 (0)	26.61	41.41	4	15	294
Cu	PB *	0.2 (0)	48.88	79	0.5	21.8	726	0.2 (0)	48.92	73.69	1.4	20	556
	NPB	0.2 (0)	66.36	90.89	1.7	34.9	726	0.2 (0)	71.55	83.32	2.6	41.65	556
	SPB	0.2 (0)	21.39	42.75	0.5	8.7	438	0.2 (0)	7.73	8.49	1.4	5.2	47.4
Hg	PB *	0.01 (0)	0.1	0.1	0.02	0.07	0.54	0.01 (9.0)	0.03	0.03	<0.01	0.02	0.14
	NPB	0.01 (0)	0.13	0.08	0.02	0.11	0.54	0.01 (5.7)	0.04	0.03	<0.01	0.03	0.14
	SPB	0.01 (0)	0.05	0.02	0.02	0.05	0.11	0.01 (14.9)	0.02	0.01	<0.01	0.01	0.08
Mn	PB *	5 (0)	606.2	941.5	13	308	8590	5 (0)	826.32	933.84	69	547	6420
	NPB	5 (0)	710.33	1136.67	27	318	8590	5 (0)	950.10	1050.42	74	609.5	6420
	SPB	5 (0)	440.04	453.61	13	300	2970	5 (0)	600.94	617.48	69	428	3270

Table 2. Cont.

Element	Region	Surface Soil						Stream Sediments					
		LLD (% < LLD)	Mean	SD	Min	Med	Max	LLD (% < LLD)	Mean	SD	Min	Med	Max
Mo	PB *	0.05 (0.5)	0.85	0.9	<0.05	0.48	6.34	0.05 (0)	0.57	0.60	0.06	0.36	3.49
	NPB	0.05 (0)	1.16	1.02	0.06	0.84	6.34	0.05 (0)	0.75	0.68	0.11	0.545	3.49
	SPB	0.05 (1.4)	0.36	0.35	0.025	0.26	2.17	0.05 (0)	0.24	0.13	0.06	0.23	0.76
Ni	PB *	0.2 (0)	21.47	87.8	0.7	6.3	1260	0.2 (0)	15.73	32.24	1.1	6.9	273
	NPB	0.2 (0)	28.20	110.36	0.8	8.3	1260	0.2 (0)	20.95	38.76	1.2	9.7	273
	SPB	0.2 (0)	10.89	22.43	0.7	4.6	220	0.2 (0)	6.21	7.97	1.1	4.2	47.1
V	PB *	1 (0)	81.09	87.3	1	43	435	1 (0)	50.37	57.18	2	29	410
	NPB	1 (0)	111.46	93.79	4	89	435	1 (0)	68.57	63.63	2	43	410
	SPB	1 (0)	33.90	45.80	1	18	369	1 (0)	17.22	12.81	4	14	75
Zn	PB *	2 (0.5)	22.35	25.7	<2	16	202	2 (0)	30.04	40.99	3	19	304
	NPB	2 (0.9)	23.52	30.92	<2	14	202	2 (0)	39.28	48.40	3	24	304
	SPB	2 (0)	20.53	13.95	4	18	120	2 (0)	13.22	6.80	4	13	40

Note: The concentration unit is expressed in mg kg⁻¹, except for Fe and Al in wt.%; DL = Lower limit of detection; % < DL = % of data below LLD; Mean = Arithmetic mean; SD = Standard deviation; Min = Minimum; Med = Median; Max = Maximum; '*' = Surface soil data from [24].

The use of intersection function under geoprocessing environment allowed plotting and merging of soil samples with stream sediment catchment areas. It is important to highlight that a single microcatchment, which is represented by only one stream sediment sample, can be merged to multiple soil samples, or even none in the rare cases of no collected samples in the catchment area. Scatter plots comparing the concentrations of selected elements in surface soil (y-axis) and stream sediment (x-axis) samples were constructed to verify a possible relationship between them by using linear regression analysis (Figure 5 and Figure S4). Spearman's correlation coefficient (ρ) and p -value of the linear regression are presented. In general, the majority of the selected elements presented a significant correlation ($p < 0.05$), excepting for Cd, Ba, B, and Zn ($p > 0.05$; Figure S4). Three groups were observed: (i) Strongly ($\rho \geq 0.5$) correlated materials: Fe, As, Cu, and U in Figure 5; Bi, Sn, Mo, and V in Figure S4; (ii) Moderately ($0.49 < \rho \leq 0.3$) correlated materials: Hg, Ni, Cr, and Sb in Figure 5; (iii) Weakly ($\rho \leq 0.29$) to non-significant ($p > 0.05$) correlated materials: Al, Mn, and Co in Figure 5; Se, Ag, Pb, Cd, Ba, B, and Zn in Figure S4.

In this study, geochemical threshold concentration values were determined for all 22 studied elements in soils and stream sediments, but contrarily to the approach adopted in previous studies [24,58], distinct threshold values for the NPB and SPB were calculated, by using a variety of statistical methods (M_{MAD} , TIF, and percentile-based techniques, e.g., P98 and P95; Table 3). Threshold values of each individual subregion were then compared to threshold values proposed for the whole PB, determined in previous studies of soil [24] and stream sediments [58].

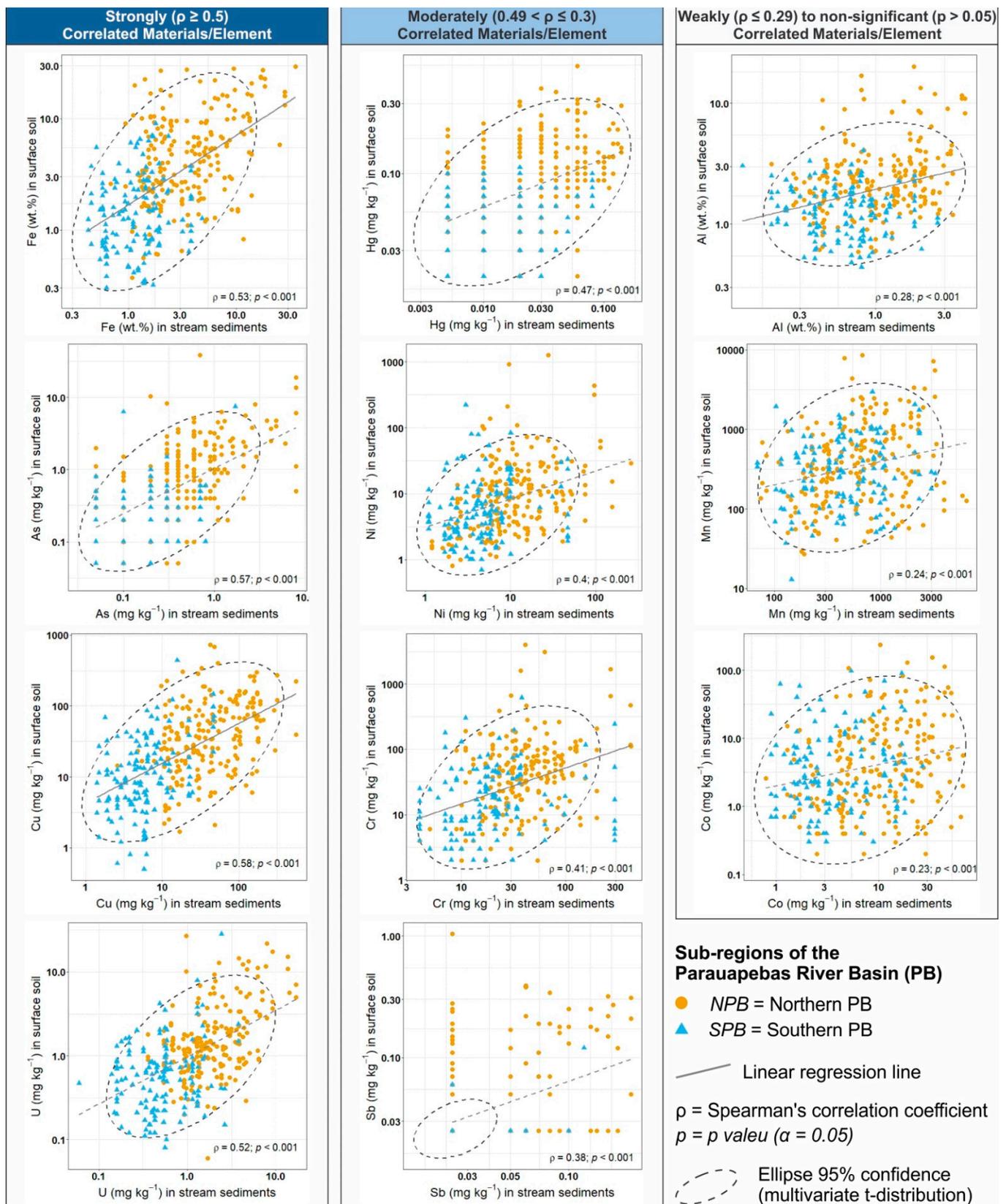


Figure 5. Scatter plot comparing the concentrations of selected elements in surface soil samples against stream sediment samples. Three groups of elements were observed: (i) Strongly correlated materials (e.g., Fe, As, Cu, and U); (ii) Moderately correlated materials (e.g., Hg, Ni, Cr, and Sb); (iii) Weakly to non-significant correlated materials (e.g., Al, Mn, and Co); Additional scatter plots for the remaining elements are presented in Figure S4.

Table 3. Geochemical threshold values for Fe, Al, and 10 potentially toxic elements (PTE; As, Co, Cr, Cu, Hg, Mn, Mo, Ni, V, and Zn) in surface soils and stream sediments, estimated by a variety of methods [Median + 2 Median Absolute Deviation (M_{MAD}), Tukey's inner fences (TIF), the 98th (P98) and 95th (P95) percentiles]. Values are provided for the entire Parauapebas River Basin (PB, retrieved from previous studies), for the northern (NPB) and the southern (SPB) regions separately, determined in the present study. Guideline values reposted by Brazilian environmental agencies are presented as references. Refer to Table S2 for the results of the remaining elements.

Element	Regions	Geochemical Threshold in Surface Soil				Soil Guidelines		Geochemical Threshold in Stream Sediments				Stream Sediment Guidelines	
		M_{MAD}	TIF	P98	P95	QRV ^b	PGV ^c	M_{MAD}	TIF	P98	P95	L1 ^d	L2 ^d
Fe	PB ^a	25.7	58.21	24.55	18.2			12.02	29.51	17.76	12.94		
	NPB	34.24	68.63	27.51	22.65			22.93	42.89	26.74	16.73		
	SPB	6.93	12.24	6.92	5.99			3.54	5.20	3.74	2.88		
Al	PB ^a	5.62	8.51	11.22	8.32			▲	▲	3.32	2.76		
	NPB	6.51	8.89	12.45	10.57			6.25	10.72	3.44	3.16		
	SPB	3.34	4.74	3.05	2.65			2.87	3.63	2.01	1.51		
As	PB ^a	7.2	14.1	7.2	4.5			2.4	4.6	3.9	2.4		
	NPB	7.0	14.9	9.4	5.2	3.5	15	2.3	6.1	4.5	2.9	5.9	17
	SPB	1.6	3.2	1.1	0.6			1.6	1.6	0.8	0.5		
Co	PB ^a	69.2	201.8	79.4	47.9			▲	▲	51.4	42.5		
	NPB	96.4	284.9	96.5	48.9	13	25	93.2	190.1	52.2	48.3		
	SPB	35.7	91.7	64.5	37.0			16.7	39.6	18.3	16.3		
Cr	PB ^a	562	1413	468	191			191	331	275	138		
	NPB	564	1401	661	254	40	75	160	277	348	139	37.3	90
	SPB	161	529	204	117			68	121	134	89		
Cu	PB ^a	398.1	1216.2	275.4	162.2			512.9	▲	288.5	177.0		
	NPB	365.9	926.3	302.7	223.7	35	60	482.4	1223.9	306.0	190.5	35.7	197
	SPB	72.7	203.1	101.9	70.7			20.0	35.1	37.8	22.8		
Hg	PB ^a	0.40	0.55	0.32	0.27	0.05	0.5	0.16	▲	0.13	0.10		
	NPB	0.14	0.25	0.10	0.09			0.23	0.31	0.13	0.11	0.17	0.486
	SPB	0.14	0.25	0.10	0.09			0.08	0.06	0.06	0.04		
Mn	PB ^a	3890	8810	2884	1995			3548	6383	3387	2564		
	NPB	4835	14,783	3908	2359			4503	8660	3732	3117		
	SPB	2538	5083	1793	1250			3079	4643	2766	1839		
Mo	PB ^a	4.79	10.59	3.31	2.88			1.95	▲	2.92	1.69		
	NPB	6.11	11.43	3.60	3.14	<4	30	2.82	4.63	3.02	2.36		
	SPB	1.10	1.58	1.70	0.99			0.73	1.02	0.51	0.46		
Ni	PB ^a	60.3	142.9	107.2	52.5			45.7	88.1	100.3	46.8		
	NPB	98.8	173.0	174.2	64.1	13	30	56.4	127.0	137.3	71.0	18	35.9
	SPB	32.6	80.0	78.7	33.5			12.6	19.5	36.4	17.5		
V	PB ^a	891	2512	331	269			234	▲	188	162		
	NPB	769	1831	344	284			360	931	239	183		
	SPB	141	288	160	121			61	112	47	40		
Zn	PB ^a	63	89	115	65			60	88	27	18		
	NPB	53	84	144	74	60	300	83	169	216	114	123	315
	SPB	54	75	55	43			47	55	27	24		

Note: The concentration unit is expressed in mg kg⁻¹, except for Fe and Al in wt.%; *Italic* or "▲" (value not available): threshold values greater than the maximum value; ^a Results reported in previous studies of soil [24] and stream sediments [58] of the PB; ^b Quality reference value (QRV) reported by the Sao Paulo Sanitation Technology Company (CETESB) [59]; ^c Prevention guideline value (PGV) reported by the National Council of the Environment (CONAMA) of Brazil [50]; ^d Threshold levels 1 (L1) and 2 (L2) reported by CONAMA [60]. Blank entries indicate data not available.

5. Discussion

5.1. Regional Geochemical Distribution of Fe, Al, and PTE in Soils and Stream Sediments

The geochemical signature of an element in a given sampling medium provides important information about external controlling conditions, either natural or anthropic. The geochemical maps for Fe, Al, and 20 PTE (Figures 2 and 3, Figures S1 and S2) in the two-sampling media, as assessed by visual inspection, are notoriously similar. The composition of soils and stream sediments appears to be strongly controlled by bedrock lithologies in the area (Figure 1c), with evident differences between the north and south of the study

area. Higher concentrations for the majority of the elements in both sampling media are observed in the NPB in comparison to SPB (Figure 1b).

The spatial distribution of these elements is well-documented in previous studies of soil [24,44] and stream sediment [45,58]. For instance, the concentrations of Fe, V, As (Figure 2) (\pm Cd, Sb and Ag; Figure S1) and relative concentrations of Al, Ba, Mn, and Zn (Figures 2 and 3, Figure S2), along with two E-W corridors (tectonic trend of the region) in the NPB are controlled by the occurrences of Fe-Al-rich duricrusts, formed by the intense weathering of metamafic rocks and BIF of the Carajás Formation, which hosts the world-class Fe deposits (N4, N5, and S11D) of Carajás [61–63].

Similarly, the concentrations of Ni, Cr, Co, and \pm V (Figure 3) are strongly controlled by the metavolcanic rocks of the Parauapebas Formation, generally intercalated with rocks from the Carajás Formation, and cross-cut by local mafic to ultramafic rocks of the Cateté Intrusive Suite (the Luanga Complex, located in the NE of the NPB; the Vermelho Complex, in the southern area of the NPB) [37,64]. Local anomalies also occur in the south of the SPB, due to the occurrences of Sapucaia greenstone belt [65].

The spatial distribution of Cu, Mo (Figure 2), and to a lesser extent Se (Figure S1) is a response of mineralization zones along two E-W corridors (northern and southern copper belts [27]) in the NPB, similarly observed for Fe and related elements. To some extent, higher concentrations of Se (Figure S1) were observed in stream sediments and, especially, in soils of the north of NPB, along the northern copper belt in comparison to the southern copper belt. This evidence indicates that these two corridors do not share common surface multi-element signatures, perhaps, due to different metallogenic evolution [27].

Uranium, Pb, and Sn tend to concentrate in quartz-feldspar rocks, such as granites and felsic granulites, particularly those with an alkaline tendency. In the NPB, the main sources for the enrichment of these elements are A-type granitoids (e.g., Estrela and Igarapé Gelado granites) and Paleoproterozoic anorogenic granites (e.g., Seringa and Serra dos Carajás granites) [38]. In addition, unusually high concentrations of Mn, Co, and Ba (Figure 3 and Figure S2) in soils and stream sediments and B in soils (Figure S1) were observed in the NW region of the SPB, under the influence of charnockitic rocks (Figure 1d) of the Diopside-Norite Pium unit [28].

Using integrated geochemical maps is important not only for understanding the regional distribution of a given element but also to compare two (or three) different sampling mediums in terms of concentration magnitude and source. Although, as described, the different lithologies of the area are the main source of enrichment for Fe, Al, and the 20 PTE. However, anthropogenic contributions cannot be disregarded and further studies should be conducted.

5.2. The Geochemical Compartmentation of PB as Subsidy to Territorial and Watershed Management

Watershed management is essential for planning the sustainable use of natural resources. It supports many kinds of human needs in terms of water consumption, food production, recreation, and most importantly the maintenance of ecologic function [66]. Each watershed has its own particularities, for instance, climate conditions, land use, human occupation, and, for the purpose of the present study, geochemical background. All these multidisciplinary concerns have increased the need of developing robust watershed-management strategies aiming for realistic environmental policies [67].

As presented in previous studies, the chemical composition of soils [24,44] and stream sediments [45] changes with the geological domain across the IRW, including the study area (Figure 1b). Nevertheless, minor differences were also observed between the BD and CB in terms of spatial distribution for many elements, as discussed previously. The boxplots for the studied elements (Figure 4 and Figure S3) display the difference among the geological domains of the PB area (Figure 1d), suggesting that many elements actually present similar distribution (e.g., Al, As, Bi, and Cr; Figure 4). For this reason, the element concentration in soil and stream sediment samples from these two domains were statistically compared using the MWW test (Table 1). The obtained results suggest that dividing the study area

into NPB and SPB is statistically acceptable, at least for surface geochemical studies at a regional scale. However, the geochemical data of Cu in the PB represents a clear exception to this approach. Not only the MWW test revealed different statistical distribution between BD and CB (p -value < 0.05; cf. Table 1), but also the boxplots (Figure 4 and Figure S3) and the integrated geochemical map (Figure 2). The Cu signature in the PB is a clear response from highly mineralized areas that constitute a geochemical and metallogenic province [68], which cannot be generalized in terms of watershed management.

5.3. The Relationship between Surface Soil and Stream Sediment Geochemistry

A visual inspection of the boxplots (Figure 4 and Figure S3) and the comparison of descriptive statistics results (Table 2 and Table S2) revealed that element concentrations in soils are generally greater than in stream sediments of PB. This is particularly true for Fe, Al, Ag, As, B, Bi, Cd, Cr, Cu, Hg, Mo, Sb, V, Se, and Sn, and it is not observed for Ba, Co, Mn, Ni, Zn, Pb, and U. By using geoprocessing techniques, it was possible to identify the soil samples that are geographically located at a given catchment area, which is represented by a stream sediment sample collected at the outlet, and compare them. Scatter plots used to evaluate the relationship between surface soil and stream sediment samples revealed that these sampling media are strongly to moderately correlated for many elements (Fe, As, Bi, Cr, Cu, Hg, Mo, Ni, Sb, Sn, U, and V; Figure 5 and Figure S4), but weakly to other elements (Al, Ag, B, Ba, Cd, Co, Mn, Pb, Se, and Zn; Figure 5 and Figure S4). In terms of source apportionment, in the case of the elements with strong to moderate correlations the composition of soils and stream sediments seems to be both controlled by the bedrock lithologies or, alternatively, the soils themselves are the primary source for the constitution of stream sediment, driven by erosion processes that have been directly influenced by the deforestation in the area over the past decades [69]. The weak correlations may be due to three reasons: (i) Mineralogical sorting during hydrodynamic and sedimentation processes. For instance, Al is a major constituent of kaolinites, which is a naturally occurring mineral in the soils of the Amazon [70], but to a lesser extent in active river sediments; (ii) low sensitivity of the analytical method, which is clearly the case for Ag, B, Ba, Cd, and Se; (iii) Different sources contributing to the enrichment of an element in a given sampling media. For this case, Ba, Co, Mn, Pb, and Zn captured our attention because these elements are well-known for being part of important biogeochemical processes that take place in nature [71].

5.4. Geochemical Threshold Variation in Soils and Stream Sediments vs. Environmental Guidelines

The existence of solid legislations proposing reference-quality guideline values for different regions, demarked by considering a multidisciplinary approach, including the definition of geochemical compartments, instead of simply using political boundaries would be ideal. Under this context, the variation of the background concentrations in soils and stream sediments of the PB and the quality guideline values proposed by Brazilian environmental agencies [50,59,60] should be critically evaluated.

Firstly, the threshold values calculated by using statistical techniques widely applied in geochemical studies [72–74] pointed out different results among each statistical method (Table 3 and Table S3). These differences occur due to the statistical approach and the central criteria of the method, which is widely discussed in the literature [17,22,23,44,45]. In general, the highest background values were obtained by the TIF method, with several overestimated values (cf. Table 3 and Table S3). The P98 and P95 deliver threshold values by considering a fixed percentage of outliers, within the range of values in the data set, which is not entirely appropriate. Among the methods used herein to derive threshold concentration values, the M_{MAD} appears to derive more consistent and realistic results. This conclusion has been also achieved in other studies [17,22,23]. For this reason, the following discussion will be addressed by using the M_{MAD} results (Table 3 and Table S3).

The comparison of the threshold values, in both sampling media, between the NPB and the SPB regions revealed significant discrepancies. For instance, the threshold concen-

trations of Fe in soils of the NPB and SPB are 34.24 and 6.93 wt.%, respectively, and in stream sediment are 22.93 and 3.54 wt.%, respectively (Table 3). Similar behavior is observed for the majority of the studied elements (cf. Table 3 and Table S3). The differences observed in each region are a direct influence of the natural geological/geochemical variation, already described in this study, confirming the consistency of the results presented here.

The previous results demonstrated the existence of a large natural spatial variation of PTE in the territory of PB and indicated that establishing threshold values for the NPB and SPB regions is more adequate than assuming a uniform value for the entire PB. This conclusion is also relevant in terms of defining quality guideline values for large areas elsewhere. For instance, the comparison of threshold values in NPB and SPB (cf. Table 3 and Table S3) for some PTE [As (NPB = 2.3; SPB = 1.6), Cd (NPB = 0.16; SPB = 0.01), Pb (NPB = 24.4; SPB = 14.2), and Zn (NPB = 83; SPB = 47; all values in mg kg^{-1})] contemplated in the Brazilian environmental resolution of stream sediments [60] shows that they have their threshold concentrations below the Level 1 (L1; also known as the Threshold Effect Level—TEL [75]) proposed by the National Council of the Environment (CONAMA) of Brazil [60] for the mentioned elements (cf. Table 3 and Table S3). Mercury exhibits a threshold value in NPB (0.23 mg kg^{-1}) greater than the L1 (0.17 mg kg^{-1}), but the referenced value in SPB (0.08 mg kg^{-1}) is lower than L1. Nickel shows in NPB threshold value (56.4 mg kg^{-1}) greater than the Level 2 (L2, also known as the Probable Effect Level—PEL [75]; L2 of Ni = 35.9 mg kg^{-1}), but in the SPB the obtained value (12.6 mg kg^{-1}) is lower than L1 (18 mg kg^{-1}). The greatest differences were observed for Cu (482.4 mg kg^{-1}) and Cr (160 mg kg^{-1}), for which threshold values in the NPB are considerably greater than the L2 (Cu = 197; Cr = 90 mg kg^{-1}). On the other hand, the threshold values in SPB for Cr (68 mg kg^{-1}) are between the L2 and L1 (respectively, 90 mg kg^{-1} and 37.3 mg kg^{-1}), and for Cu (20 mg kg^{-1}) below L1 (35.7 mg kg^{-1}).

The quality guidelines of soils in Brazil are based on two resolutions, a Federal resolution [50] applicable for the entire Brazilian territory, which presents Prevention Guideline Values (PGV), and a State resolution for the definition of Quality Reference Value (QRV), which corresponds to the geochemical background. In the absence of QRV for the State of Pará (PA), where the PB is situated, the State Secretariat of the Environment and Sustainability (SEMAS-PA) adopted for the Pará territory the same QRV presented by the São Paulo Sanitation Technology Company (CETESB) [59], derived for the State of São Paulo.

Firstly, it should be emphasized that it is profoundly inadequate to establish geochemical background values for a given area (e.g., the PB situated in the State of Pará) based on values of another region (e.g., the State of São Paulo), with completely different environmental, geological and geochemical characteristics. This is clear when comparing the threshold values of the PTE with the QRV proposed by the State resolution [59]. Among the 14 PTE contemplated in the resolution, ten (As, Ba, Co, Cr, Cu, Hg, Mo, Ni, Pb, and Se) presented generally, in both NPB and SPB, higher threshold values in comparison to the QRV. From this group, when compared to the PGV, which values are somewhat higher than those of QRV (Table 3 and Table S3), the discrepancies with assumed background values of PB are reduced. In contrast, Ag, Cd, and Zn presented lower threshold values than the proposed QRV and PGV, whereas Se showed in NPB and SPB background values higher than QRV and lower than PGV (Table 3 and Table S3).

Secondly, instead of defining realistic threshold values for the entire State and some relevant areas, it appears that environmental agencies tend to define even more conservative QRV values, which is clearly seen by comparing the QRV and PGV values (Table 3 and Table S3). It is highly recommended that new QRV values should be established for the different large geological domains of the State of Pará, in particular for the Carajás region, by using soil samples from the area of investigation and considering the complexity of the geological setting, as similarly conducted in previous studies in the State of Pará [76,77].

The issues addressed above show how understanding the variation of the geochemical background is important for territorial and watershed management. Therefore, the source

of the anomalies of the PTE needs to be carefully investigated on a case-by-case basis, considering the local scenario (geology, land use, possible anthropic interventions). It is not demonstrated that high concentrations of some PTE, above the threshold values, are indeed influenced by anthropogenic activities. In the case of PB, the majority of the soil and stream sediment samples with values above the threshold is actually due to bedrock lithologies and hydrothermal mineralized zones (e.g., northern and southern copper belts) that naturally occur in the area. This reinforces the need for new environmental resolutions, which consider the regional characteristics and can thus provide more realistic guideline values.

6. Conclusions

Soils and stream sediments of the PB are strongly influenced by the geological environment of the region. The geochemical maps revealed substantial differences between the NPB and the SPB regions. At the regional scale, the local anomalies are mostly influenced by the bedrock lithologies rather than by any anthropogenic impact. Significant evidence has shown that the metavolcanosedimentary rocks of the CB and, particularly, the mineralizations along the northern and southern Cu belts in the NPB are the main source for several anomalous concentrations of PTE in both sampling media. Considering the elements under investigation in the PB area, the geochemical compositions of soils and, especially, stream sediments of the BD and CB are statistically similar. The soils and stream sediments are strongly to moderately correlated for many elements (Fe, As, Bi, Cr, Cu, Hg, Mo, Ni, Sb, Sn, U, and V), which suggest the same rock source or, in some cases, the soils themselves as the primary source for the constitution of stream sediments, driven by erosion processes and intensified by the deforestation in the area. The comparison between new statistically derived threshold values of the NPB and SPB regions with the threshold values of the whole PB and to quality guidelines proposed by Brazilian environmental agencies demonstrates that a uniform value of quality guideline is not adequate, because it does not consider the natural geological/geochemical variation of the area. For this reason, geochemical compartments, instead of political boundaries, should be considered prior to defining new guideline values. The integrated assessment used here is easily replicated and remarkably useful for territorial and watershed management, important for the Sustainable Development Goals.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2571-8789/5/1/21/s1>, Figure S1 Geochemical maps for Ag, B, Cd, Sb, and Se; Figure S2: Geochemical maps for Ba, Bi, Pb, Sn, and U; Figure S3: Boxplots for 8 potentially toxic elements (PTE; Ag, B, Cd, Mo, Sb, Sn, Pb, and U); Figure S4: Scatter plot comparing the concentrations of the studied elements in surface soil and stream sediment samples; Table S1: Descriptive statistics for 10 potentially toxic elements (PTE; Ag, B, Ba, Bi, Cd, Pb, Sb, Se, Sn, and U) in surface soils and stream sediments; Table S2. Geochemical threshold values for 10 potentially toxic elements (PTE; Ag, B, Ba, Bi, Cd, Pb, Sb, Se, Sn, and U) in surface soils and stream sediments.

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