minerals

Article

Geochemical Mapping and Reference Values of Potentially Toxic Elements in a Contaminated Mining Region: Upper Velhas River Basin Stream Sediments, Iron Quadrangle, Brazil

Raphael Vicq [1], Mariangela G. P. Leite [2], Lucas P. Leão [2], Hermínio A. Nallini Júnior [2] and Teresa Valente [1,*]

[1] Earth Science Institute, Pole of the University of Minho, Campus Gualtar, 4710-057 Braga, Portugal; raphaelcosta@dct.uminho.pt

[2] Department of Geology, Federal University of Ouro Preto, Morro do Cruzeiro Campus, Ouro Preto 35400-000, MG, Brazil; mgpleite@ufop.edu.br (M.G.P.L.); lucas.leao@ufop.edu.br (L.P.L.); nallini@ufop.edu.br (H.A.N.J.)

* Correspondence: teresav@dct.uminho.pt

Abstract: The Upper Velhas River Basin, in the mining region of the Iron Quadrangle, is one of the most polluted basins in Minas Gerais, Brazil. The region has been exploited for gold and iron, among other substances of interest. In addition to abandoned mines, active works and mineralized rocks contribute to the discharge of contaminated waters into the rivers and streams. Thus, high-density geochemical mapping with the determination of reference values has become very important, as it allows the spatial distribution of contaminant elements to be obtained, contributing to the recognition of areas with deviant values in the basin. Two hundred and eight sediment samples were collected from streams throughout the Velhas River Basin, with a density of one sample per 15 km^2. Geochemical maps were compiled using the distance-weighted inverse interpolation method, and concentrations were distinguished from anomalies using the box plot Upper Inner Fence technique. It was found that 73–78% of the basin area does not present geogenic and anthropic anomalies, with values up to the third quartile for As, Cd, Cr, Ni, Cu, Pb, and Zn. However, anomalies related to human actions, mainly mining works and rock types, occupy 2 to 11% of the area. This first high-density mapping in the Upper Velhas River Basin found numerous streams with concentrations of the elements studied above the Probable Effect Level, allowing us to determine which locations, cities, and river sub-basins are exposed to environmental risks and should be monitored and protected.

Keywords: high-density geochemical mapping; reference values; mining contamination; Brazil

check for updates

Citation: Vicq, R.; Leite, M.G.P.; Leão, L.P.; Nallini Júnior, H.A.; Valente, T. Geochemical Mapping and Reference Values of Potentially Toxic Elements in a Contaminated Mining Region: Upper Velhas River Basin Stream Sediments, Iron Quadrangle, Brazil. *Minerals* **2023**, *13*, 1545. https://doi.org/10.3390/min13121545

Academic Editor: Bohdan Křibek

Received: 13 November 2023
Revised: 7 December 2023
Accepted: 11 December 2023
Published: 14 December 2023

1. Introduction

Mining works typically drive river system degradation, including water and sediment reservoirs. Contaminated sediments are considered the problem that most contribute to aquatic ecosystem degradation, acting diffusely. This makes it challenging to control pollution and is therefore considered an eminent concern to be solved for preserving water resources [1]. This environmental compartment has a great capacity for the absorption/adsorption of potentially toxic elements (PTEs), which can cause harm to human health [2]. In addition, factors such as the lack of rainfall and the consequent reduction in flow cause greater concentrations of these pollutants in the sediments [3,4]. Geochemical mapping of stream sediments contributes significantly to the control of pollution, which is important for the sustainable growth tripod (environmental, social, and economic development) [5,6]. Hence, this issue has been relevant in environmental analysis studies in the last few years [7]. The maps generated allow the visualization of the spatial distribution of chemical elements in a specific area, contributing to recognizing regions with anomalous values and identifying their main sources, whether natural or associated with anthropic activities, mainly mining [8–11]. New areas for mineral exploration can be delineated from these mappings, and reference and safety concentrations can be established so that the population may become aware of potential environmental risks and environmental policies may be implemented [6].

Due to the long history of mining and the geological complexity, the upper basin of the Velhas River, in the Iron Quadrangle (IQ) region, was the subject of several geochemical studies that reported high levels of PTEs in stream sediments [12–20], all using aqua regia as an extraction method and a particle size fraction below 63 µm. Table 1 summarizes the most well-known survey areas, with the number of monitored points and the concentration values characterized by local and low-density studies.

Table 1. Summary of main geochemical studies in the Upper Velhas River Basin—Iron Quadrangle—Minas Gerais, Brazil. Min—Minimum; Max—Maximum; Q3—Third quartile.

References	Basin/Cities	No of the Sampled Points	Stream Sediments (mg kg^{-1})				
Deschamps Matschullat (2007) [15]	Velhas River—Nova Lima and Rio Acima	24		Min	Mean	Q3	Max
			As	47	140	----	3300
Mendonça (2012) [18]	Mata Porcos Riverside—Itabirito	12		Min	Mean	Q3	Max
			As	1.6	7	1.6	69
			Cr	8	79	94	198
			Cu	0.3	41	48	180
			Pb	1	26	33	47
			Ni	0.6	19	30	47
			Zn	30	60	72	119
Pereira et al. (2007) [16]	Velhas River—Ouro Preto, Itabirito, Rio Acima, Nova Lima, Raposos, Belo Horizonte, and Sabará	19		Min	Mean	Q3	Max
			As	2	-----	35	580
			Cr	30	-----	180	510
			Cu	20	-----	60	110
			Ni	5	-----	95	480
			Zn	40	-----	105	380
Gonçalves (2010) [17]	Microbasins of Andaime and D'Ajuda Stream—EPA Cachoeira das Andorinhas and Floresta do Uaimii	8		Min	Mean	Q3	Max
			As	1.6	50	77	167
			Cr	197	393	520	632
			Cu	8	43	48	97
			Pb	1	10	17	50
			Ni	65	146	177	220
			Zn	50	84	104	131
APA SUL (2005) [14]	Middle Velhas River—Itabirito, Rio Acima, Nova Lima, Caeté, Raposos	44		Min	Mean	Q3	Max
			As	4.1	91	85.3	873
			Cd	1.6	7.3	9.3	12,2
			Cr	44	293	363	1077
			Cu	17	85.4	87.5	841
			Pb	7	20	27	47
			Ni	10	74	84	332
			Zn	28	73	85	175

These surveys are scattered in several sub-basins of the Velhas River; so far, no high-density sampling study covers the whole basin area and relates the results obtained with the diversity of existing lithotypes. Aiming to fill this gap, a high-density geochemical mapping was carried out in the upper course of the Velhas River Basin. Pollutants of ecological and human health concerns, like the PTEs (As, Cd, Cr, Ni, Cu, Pb, and Zn), were surveyed and mapped for the river sediments in this catchment.

2. Materials and Methods

The Upper Velhas River region is inserted in the Iron Quadrangle in the central region of the state of Minas Gerais, covering an area of 3200 km^2, comprising nine municipalities, with the city of Ouro Preto as the south–southeast limit, the municipalities of Belo Horizonte and Sabará as the border with the north, Serra da Moeda (Itabirito) as the west limit and Serra da Piedade (municipality of Caeté) delimiting its east–northeast region (Figure 1).

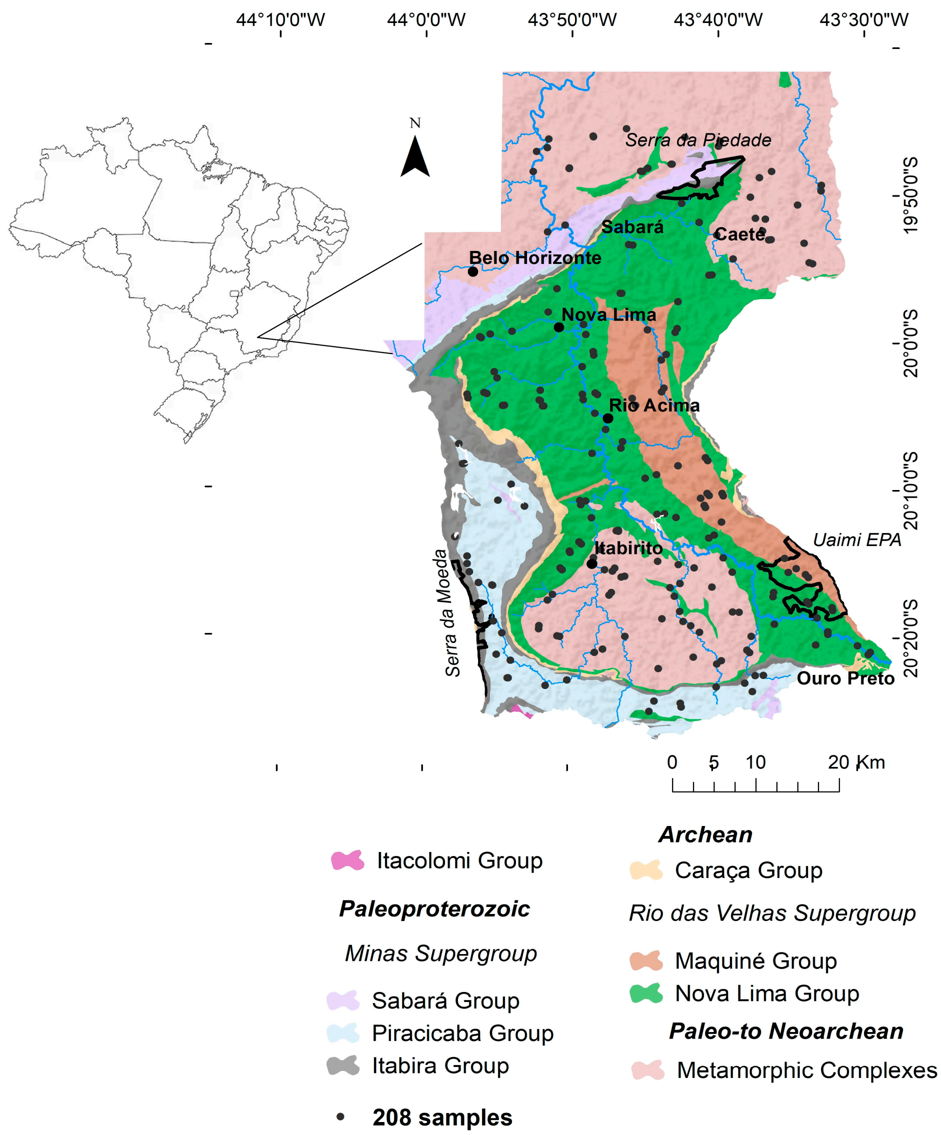

Figure 1. Simplified geological map of the Upper Velhas River Basin.

Four major lithostratigraphic units mainly define the regional geology (Figure 1). At the base, there are the granite–gneiss metamorphic complexes (Bonfim, Santa Rita, Caeté, Belo Horizonte, Santa Bárbara, and Bação), which represent the crystalline basement of the region, formed by poly-deformed gneissic rocks of tonalitic composition and granite, granodiorite, mafic and ultramafic intrusions [21]. Following the three metamorphic units, (a) Velhas River Supergroup, consisting of metasedimentary and metavolcanic rocks, forms the Rio das Velhas Greenstone Belt (RVGB). The RVGB rocks are constrained in the Homonymous Supergroup, which comprises two groups (from bottom to top): (i) Nova Lima Group (metavolcanic–sedimentary sequence) and (ii) Maquiné Group (siliciclastic metasedimentary rocks) [22,23]. The upper Nova Lima Group comprises a basal volcanic unit ranging from tholeiitic to komatiitic, associated with a large amount of chemical sedimentary rocks. This group is subdivided into three units, named Catarina Mendes, Córrego da Paina, Córrego do Sítio, Mindá, and Fazenda Velha, which presents the predominance of volcanic–sedimentary rocks composed of carbonate schists, metacherts, ferriferous formations, and phyllites. The Maquiné Group, which presents metaconglomerates at the base, overlapped by massive and sericitic quartzites, sericite quartz schists, and phyllites [22,23]; (b) Minas Gerais Supergroup, divided into three groups (from bottom to top): Itabira, Piracicaba, and Sabará, whose basal units are composed of metaconglomerates and metarenites grading for marine metapelites, which were covered by a sequence of chemical sediments. The Itabira Group consists of banded iron formations in the Cauê Formation and carbonate rocks in the Gandarela Formation. The Piracicaba Group comprises quartzites and ferruginous schists, conglomerates with itabirite pebbles, and carbonaceous phyllites deposited in a shallow to deep marine environment [22]. The Sabará Group is the youngest unit of the Minas Supergroup. It is positioned above the Piracicaba Group and is composed of essentially terrigenous sedimentation, with a base marked by conglomeratic phyllite, schists, and quartzites [22,23]. The Itacolomi Group is above the Minas Supergroup, following the crystalline base from bottom to top. Locally, Tertiary deposits and Quaternary sediments occur, forming polymictic conglomerates, sericitic quartzites, and pelites [23].

The region's estimated population is 4.3 million [24], which represents 22% of the total population of Minas Gerais state, which is the largest urban concentration area in the state. The region's production corresponds to 26.8% of Minas Gerais gross domestic product. The population's average income varies between 1 and 3.5 minimum wages, and only 23% has completed secondary education. The regional economy is based on mining and tourism with additional intense industrial activities, particularly in the steel sector and metallurgy [24]. Among mining activities, there are essential iron mines, as well as vast resources of gold, limestone, dolomite, bauxite, manganese, topaz, and clay, among others, making it one of the most important productive mineral provinces in the country and the most well known in geological terms [19]. This socioeconomic importance is also increased since the area provides water for the entire metropolitan area of Belo Horizonte, which concentrates 70% of the basin's population [25].

A total of 208 stream sediment samples were collected throughout the study area (3200 km^2), providing a density of 1 sample per 15 km^2. The selection of the sampling points was carried out with the collection of sediments being carried out in the mouth of the third-order basins [26], which were determined from the ArcGis 10.8 software, with the hypsometric, topographic, and hydrographic maps of the region on the scale of 1: 25,000, provided by the Institute of Water Management and by the Company of Mineral Resources Production.

All sediment samples were collected along a 300 to 500 m stretch, in which nine subsamples were taken, to cover different patterns of the fluvial geomorphology (riffles, pools, and transition). In each morphological type, samples were collected in the right margin, left margin, and middle of the channel. The samples of the margins were collected at 0.50 m from the riverbed, always trying to avoid the collection of organic matter and still in the field. The subsamples were mixed to obtain a representative sample of the stretch [27]. After complete homogenization, a 500 g sample was packed in plastic bags [27].

The sediment samples were dried at room temperature and sieved, and 1 g of the granulometric fraction smaller than 63 μm was subjected to digestion by aqua regia (HCl mixed with HNO_3, 3:1), carried out at the Laboratory of Geochemistry of the University Federal of Ouro Preto. After forming sediment "pulp" with Milli-Q water, in a volumetric flask to 100 mL total volume, 7.0 mL of concentrated HCl and 2.3 mL of concentrated HNO_3 (Merck p.a.) were added. The samples were allowed to stand at room temperature for 16 h in the exhaust hood. After this period, the beakers were heated (hot plate) to 100 $\pm$ 5 °C for 2 h for volume reduction, then cooled to room temperature and filtered through 0.45 μm pore filter paper. After that, the solution was diluted with Milli-Q water in a volumetric flask to 100 mL total volume [28]. To evaluate the accuracy of analyses, blank samples were produced at every tenth sample, and 10% of the samples were performed in duplicate. The results were additionally controlled for accuracy using certified reference material (LKSD-01, CCRMP, Ottawa, Ontário, Canada). Recovery rates were always between 93 and 107%. The digestion with aqua regia is called pseudo-total digestion. It allows the extraction of the elements associated with oxy-hydroxides, sulfides, clay minerals, and elements bound to organic matter, which are of greater environmental interest [8,29,30].

After the digestion, the samples were analyzed in the Spectrophotometer of Atomic Emission with Inductively Coupled Plasma Source (ICP-OES), brand Spectro/Ciros CCD, where the concentrations of Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Ti, and Zn were obtained. Detection limits are provided in Table 2. From the database obtained, iso-values maps were prepared for the potentially toxic elements (PTEs). The GIS environment was designed according to the World Geodetic System 1984 (WGS84) [31] datum, and the IDW (inverse distance weighted) geostatistical tool of interpolation was used, applying as a neighborhood technique the choice of 12 points [8,9,32]. The whole dataset of stream sediment chemical analyses was submitted to exploratory data analysis using Minitab 18 software, and box plot graphs were created. The analytical data that presented values below the detection limit were replaced by 0.8 LLD (Lower Limit of Detection) [8]. To distinguish between normal concentrations and anomalies, the quartile separation technique (Q1, Q2, and Q3) was adopted to classify the data into reference values, high values (reference), and outliers, in which anomalies are defined by the box plot Upper Inner Fence (UIF). This is obtained by multiplying by 1.5 times the interval between quartiles (IQR), which means the anomaly threshold = Q3 + (Q3 − Q1) × 1.5 [7,33,34].

Table 2. Detection limits for major, minor, and trace elements determined by ICP-OES.

Elements	Detection Limit (mg kg^{-1})
Al	2.6
As	1.6
Ca	1.0
Cd	0.4
Cr	0.2
Cu	0.3
Fe	0.8
Mg	0.1
Mn	0.1
Ni	0.6
Pb	1.0
Zn	0.1

3. Results

The statistical parameters of the element concentrations of the 208 sediment samples and the medians of the projects in Europe, Australia, Portugal, and Italy are shown in Table 3.

Table 3. Descriptive statistics of sediment samples from Upper Velhas River; IQ region, Minas Gerais, Brazil, compared to data from Europe (EUR), Australia (AUS), Portugal (Port), and Italy.

Elem	Unit	Min	Max	Mean	Median	Avg Crust	Q1	Q3	EUR*	AUS**	Port***	Italy
Al	%	0.2	8	2.5	1.9	---	1.0	3.8	5.5	1.5	1.6	1.5
Ca	%	7.6×10^{-4}	1.8	0.1	0.1	---	0.1	0.2	1.7	0.3	0.2	6.4
Fe	%	1.1	62.2	12.9	10.4	---	5.4	16.6	2.0	2.3	2.5	2.1
Mg	%	1.3×10^{-4}	1.3	0.1	0.1	---	0.1	0.1	0.7	0.3	0.4	0.6
As	mg kg^{-1}	<LLD	1687	32.3	2.0	2	1.6	20.6	6	2.1	9	5.7
Cd	mg kg^{-1}	<LLD	14.7	1.1	0.4	0.1	0.4	1.1	0.3	0.1	n.d.	0.2
Cr	mg kg^{-1}	6.5	572	115	92.8	126	41.7	151.3	21	29.4	23	20
Cu	mg kg^{-1}	<LLD	233	27.7	22.3	25	12.7	37.9	14	16.5	22	30
Mn	mg kg^{-1}	41	10,000	1317	756	---	305	1771	452	387	411	811
Ni	mg kg^{-1}	1.2	157	36.3	30.5	56	11.2	56.9	16	13.8	19	21
Pb	mg kg^{-1}	<LLD	70.2	22.5	20.2	15	14.6	28.4	14	10.5	19	22
Zn	mg kg^{-1}	18.6	181	53.8	48.7	65	38.4	63.1	60	37.3	74	71

European, Australian, Portuguese, and Italian data refer to median values. Q1: First quartile; Q3: Third quartile. EUR*: Data from European Stream Sediment Survey [27] with Al, Ca, Mg, K, Ti, Cd, co-analyzed by WD-XRF. AUS**: Data from the Australian National Geochemical Survey with all elements obtained on the fraction <75 µm (aqua regia) [6]. Port*** = Data from Portugal low-density geochemical mapping [30]. Italy: Data from Campagna Region [8]. LLD—Lower Limit of Detection.

The concentration values and the classification of concentration ranges, with all values above the UIF being considered anomalies, are represented in Table 4, with the limits of intervention established by Brazilian legislation, which adopts the same values as Canadian and the average distribution of elements in the upper continental crust [33].

Table 4. Regional concentration values (RCV), reference value classification (RVC), CONAMA 454/2012 (Probable Effect Level) established by the Brazilian legislation, and the average distribution of elements in the upper continental crust [32] to PTEs in the Velhas River Basin, IQ region, Minas Gerais, Brazil. Reference Range (RR), High Reference Values (HRV).

Element	RCV (mg kg^{-1})	RVC	CONAMA 454 [1] (mg kg^{-1})	% of Concentration Range to Total Area
As	1.6–20.6 >20.6–49 >49	RR HRV Anomalies	17	78 11 11
Cd	0.4–1.02 >1.02–1.96 >1.96	RR HRV Anomalies	3.5	76 15 09
Cr	6.48–151.3 >151.3–315.7 >315.7	RR HRV Anomalies	90	74 24 02
Cu	0.3–37.9 >37.9–75.6 >75.6	RR HRV Anomalies	197	76 22 02
Pb	0.4–28.4 >28.4–49 >49	RR HRV Anomalies	91.3	78 18 04
Ni	1.1–56.9 >56.9–125.7 >125.7	RR HRV Anomalies	35.9	77 18 05
Zn	18.6–63.1 >63.1–100.2 >100.2	RR HRV Anomalies	315	75 21 04

3.1. Arsenic (As)

The pattern of behavior can be observed in the geochemical map of As (Figure 2a). The 78% of the area presents values up to 20.6 mg kg^{-1} and an intermediate range with concentrations up to 49 mg kg^{-1}, closely related to carbonate–quartz schist and sericite schist rocks that are part of the Nova Lima Group. This appears mainly in Ouro Preto, Itabirito, Rio Acima, Nova Lima, and Caeté.

The areas with concentrations above these values correspond to 11% of the studied area and are represented by 21 points with concentrations between 50.6 and 1687 mg kg^{-1}. Fifteen of those points are in third-order basins, with more than 60% draining on the aforementioned rocks in locations with intense historical gold mining activity, urbanization, and land occupation.

According to the Guideline Values for Sediment Quality (GVSQ), 61 points with a concentration of As higher than the limit of intervention determined by Brazilian legislation were found, most of them located in rural and peri-urban locations, which generally have a low-income population with low education level, unaware of the risk they are exposed to. The As mobility only occurs if pH and Eh are low [35], which does not occur in most sampled areas, where measured pH values were close to neutral to moderately alkaline (6 to 8), but negative Eh values were found in urbanized locations.

3.2. Cadmium (Cd)

The spatial distribution of Cd presented 76% of the area with values below 1.02 mg kg^{-1} (Figure 2b), which can be considered a reference range. There was also an intermediate interval with contents up to 1.96 mg kg^{-1}, which covers 15% of the basin (HRV), and a third set of data with concentrations between 1.96 and 14.73 mg kg^{-1}, classified as anomalies. Eighteen points form this group, and the vast majority drains on carbonate–quartz schist and sericite schist from the Nova Lima Group.

The influence of these rocks on the Cd concentration must be relevant since it was found that the median and third quartile values of 2.1 and 2.4 mg kg^{-1}, respectively, were statistically higher than the other lithologies that drained in the basins. In an area with intense mining exploration in the 90 s, 2.4 to 5.7 mg kg^{-1} values were observed in the upper part of the basin. However, in the intermediate portion of the study area (municipalities of Caeté and Nova Lima), the highest concentration points ranged from 3 to 14.7 mg kg^{-1}

Cadmium demonstrated a similar spatial distribution to As, with higher values in the same regions. However, higher levels were found in the southwestern portion of the Basin, in the Mata Porcos stream sub-basin, a region characterized by intense iron mining activity and previous gold exploration.

Regarding the intervention limits, 11 streams in urbanized, industrialized, and mining-impacted areas have concentrations higher than those established by environmental legislation.

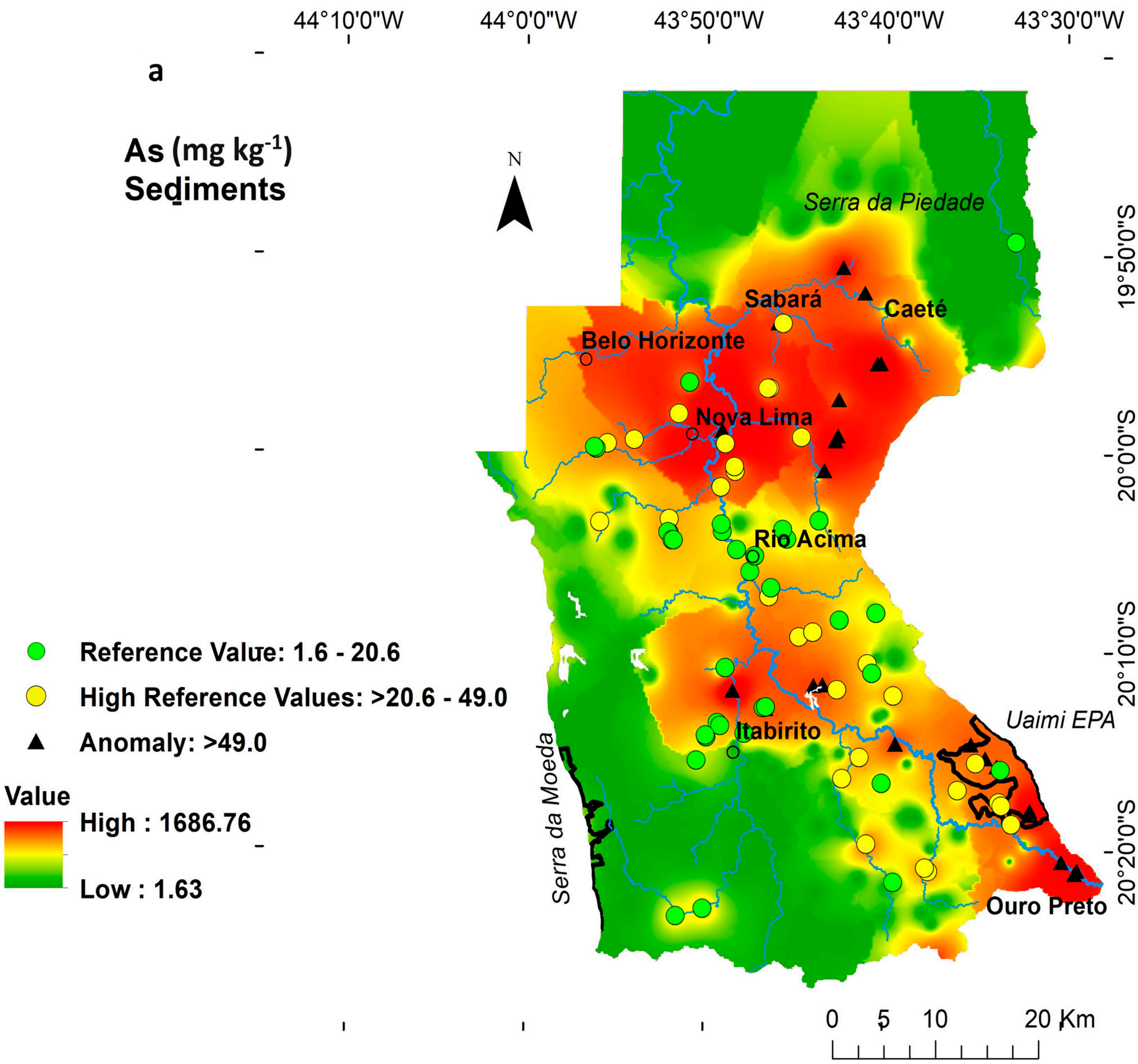

Figure 2. *Cont.*

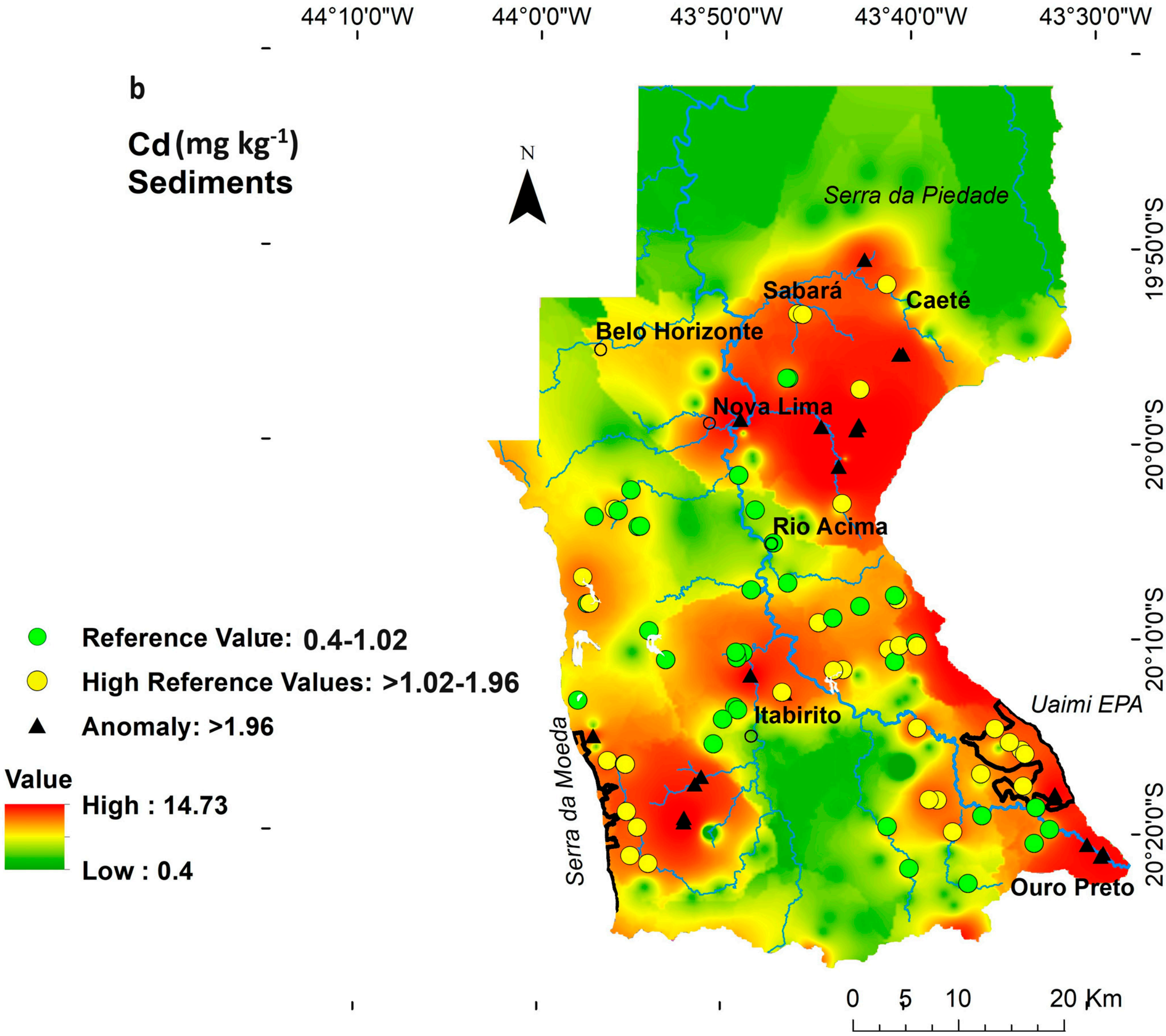

Figure 2. (**a**,**b**) As and Cd geochemical map—Upper Velhas River Basin, IQ region, Minas Gerais, Brazil.

3.3. Lead (Pb)

Lead showed an average value of 22.5 mg kg^{-1}, 1.5 times higher than the continental crust average [33]. The behavior of lead can be observed in Figure 3a, with 78% of the area showing points with concentrations ranging from 0.4 to 28.4 mg kg^{-1}. A second group, with HRV ranging from 28.4 to 49 mg kg^{-1}, covers 18% of the region and has a close relation with geology since most of the points are in basins where itabirites and phyllites of the Minas Supergroup or the sericite quartzites of the Maquiné Group predominate.

3.4. Zinc (Zn)

The distribution of Zn values (Figure 3b) showed a variation between 18.6 and 181.2 mg kg^{-1}, with an average of 53.8 mg kg^{-1}, slightly below the one of continental crust. Also, 11 points with values greater than the UIF (100.2 mg kg^{-1}) were verified.

It is a region highly affected by gold mining and urbanization, with 25 high reference values and anomalies, showing concentrations between 65.7 and 157 mg kg^{-1}, all draining metabasalts and quartz–carbonate schists of the Nova Lima Group.

In the municipality of Itabirito, draining on the hematite, itabirite, and phyllites of the Minas Supergroup, six points with excessive concentrations ranging between 72.8 and

120 mg kg^{-1} were found, which are located in intensely impacted areas by iron mining and also presented anomalies for Fe and Pb.

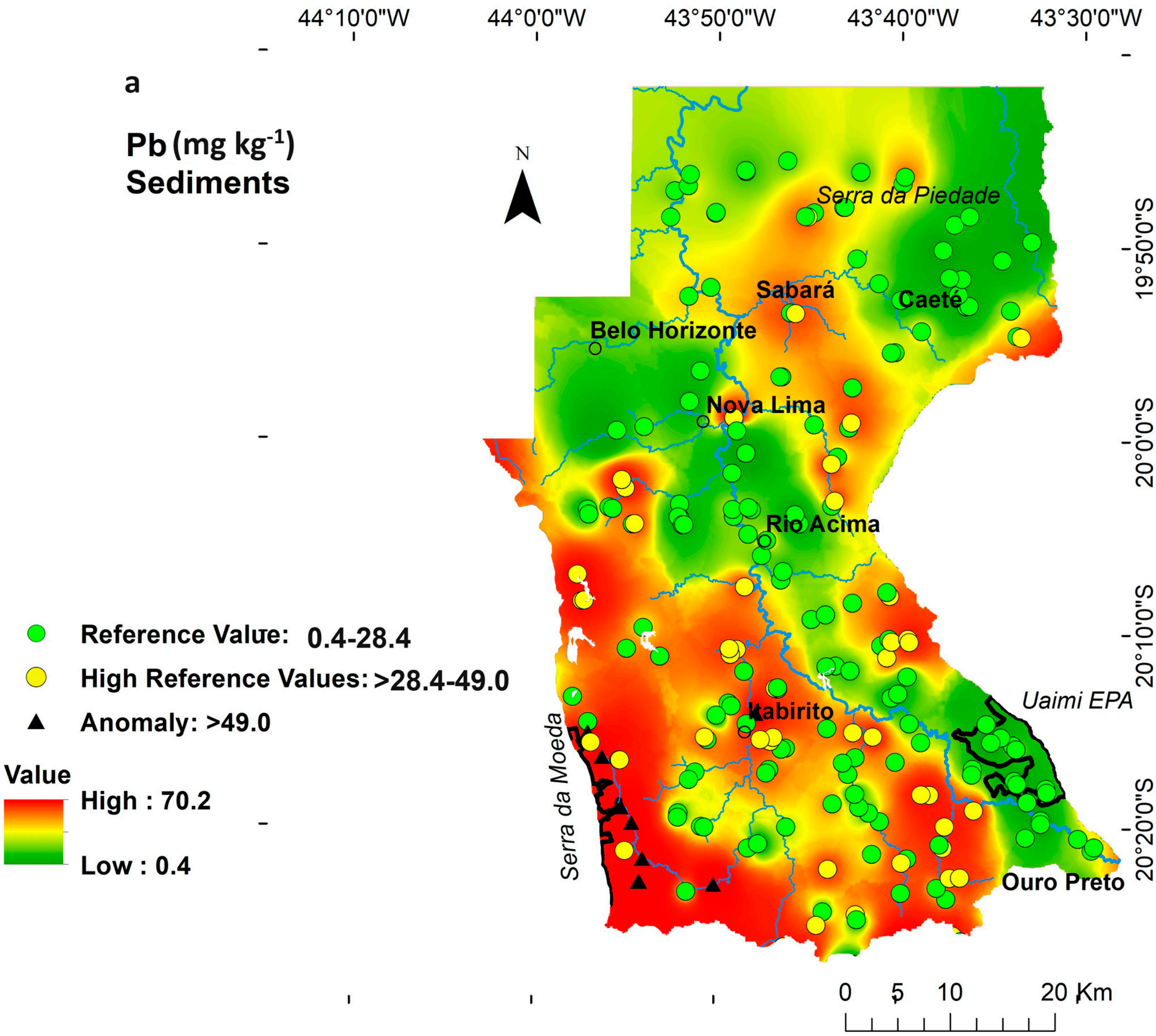

Figure 3. *Cont.*

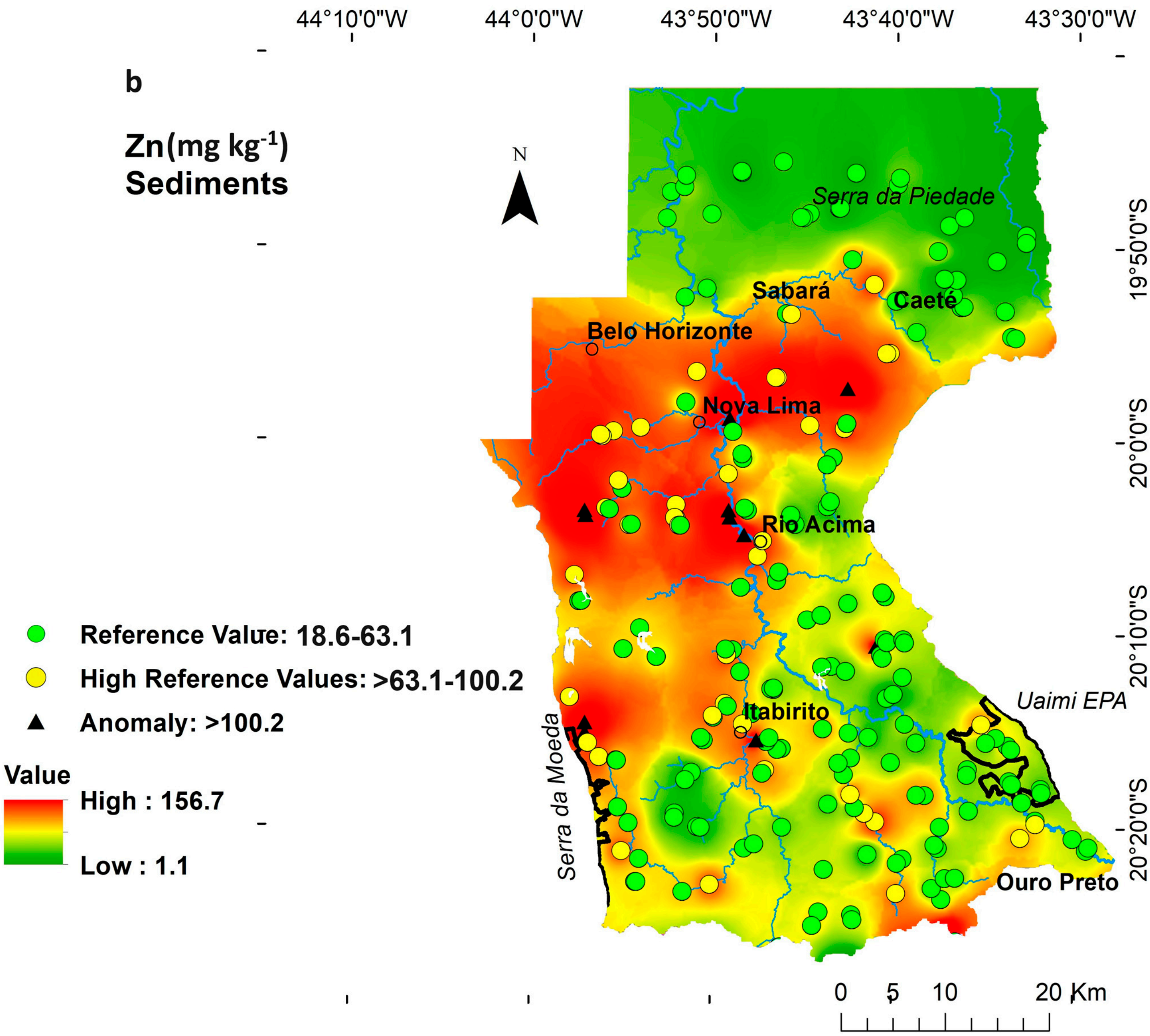

Figure 3. (**a**,**b**) Pb and Zn geochemical map—Upper Velhas River Basin, IQ region, Minas Gerais, Brazil.

3.5. Chromium (Cr)

The distribution of Cr in the Upper Velhas River presented a very strong correlation with Ni (70% of the points presented joint anomalies). The pattern showed a group with concentrations up to 151 mg kg^{-1} covering 74% of the basin, which can be observed in Figure 4a. A second set with values between 151.3 and 315.7 mg kg^{-1} was observed, comprising 24% of the area, located mainly in the central region of the study area, which showed a close relation with the rocks of the Nova Lima Group (carbonate–quartz schist, quartz–carbonate schist, and sericite schist).

The Cr had 106 points (51% of total points) with concentrations above the intervention limits [1]. Most of these streams are tributaries of the rivers Itabirito, Maracujá, and the Velhas River, which are responsible for the water supply of many regional cities and neighborhoods. In addition, these streams cross through numerous rural communities, where water is captured directly for human consumption.

3.6. Nickel (Ni)

Ni presented values up to 56.9 mg kg^{-1} in 77% of the study area, which can be considered a reference range. It deserves attention because they exceed Level 2 of intervention limits (35.9 mg kg^{-1}). A second group with HRV comprises 18% of the area, including concentrations between 56.9 and 125.7 mg kg^{-1} in 47 streams (Figure 4b).

According to the Guide Values for Sediment Quality (GVSQ), Ni presented 94 points with values above the intervention limits [1], located in the urban areas of Itabirito, Rio Acima, Caeté, in rural communities, and through peri-urban localities where water has been used directly for human consumption for several years, which causes the exposure of a large population contingent to significant environmental risks.

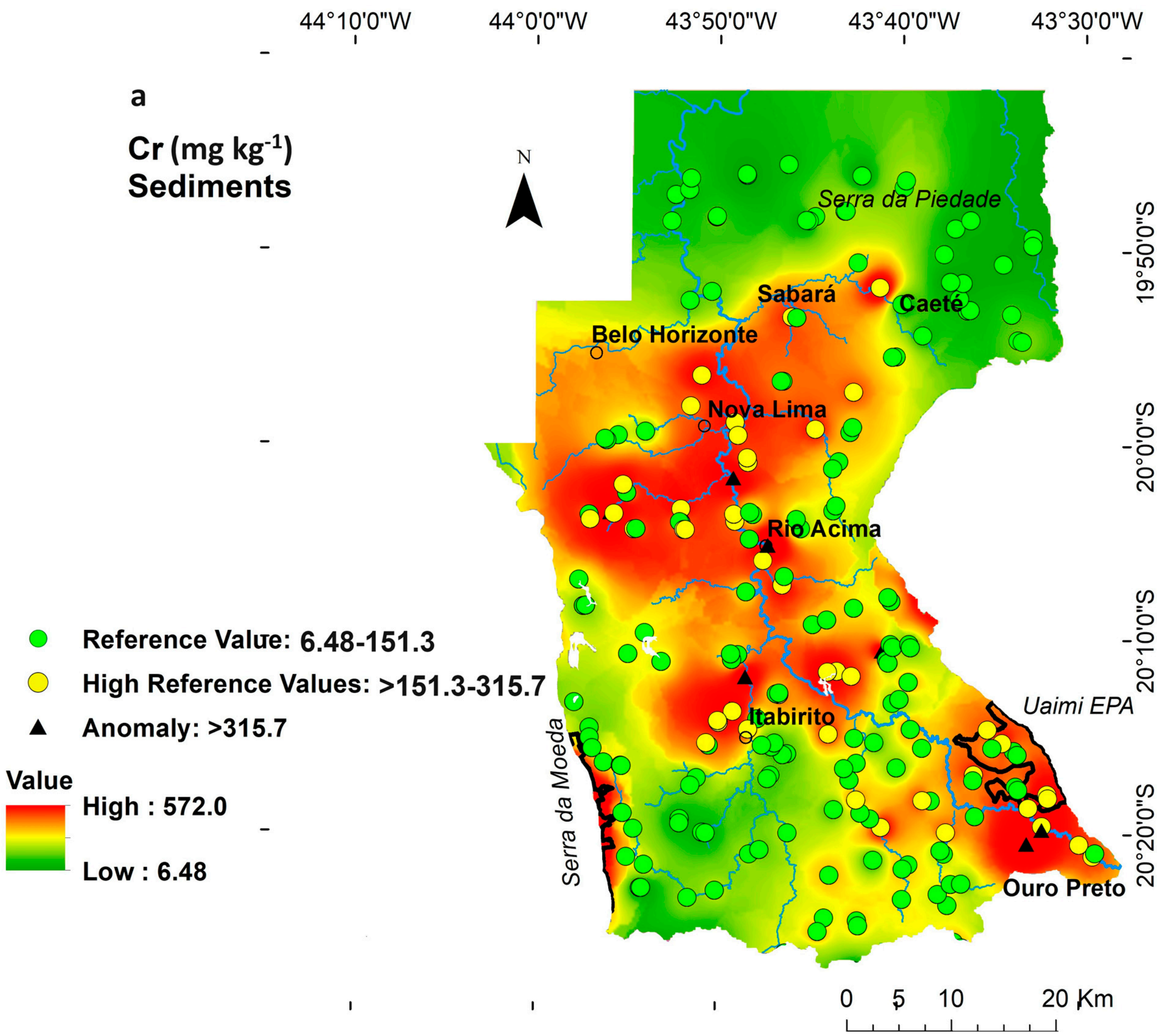

Figure 4. *Cont.*

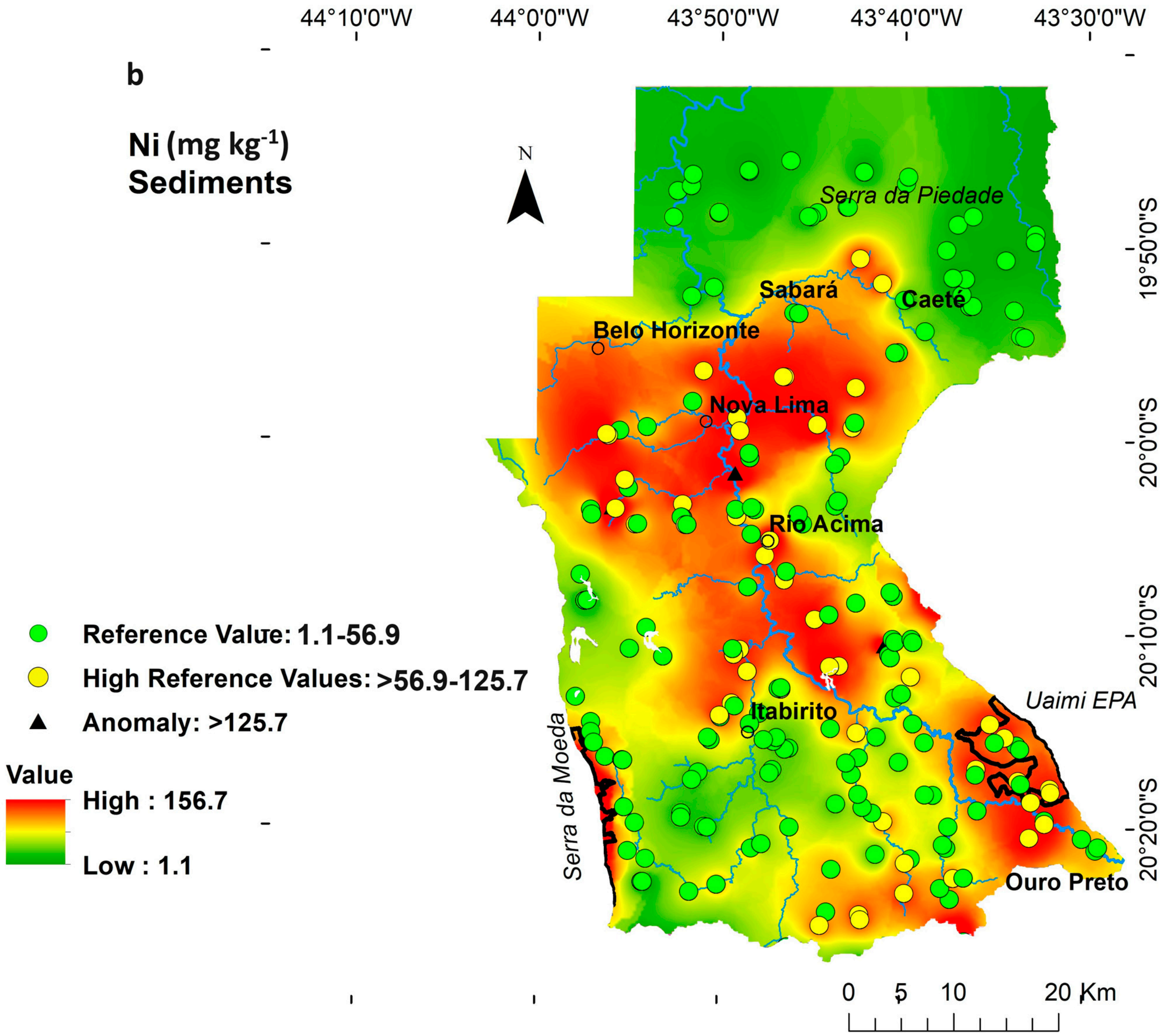

Figure 4. (**a**,**b**) Cr and Ni geochemical map—Upper Velhas River Basin, IQ region, Minas Gerais, Brazil.

3.7. Copper (Cu)

Due to its chalcophile character and high concentration of sulfide minerals, Cu presented a geochemical signature strongly related to the basic volcanic rocks in the Nova Lima Group (Rio das Velhas Supergroup) within a characteristic association between Cu-As-Ni-Cr and Cu-Zn.

The distribution of Cu in the basin (Figure 5) presented levels of up to 37.9 mg kg^{-1} in 76% of the area. Considering that the HRV is 37. 9 to 75.6 mg kg^{-1}, 41 drainage segments are within this range, of which nine points are located in rural communities and environmental preservation areas (EPA) draining on the quartz–carbonates schists of the Córrego do Sítio and Catarina Mendes Units. Thus, weathering allied to the erosive processes can release elements to the sediments in important concentrations even in low-anthropogenic interference.

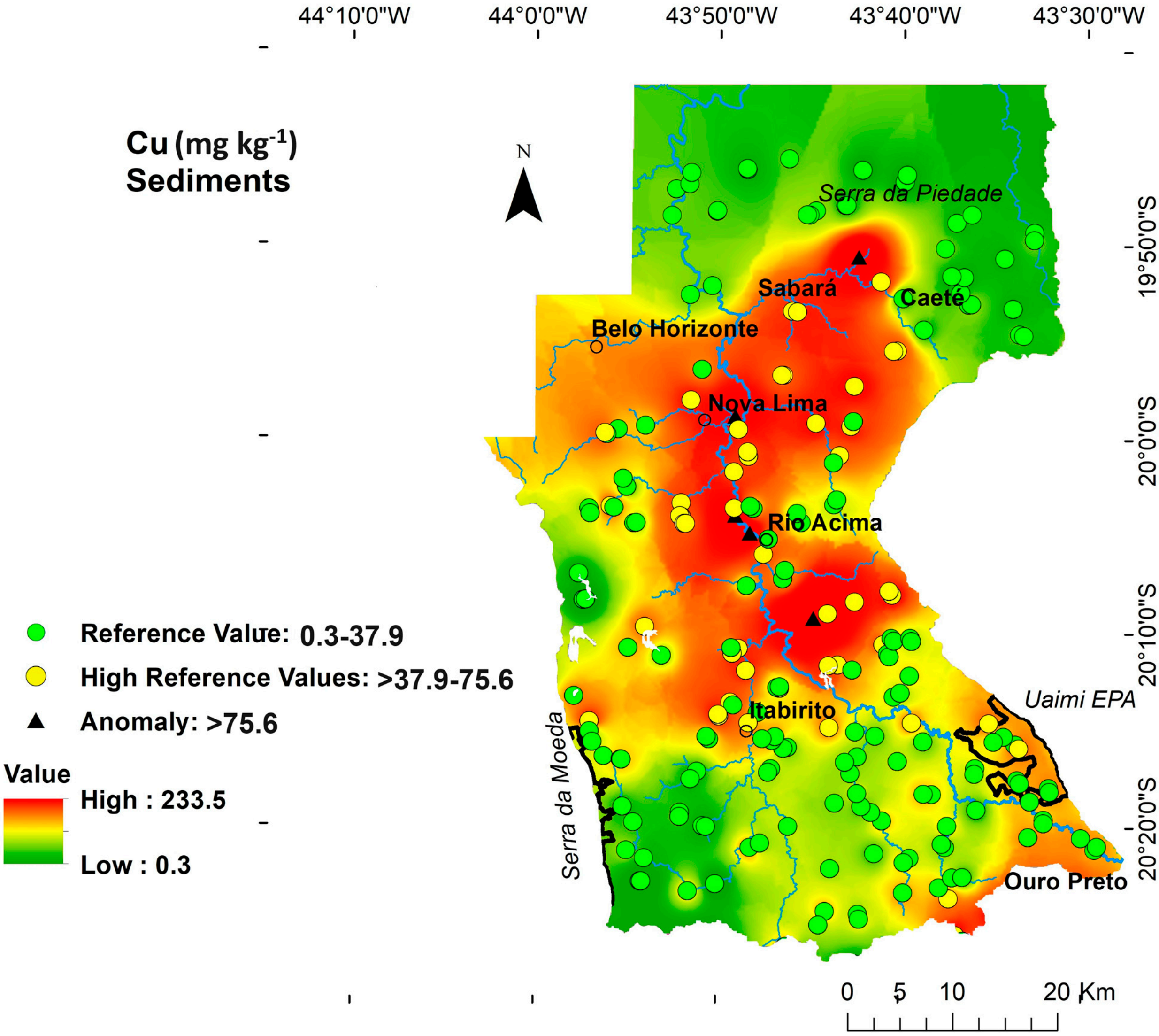

Figure 5. Cu geochemical map—Upper Velhas River Basin, IQ region, Minas Gerais, Brazil.

4. Discussion

The As and Cd showed to be remarkably abundant, with average concentrations 16 and 11 times higher than the average continental crust, respectively [33]. Cu and Pb, although above the crustal average, are only 1.1 and 1.5 times higher, respectively. The other elements are below the earth's average crust [33].

When these results are compared with studies carried out in Europe, Australia, Portugal, and Italy [8,30], it is possible to observe that sediments from the Upper Velhas River present average contents of Fe, Cd, Cr, Mn, and Ni considerably higher, showing a relative enrichment, which results from the presence of geogenic anomalies, associated with the availability of these metals through the mining activity. The high Fe concentrations reflect tropical weathering and iron enrichment processes. On the other hand, the elements that act as plant nutrients (e.g., Ca and Mg) demonstrate strong relative depletion, typical of soils and sediments originating from ancient geological and pedological environments, characteristic of subtropical regions.

The environmental mobility of these elements, the very long weathering time (the youngest rocks are at least 2.1 Ga old), and the climate situation (subtropical) explain their deviation from the average conditions of other studies. This context confirms the need to define regional backgrounds to have anomalous values truly representative of the area.

It is observed that 74–78% of the basin area shows values up to the third quartile for As, Cd, Cr, Ni, Cu, Pb, and Zn. Furthermore, it is verified that 11 to 24% of the area demonstrated HRV derived from geogenic sources, which was possible to conclude from the overlap of geological maps and geochemical maps. This, together with statistical analyses (e.g., Cluster analysis) indicates a behavioral pattern of elements in certain lithologies. Also, 2 to 12% of the whole basin has anomalies, which may be related to lithologies as well as to the anthropic influence, mainly due to the land occupation and mining activities associated with the extraction of gold and iron

Regarding As, the relation between high concentrations and lithology is evidenced in the elevated portion of the basin, which was mined for gold in the past. This process accelerated the mobilization of trace elements to the environment [7]. In this area, current EPA Cachoeira das Andorinhas, where intense gold mining occurred in the river's headwaters in the past centuries, concentrations between 130 and 306 mg kg^{-1} were observed, considerably higher than in previous studies [17]. Extending along the river's course in rural communities (São Bartolomeu and Glaura) and in the EPA Floresta do Uaimii, there was a high density of anomalous points. In this region, it was observed that in an area of 7.6 km^2, there are eight points with values ranging from 60.6 to 374.1 mg kg^{-1}. In these locations, anomalies also occur in the sediments that drain into the sericitic quartzites and quartz–sericitic schists, which are also higher than in previous research [16,17]. The presence of As in these lithotypes is based on the occurrence of minerals such as arsenopyrite, lollingite, realgar, and arseniferous pyrite, which are abundant in these rocks [15]. In addition, As is associated with sediments through adsorption in iron oxides (goethite) and as a function of the precipitation of secondary minerals of arsenic as scorodite [35,36].

In the municipality of Itabirito, several tributaries of the Velhas River also presented relatively high values, up to 122 mg kg^{-1}. In the rural communities of this city, 31 and 83 mg kg^{-1} concentrations were observed, which have upstream gold mining. In the Portões community, still in Itabirito city, concentrations ranging from 13 to 122 mg kg^{-1} were observed in streams with low anthropic interference and draining on the granite, granodioritic, and gneiss rocks of the Bação complex. This was a relevant detection since these rocks are not normally enriched with As, which may suggest a dispersion of geogenic sources or anthropogenic influence, which was not found in previous studies [14,16–18].

Continuing upstream, in the cities of Rio Acima, Nova Lima, Caeté, and Sabará, there is also a great density of anomalous points: in an area of 74 km^2, samples 32 samples were collected, whose 19 had high reference values or anomalies, 10 with concentration in the range of 20.6 to 49 mg kg^{-1}, three presented As values between 49.1 and 255 mg kg^{-1} and six showed concentrations between 255 and 1687 mg kg^{-1}. These values are similar to previous studies and confirm the intense As pollution in these cities [14–16]. All these streams drained predominantly on Nova Lima Group (quartz–carbonate–mica–chlorite schists lithology). In the municipality of Nova Lima, still, over the same lithology, anomalous concentrations were found in rural communities in the sub-basin of Ribeirão dos Macacos, a fact corroborated by several studies [11,15,19]. The highest concentration of As of the entire basin, 1687 mg kg^{-1}, occurred in the Água Suja stream, one of the tributaries of the Velhas River, and showed As contents in the waters of 414 µg L^{-1} [11].

Despite the remarkable presence of the quartz–carbonate–mica–chlorite schists of the Nova Lima Group and its relationship with the sulfide deposits, the anthropic influence and mineral exploitation probably also determine the availability of As in the environment. In the cities mentioned above, where there was intense gold mining between the 17th and 19th centuries, extending to the present day, there is abundant evidence of the extraction and mineral processing, including mines and abandoned mining tailings. This activity accelerates sulfide oxidation and contamination by providing various chemical elements to the waters and secondary minerals in the sediments [36,37].

Regarding Cd, in sections where significant anomalies were observed, these were often associated with high concentrations of Pb and Zn, which has already been reported in another research [14,38]. Parallel to this, the albite and ilmenite minerals that usually host the Cd in their structures are associated with these rocks [33]. This association was verified very clearly in the Mata Porcos stream sub-basin, a region characterized by intense iron mining activity and previous gold exploration, and which, until then, had not demonstrated anomalies for Cd [18].

The Pb demonstrated eight HRV and anomalies in the central portion of the basin (Ouro Preto and Itabirito) in places where the granitic and granodioritic rocks of the Bação metamorphic complex predominate, which was not found in previous studies [14,16–18]. These points are divided into two distinct cities: Ouro Preto, with values between 33.8 and 40.8 mg $kg^{-1,}$ and Itabirito, with concentrations of 39.6 and 61.2 mg kg^{-1}. As Pb mobility is low in any environment [19,33], it can be concluded that there is a geogenic source in these regions.

In the rural communities of Itabirito, a cluster of points with high Pb levels, between 37.9 and 41.6 mg kg^{-1}, was also observed, which occurs in basins where there is a predominance of sericites and sericite schists of the Maquiné Group, with occurrences associated with the "greenstone Belts" of the Rio das Velhas Supergroup associated with mineralization. Furthermore, it is essential to highlight that these streams are located downstream of a gold mine.

Furthermore, nine points with levels above 35.9 mg kg^{-1} are located mainly in the southwestern portion of the basin, in the Mata Porcos stream, a region that notably presents the release of Pb into the environment. An advanced stage of silting with a large amount of sediment was also observed at these collection points. In addition, Pb concentrations in streams decrease significantly with increasing distance from iron ore miners (Figure 3a). This element showed a significant correlation with Fe, with 78% of the points showing joint anomalies; this affinity may be related to the presence of Pb in iron minerals (e.g., hematite and magnetite) [33], intensely explored in the region. There is also the process of co-precipitation of Pb with Fe compounds, which has already been reported [39,40].

The Cr anomalies were found to begin at the headwaters of the basin, in the city of Ouro Preto, in a region with an environmental preservation area and two rural communities, which were targets of gold mining in the past [15,16]. In this area, 10 high reference values and anomalies with concentrations between 155 and 365 mg kg^{-1} were found in the stream where rocks from the Nova Lima Group predominate. Furthermore, on the same lithology, in the municipalities of Rio Acima, Nova Lima, Caeté, and Sabará, which have urbanization and mining activity mainly related to gold, 22 HRV and anomalies were found with concentration values varying between 170 and 572 mg kg^{-1}.

Demonstrating a strong correlation with Cr, Ni anomalies also started in the Rio das Velhas headwaters, with an area of 10 km^2 in which nine sampled streams presented concentrations between 57.4 and 93.0 mg kg^{-1}. In the intermediate portion of the study area, in Itabirito, five points were observed draining over the granite rocks and gneisses of the Bação Metamorphic Complex, which also presented high Ni and Cr contents (Figure 4b). Also, the highest concentration of anomalous points was observed in this region, where quartz–carbonate–sericitic schists from the Córrego do Sítio and Mestre Caetano Units predominate. In this area, samples were collected at 33 points, of which 25 showed concentrations above RR or HRV, with values between 56.9 and 156.7 mg kg^{-1}. As with As, Cu, and Zn, the Ni and Cr also presented anomalies related to sulfide mineralization in the northernmost part of the upper Velhas River.

Concerning Cu, the highest concentration of points with a high reference value occurred in the municipalities of Rio Acima and Nova Lima, where sediments were collected in an area of 20 $km^{2,}$ and 15 samples showed values ranging from 39.4 to 147.5 mg kg^{-1}, all draining on quartz–carbonate–sericitic schists from the Córrego do Sítio and Mestre Caetano Units. It is important to highlight that 15 streams presented HRV and anomalies, of which 12 presented values between 39.4 and 68.4 mg kg^{-1}, the vast majority in areas with less anthropogenic impact and three points with the highest concentration (between 93.5 and 147.5 mg kg^{-1}) were in urban areas. Above the UIF, five points were found in the cities of Itabirito, Rio Acima, Nova Lima, and Caeté, in highly urbanized areas with intense industrial and mining activity (gold). These points drain over the rocks mentioned above, hosting chalcopyrite, and may have the capacity of Cu adsorption due to the presence of iron oxides, hydroxides, and clay minerals [34]. This region also presented As, Cd, Cu, and Ni anomalies, which reflects the intense anthropogenic interference observed through gold mining and the high degree of urbanization.

Regarding Zn, in contrast to most of the elements, the highest concentrations of this element did not show a direct relation with a specific lithotype since excessive concentrations were found in the carbonate–quartz schists rocks, quartz–carbonate–sericite schists from the Rio das Velhas Supergroup that is associated with sulfide mineralization, as well as in the phyllites and itabirites of the Minas Supergroup. Concentrations of Zn above 90 mg kg^{-1} can be attributed to the combination of the geology factor with anthropogenic interference. This undefined behavior of Zn can be partially explained by its ability to substitute Fe and Mn in oxides and silicates, which provides its presence in clay minerals, iron oxides, and organic compounds. This allows its occurrence even in regions far from the source areas [32]. As with As and Cu, the Zn also showed anomalies related to sulfide mineralization in the municipalities of Caeté, Sabará, Rio Acima, and Nova Lima.

Mining works or mining accidents (e.g., Aznarcollar in Spain [41] and Brumadinho in Brazil [42]) are important sources of sediment contamination. The present work provides knowledge about PTEs in stream sediment, highlighting the pollution problem and may help mitigate or manage the affected river basins.

5. Conclusions

For the first time, reference values for stream sediments were determined in the upper portion of the Velhas River Basin. In addition, the high-density geochemical mapping allowed anomalies to be detected in places where they had not previously been reported, for example, the Cr, Ni, and Cd on the basin headwater (EPA Cachoeira das Andorinhas) and the Pb and Cd on the Itabirito river basin.

The high sampling density allowed for assessing the lithology control in the geochemistry of the sediments and established a pattern of well-defined behavior of the elements for each type of rock. This allowed the detection of anomalies due to anthropic interference, which was verified with Pb, Mn, and Cd in regions close to the iron mines in the Itabirito River Basin.

The anomalous concentrations of several elements are scattered throughout the basin on a greater or smaller scale. Numerous streams with As, Cd, Cr, Cu, Ni, Pb, and Zn concentrations above the intervention limits were found throughout the region, often demonstrating clear mining interference. They need to be monitored since any changes in pH and Eh (redox potential) that may occur due to the discharge of effluents or mine-influenced waters could modify the environmental conditions and promote the availability of the toxic elements to the water system and, consequently, to the whole food chain.

Rio Acima, Nova Lima, Caeté, and Sabará regions had the highest density of As, Cd, Cu, Ni, Cr, and Zn anomalies. The high concentration of these elements occurs due to the interaction between geology and anthropic interference. Many of these points present a high concentration of PTEs due to mining influence. Therefore, in many cases, the sites are monitored internally or externally according to the constraints established in environmental legislation. However, many localities have demonstrated anomalous concentrations due to the natural weathering process of the geological material. With this, a hidden ecological risk is not monitored, but it begins to unravel in the face of the mapping performed.

There were notable differences in the concentration of various elements between the geological domains of the basin, which points to the need to determine different reference values for each specific lithotype, as exemplified by Fe and As.

Geochemical mapping in third-order basins proved extremely useful for identifying anomalous values for environmental concerns. This approach accurately confirmed the influence of local lithologies and human action in the Upper Velhas River Basin.

The reference values for Cr and Ni are higher than the limits of intervention established by Brazilian legislation, and the high reference values for As are similar to this level. It is possible to conclude that working with uniform values of sediment quality guidelines is not appropriate.

The results reflect the true geochemical signature of the river sediments of the basin, which is the most polluted in the state of Minas Gerais and is located in one of the most important mining provinces in the world. In addition to the scientific aspect, this research may prove useful for formulating environmental policies in Brazil, for example, in defining geochemical guidelines. Knowledge of the elements' natural or geogenic distribution will help define environmental background values and cleaning levels for ecotoxicological studies.

The mobilization of PTEs from sediments is dangerous, not only for the ecosystem but also for drinking water supplies. In addition, high-density mapping has demonstrated which locations, cities, and sub-basins are exposed to environmental hazards and thus need to be protected.

Author Contributions: Conceptualization, R.V., T.V., M.G.P.L., L.P.L. and H.A.N.J.; Methodology, R.V., M.G.P.L. and L.P.L.; Validation, R.V. and T.V.; Writing—original draft, R.V., T.V., M.G.P.L., L.P.L. and H.A.N.J.; Supervision, R.V. and T.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by FCT (Fundação para a Ciência e a Tecnologia, Portugal) through projects UIDB/04683/2020 and UIDP/04683/2020) and by the institutions CNPq, FAPEMIG and mainly CAPES for the scholarship Proc. Nº 10228/13-6.

Data Availability Statement: Data are available on request from the authors. The data are not publicly available due to the large dimensions of the database.

Acknowledgments: The authors are grateful to the anonymous reviewers and editors for their contributions to improving the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. *Resolution No. 454/12*; Establishing General Guidelines to the Evaluation of Dredging Material in Brazilian Jurisdictional Waters. CONAMA. Environmental National Council: Washington, DC, USA, 2012.
2. Giripunje, M.D.; Fulke, A.B.; Meshram, P.U. Remediation techniques for heavy-metals contamination in lakes: A mini-review. *Clean–Soil Air Water* **2015**, *43*, 1350–1354. [CrossRef]
3. Vicq, R.; Matschullat, J.; Leite, M.G.P.; Nalini, H.A., Jr.; Mendonça, F.P.C. Iron Quadrangle stream sediments, Brazil: Geochemical maps and reference values. *Environ. Earth Sci.* **2015**, *75*, 25–35. [CrossRef]
4. Gomez, P.; Valente, T.; Braga, M.A.S.; Grande, J.A.; Torre, M.L. Enrichment of trace elements in the clay size fraction of mining soils. *Environ. Sci. Pollut.* **2016**, *23*, 6039–6045. [CrossRef] [PubMed]
5. Carranza, E.J.M. Geochemical Anomaly Mineral Prospectivity Mapping in. In *G.I.S. Handbook of Exploration and Environmental Geochemistry*; Elsevier Publications: Budapest, Hungria, 2009; Volume 11, 310p.
6. Caritat, P.; Cooper, M. *National Geochemical Survey of Australia: The Geochemical Atlas of Australia*; Record; Geoscience Australia: Symonston, Australia, 2011; Volume 2, 557p.
7. Smith, D.B.; Smith, S.M.; Horton, J.D. *History and Evaluation of a National Scale Geochemical Data Sets for the United States*; Geoscience Frontiers: Beijing, China, 2012.
8. Albanese, S.; Devivo, B.; Lima, A.; Cicchella, D. Geochemical background and baseline values of toxic elements in stream sediments of Campania region (Italy). *J. Geochem. Explor.* **2006**, *93*, 21–34. [CrossRef]
9. Bai, J.; Porwal, A.; Hart, C.; Ford, A.; Yu, L. Mapping geochemical singularity using multifractal analysis: Application to anomaly definition on stream sediments data from Funin Sheet, Yunnan, China. *J. Geochem. Explor.* **2009**, *104*, 1–11. [CrossRef]
10. Campodonico, M.B.; Garcia, A.I.; Pasquini, B. The geochemical signature of suspended sediments in the Parana River basin: Implications for provenance, weathering and sedimentary recycling. *Catena* **2016**, *143*, 201–214. [CrossRef]
11. Vicq, R.; Matschullat, J.; Leite, M.G.P.; Nalini, H.A., Jr.; Leão, L.P. Geochemical mapping of potentially hazardous elements in surface waters and stream sediments of the Quadrilátero Ferrífero, Brazil. *Geochim. Bras.* **2018**, *32*, 243–267.
12. Borba, R.P.; Figueiredo, B.R.; Rawlins, B.; Matschullat, J. Arsenic in Water and Sediment in the Iron Quadrangle, State of Minas Gerais, Brazil. *Appl. Geochem.* **2000**, *15*, 181–190. [CrossRef]
13. Matschullat, J.; Borba, R.P.; Deschamps, E.; Figueiredo, B.F.; Gabrio, T.; Schwenk, M. Human and environmental contamination in the Iron Quadrangle, Brazil. *Appl. Geochem.* **2000**, *15*, 181–190. [CrossRef]

14. APA SUL RMBH. *Projeto de Geoquímica Ambiental, Mapas Geoquímicos Escala 1:225.000*; da Cunha, F.G., Machado, G.J., Eds.; SEMAD/CPRM: Belo Horizonte, Brazil, 2005; Volume 7:17 mapas, 80p.
15. Deschamps, E.; Matschullat, J. *Arsênio Antropogênico e Natural: Um Estudo em Regiões do Quadrilátero Ferrífero*; Fundação Estadual do Meio Ambiente—FEAM: Belo Horizonte, Brazil, 2007; 330p.
16. Pereira, J.C.; Guimarães Silva, A.K.; Nalini, J.R.H.A.; Pacheco Silva, E.; De Lena, J.C. Distribuição, fracionamento e mobilidade de elementos traço em sedimentos superficiais. *Quim. Nova* **2007**, *30*, 1249–1255. [CrossRef]
17. Gonçalves, G.H.T. Avaliação Geoambiental de Bacias Contíguas Situadas na Área de Proteção Ambiental Cachoeira das Andorinhas e Floresta Estadual do Uaimii, Ouro Preto-MG: Diagnóstico e Percepção Ambiental. Master's Thesis, Universidade Federal de Ouro Preto, Ouro Preto, Brazil, 2010.
18. Mendonça, F.P.C. Influência da Mineração na Geoquímica das Águas Superficiais e Nos Sedimentos no Alto Curso da Bacia do Ribeirão Mata Porcos, Quadrilátero Ferrífero—Minas Gerais. Master's Thesis, Federal University of Ouro Preto, Ouro Preto, Brazil, 2012.
19. Larizzatti, J.H.; Marques, E.D.; Silveira, F.V. *Geochemical Mapping of the Quadrilátero Ferrífero, Brazil and Surroundings*; (Série metais—Informes Gerais; 2); Informe de Recursos Minerais; CPRM: Rio de Janeiro, Brazil, 2014; 208p.
20. Leão, L.P.; Vicq, R.; Nalini, H.A., Jr.; Leite, M.G.P. *Mapeamento Geoquímico do Manganês e Avaliação da Qualidade de Sedimentos Fluviais e Águas Superficiais do Quadrilátero Ferrífero, Brasil*; Anuário do Instituto de Geociências—UFRJ: Rio de Janeiro, Brazil, 2019; Volume 42, pp. 444–455.
21. Teixeira, W.; Sabaté, P.; Barbosa, J.; Noce, C.M.; Carneiro, M.A. Archean and paleoproterozoic tectonic evolution of the São Francisco Craton. In *International Geological Congress*; Cordani, U.G., Milani, E.J., Thomaz Filho, A., Campos, D.A., Eds.; Tectonic evolution of South America: Rio de Janeiro, Brazil, 2000; Volume 31, pp. 101–137.
22. Dorr, J.N. *Physiographic, Stratigraphic, and Structural Development of the Quadrilátero Ferrífero, Minas Gerais*; Professional Paper; U.S. Geological Survey: Reston, VA, USA, 1969.
23. Alkmim, F.F.; Marshak, S. Transamazonian Orogeny in the Southern São Francisco Craton Region, Minas Gerais, Brazil: Evidence for Paleoproterozoic collision and collapse in the Quadrilátero Ferrífero. *Precambrian Res.* **1998**, *90*, 29–58. [CrossRef]
24. Nalini, H.A., Jr. *Estudos Geoambientais no Quadrilátero Ferrífero: Mineração e Sustentabilidade*; School of Mines; Department of Geology UFOP: Minas Gerais, Brazil, 2009; 52p.
25. Weber, A.A.; Moreira, D.P.; Melo, R.M.C.; Vieira, A.B.C.; Prado, P.S.; da Silva, M.A.N.; Bazzoli, N.; Rizzo, E. Reproductive effects of oestrogenic endocrine disrupting chemicals in Astyanax rivularis inhabiting headwaters of the Velhas River, Brazil. *Sci. Total Environ.* **2017**, *592*, 693–703. [CrossRef]
26. Bølviken, B.; Bogen, J.; Jartun, M.; Langedal, M.; Ottesen, R.; Volden, T. Overbank sediments: A natural bed blending sampling medium for large—scale geochemical mapping. *Chemom. Intell. Lab. Syst.* **2004**, *74*, 183–199. [CrossRef]
27. Salminen, R.; Tarvainen, T.; Demetriades, A.; Duris, M.; Fordyce, F.M.; Gregorauskiene, V.; Kahelin, H.; Kivisilla, J.; Klaver, G.; Klein, H.; et al. *FOREGS Geochemical Mapping Field Manual*; Guide 47; Geological Survey of Finland: Espoo, Finland, 1998; 36p.
28. United States Environmental Protection Agency (USEPA). Method 3005A—Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy. 2001; [S.l.], 5p. Available online: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3005a.pdf (accessed on 6 September 2023).
29. Calmano, W.; Förstner, U. *Sediments and Toxic Substances: Environmental Effects and Ecotoxicity*, 1st ed.; Springer: Berlin/Heidelberg, Germany, 1996; 332p.
30. Ferreira, A.; Inácio, M.M.; Morgado, P.; Batista, M.J.; Ferreira, L.; Pereira, V.; Pinto, M.S. Low-density geochemical mapping in Portugal. *Appl. Geochem.* **2001**, *16*, 1323–1331. [CrossRef]
31. National Geospatial-Intelligence Agency. *World Geodetic System 1984 (WGS 84)*; National Geospatial-Intelligence Agency: Springfield, VA, USA, 2022.
32. Cheng, Q. Spatial and scaling modelling for geochemical anomaly separation. *J. Geochem. Explor.* **1999**, *65*, 175–194. [CrossRef]
33. Reimann, C.; de Caritat, P. Establishing geochemical background variation and threshold values for 59 elements in Australian surface soil. Sci. *Total Environ.* **2017**, *578*, 633–648. [CrossRef]
34. Fernández-Caliani, J.C.; Romero-Baena, A.; González, I.; Galán, E. Geochemical anomalies of critical elements (Be, Co, Hf, Sb, Sc, Ta, V, W, Y and REE) in soils of western Andalusia (Spain). *Appl. Clay Sci.* **2020**, *191*, 105610. [CrossRef]
35. Reimann, C.; Caritat, P. *Chemical Elements in the Environment: Factsheets for the Geochemist and Environmental Scientist*; Springer: Berlin/Heidelberg, Germany, 1998; 398p.
36. Costa, A.T. Registro Histórico de Contaminação por Metais Pesados, Associadas à Exploração Aurífera no alto e Médio Curso da bacia do Ribeirão do Carmo, QF: Um Estudo de Sedimentos de Planícies de Inundação e Terraços Aluviais. Ph.D. Thesis, Federal University of Ouro Preto, Ouro Preto, Brazil, 2007.
37. Varejão, E.V.; Bellato, C.R.; Fontes, M.P.F.; Mello, J.W.V. Arsenic and trace metals in river water and sediments from southeast portion of Iron Quadrangle, Brazil. *Environ. Monit. Assess* **2010**, *172*, 631–642. [CrossRef]
38. Parra, R.R.; Roeser, H.M.P.; Leite, M.G.P.; Nalini, J.R.H.A.; Guimarães, A.T.A.; Pereira, J.C.; Friese, K. Influência Antrópica na Geoquímica de Água e Sedimentos do Rio Conceição, Quadrilátero Ferrífero, Minas Gerais—Brasil. *Geochim. Bras.* **2007**, *21*, 36–49.
39. Merian, E.; Anke, M.; Ihnat, M.; Stoeppler, M. *Elements and Their Compounds in the Environment: Occurrence, Analysis and Biological Relevance*; WILEY-VCH Verlag GmbH & Co. KGaA: Hoboken, NJ, USA, 2004; Volume 1–3, 1773p.

40. Stephens, S.; Alloway, B.; Parker, A.; Carter, J.; Hodson, M. Changes in the leachability of metals from dredged canal sediments during drying and oxidation. *Environ. Pollut.* **2001**, *114*, 407–413. [CrossRef]
41. Riba, I.; Luque-Escalona, A.; Costa, M.H. Sediment Contamination and Toxicity in the Guadalquivir River (Southwest, Spain). *Appl. Sci.* **2023**, *13*, 3585. [CrossRef]
42. Pacheco, F.; Silva, M.; Pissarra, T.; Rolim, G.; Melo, M.; Valera, C.; Moura, J.; Fernandes, L. Geochemistry and contamination of sediments and water in rivers affected by the rupture of tailings dams (Brumadinho, Brazil). *Appl. Geochem.* **2023**, *152*, 105644. [CrossRef]