



High iron content in river waters: environmental risks for aquatic biota and human health

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ABSTRACT

This study assessed the concentrations of metals in the Dourados and Brilhante Rivers, investigated the influence of landscape features surrounding these rivers on water quality, and evaluated the risks associated with metal contamination for aquatic biota and human health. Sampling was conducted at eighteen sites distributed along the rivers in June 2016. The concentrations of metals (Cu, Zn, Mn, Fe, Cr, Al and Co) in the water were analyzed by inductively coupled plasma optical emission spectroscopy. All the samples possessed Fe concentrations above the threshold value for aquatic biota (0.3 mg L^{-1}). Moreover, land use and land cover assessment of the study area revealed extensive agriculture activity, particularly in areas surrounding the Dourados River headwaters. Fe bioavailability for both rivers indicated risks for aquatic biota and human health. Overall, the elevated Fe content in these rivers was attributed to anthropogenic activity in the vicinity of these water bodies and the soil characteristics of the area. Considering the importance of river basins, it is necessary to implement public policies for their conservation, especially those related to the cultivation of forests of native species and sustainable agricultural practices, in addition to improving the effluent treatment infrastructure, which is essential to minimize the adverse effects of contamination by chemical elements in water bodies.

Keywords: aquatic ecosystems, environmental contaminants, forest fragments.

Elevados índices de ferro na água: riscos ambientais para a biota aquática e saúde humana

RESUMO

O estudo teve como objetivo avaliar as concentrações de metais nas águas nos Rios Dourados e Brilhante, investigar a influência das características da paisagem no entorno destes rios sobre a qualidade da água e avaliar os riscos associados a contaminação dos metais para a



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biota aquática e saúde humana. As amostragens foram realizadas em dezoito pontos distribuídos ao longo dos rios em junho de 2016. As concentrações de metais (Cu, Zn, Mn, Fe, Cr, Al e Co) na água foram analisadas utilizando espectroscopia de emissão óptica com plasma indutivamente acoplada. Todas as amostras possuíam concentrações de Fe acima do valor limite para a biota aquática ($0,3 \text{ mg L}^{-1}$). Além disso, a avaliação do uso e cobertura do solo nas áreas de estudo revelou extensa atividade agrícola, particularmente nas áreas de nascentes do Rio Dourados. A biodisponibilidade de Fe para ambos os rios indicou riscos para a biota aquática e humana. No geral, o elevado teor de Fe nesses rios foi atribuído à atividade antropogênicas nas proximidades desses corpos de água e as características do solo da área. Considerando a importância das bacias hidrográficas, é necessário a implementação das políticas públicas para sua conservação, principalmente as relacionadas ao cultivo de florestas de espécies nativas e práticas agrícolas sustentáveis, além da melhoria da infraestrutura de tratamento de efluentes, que é indispensável para minimização dos efeitos adversos da contaminação por elementos químicos nos corpos hídricos.

Palavras-chave: contaminantes ambientais, ecossistemas aquáticos, fragmentos florestais.

1. INTRODUCTION

The exponential expansion of agricultural frontiers and cattle farming in certain regions of Brazil, particularly in Mato Grosso do Sul, have negatively impacted the water quality of these rivers, resulting in significant environmental degradation. Moreover, intensive agriculture and cattle farming around the basins, represented by extensive crops and pastures, have promoted the reduction of riparian forests, leaving the margins of aquatic environments unprotected (Viana *et al.*, 2020). The resultant landscape comprises erosion and silted areas and degradation of the riparian forests, a natural physical barrier for contaminant waste, has caused the flow of contaminants into nearby water bodies (Dos Santos *et al.*, 2020; Riveros *et al.*, 2021).

In this context, the Dourados and Brilhante Rivers are situated in the sub-basin of the Ivinhema River, one of the main tributaries of the Paraná River in southwestern Brazil (Message *et al.*, 2016). Along the Rivers Dourados River (DR) and the River Brilhante (BR), waste generated by agricultural development, contamination of hydrological systems by urban and industrial effluents poses a severe threat to the region. Moreover, the DR watershed comprises a significant portion of the basin that forms part of the city of Dourados and several tributaries of this river pass through the urban perimeter and are further contaminated by anthropogenic activity (Paula *et al.*, 2013; Dalla Costa and Roche, 2020).

Previous studies have demonstrated metal concentrations, particularly Iron (Fe), in the rivers of the Ivinhema River sub-basin exceeding the threshold defined by the National Legislation Conama 357 of 2005 (Souza, 2007; Kottwitz, 2012; Gonçalves, 2013; Dourado *et al.*, 2017; Maceda *et al.*, 2015; Da Rocha *et al.*, 2018; Dalla Costa and Roche, 2020; Dos Santos *et al.*, 2020; Viana *et al.*, 2020). Metal enrichment in aquatic environments, even those considered essential for the maintenance of life, such as Fe, can cause toxicity, representing environmental risks to local biodiversity and compromising human health through the consumption of contaminated water and fish (Sang *et al.*, 2019; Kortei *et al.*, 2020; Yu *et al.*, 2020). Human issues include respiratory problems, severe anemia, gastrointestinal bleeding, cardiovascular collapse, clotting, liver necrosis and progressive organ failure (Maurya *et al.*, 2019; Gashkina *et al.*, 2020).

This study evaluated the metal concentrations in water, mainly Fe, and the landscape composition, including land use and land cover, in the surroundings of the Dourados and Brilhante Rivers to investigate the influence of landscape characteristics on water quality and assess the risks of metals in the water to aquatic biota and human health.

2. MATERIAL AND METHODS

2.1. Description of the study area

The DR headwaters are located at the Antônio João municipality, on the border of Mato Grosso do Sul and Paraguay and flow for 370 km before discharging into the BR. The 344-km long BR headwaters are located in the city of Sidrolândia and run through nine towns situated totally or partially in its basin, namely Angélica, Deodápolis, Douradina, Dourados, Itaporã, Maracaju, Ponta Porã, Brilhante River and Sidrolândia. The DR supplies water to municipalities in the State of Mato Grosso do Sul, including the city of Dourados, which is the second-largest in the state (IBGE, 2014). In addition to residential use, DR water is used for animal and fish farming, irrigation and the industry sectors (Pereira *et al.*, 2007). The BR flows westward and joins the Vacaria and Dourados Rivers to the east, forming the Ivinhema River (Ferreira, 2005). The BR, which receives water from the DR, has several tributaries and is surrounded by areas of extensive agricultural activity, particularly sugarcane production, which is widespread in the State of Mato Grosso do Sul (Rio Brilhante, 2017). The sampling locations were selected according to the vicinity of activities from the headwaters to the river mouth. Sites DR1 and BR1 are located in the headwaters (Figure 1).

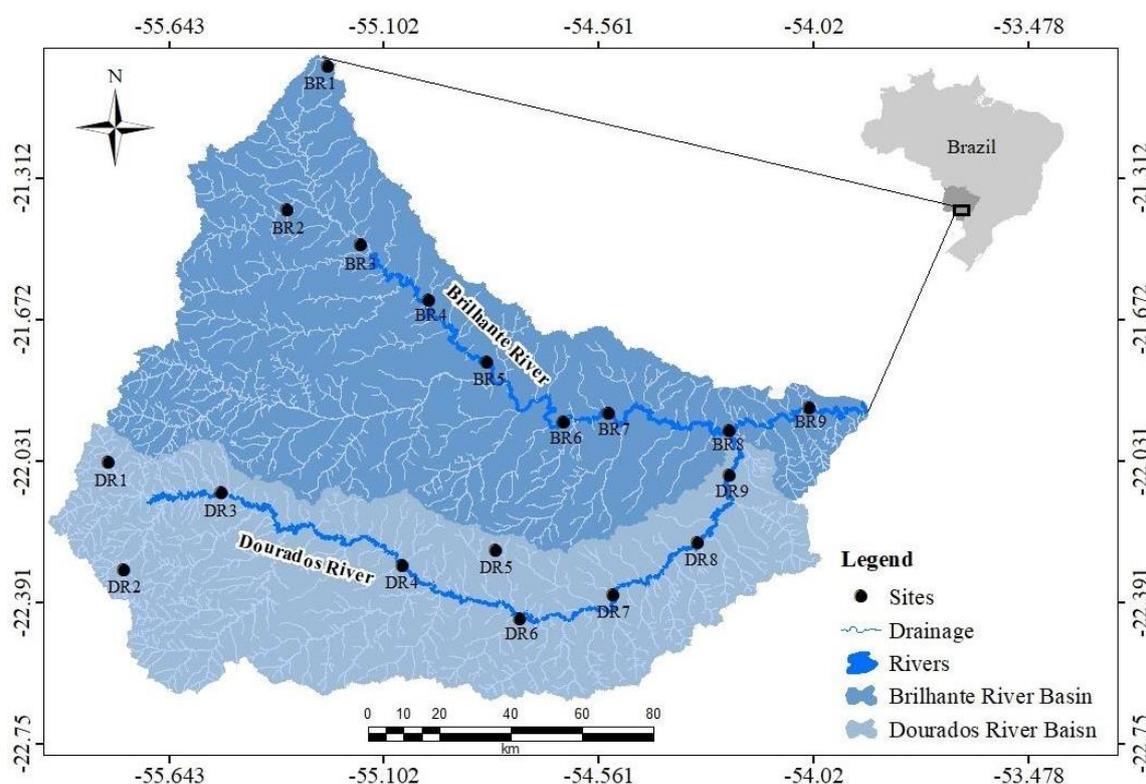


Figure 1. Sampling sites in the Dourados (DR1, DR2, DR3, DR4, DR5, DR6, DR7, DR8 and DR9) and Brilhante (BR1, BR2, BR3, BR4, BR5, BR6, BR7, BR8 and BR9) Rivers, Mato Grosso do Sul, Brazil.

2.2. Sampling and determination of metals in water

Water samples were collected at a depth of 20 cm at eighteen sampling sites along the DR (DR1, DR2, DR3, DR4, DR5, DR6, DR7, DR8 and DR9) and BR (BR1, BR2, BR3, BR4, BR5, BR6, BR7, BR8 and BR9) in June 2016. Water samples were collected in a 1 L sterile amber glass bottle, after collection, water samples were filtered using 0.45 μm membrane filter (Millipore Filtration Assembly), acidified at 1% of the volume for metal preservation (Brandão *et al.*, 2011), transported in refrigerators, and stored at 4°C until analysis. The entire procedure

was performed in triplicate. Analytical blanks were also prepared following the same procedure used for the samples.

The Copper (Cu), Zinc (Zn), Manganese (Mn), Iron (Fe), Chromium (Cr), Aluminum (Al), and Cobalt (Co) concentrations in the water samples were analyzed by Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES) (Thermo Scientific, USA, iCAP 6000® model) according to the methodology proposed by Mermet and Poussel (1995). The instrumental parameters of ICP OES were presented in (Table 1).

Table 1. ICP OES instrumental parameters.

Parameter	Setting
RF Power (W)	1250
Sample flow (L min ⁻¹)	0.35
Replicates	3
Plasma flow rate (L min ⁻¹)	12
Integration time (s)	5
Stabilization time (s)	20
Nebulization pressure(psi)	30
Plasma View	Axial
Sample Flush Time (s):	30
Pump Stabilization Time (s):	5
Nebulizer Gas Flow (L/min):	0.70
Auxiliary Gas Flow (L/Min):	0.50
Flush Pump Rate (rpm)	50
RF Power (W)	1150
Analysis Pump Rate (rpm)	50
Coolant Gas Flow (L/Min)	12

Standard solutions for calibration were prepared by suitable dilution of the stock solutions containing 1000 mg L⁻¹ of Cu and Zn and 100 mg L⁻¹ of Mn, Fe, Cr, Al and Co (Merck and Sigma Aldrich®). Standards at seven different concentrations (including a blank) were prepared (0.005 ppm; 0.01 ppm; 0.025 ppm; 0.1 ppm; 0.5 ppm; 1.0 ppm and 2.0 ppm). The metals selected in this study, wavelengths, correlation coefficients (R²), LOD and LOQ obtained by external calibration are presented in Table 2. The method was validated through the detection limit (LOD) calculated as three times the standard deviation of the blank expressed in concentration divided by slope of the analytical curve, and the limit of quantification (LOQ) was based on ten times the standard deviation of the blank divided by slope of the analytical

curve according to IUPAC (Long *et al.*, 1983). In addition, the accuracy of the methods was evaluated by addition and recovery tests, conducted in samples of water by spiking (0.5 mg/L and 1.0 mg/L of each analyte) (Table 2).

Table 2. Metals, wavelengths, limits of detection (LOD) and limits of quantification (LOQ), correlation coefficients (R^2) obtained by external calibration and validation of methods using spike concentration samples of water.

Metals	Wavelengths (nm)	LOD (mg/L)	LOQ (mg/L)	Linearity (R^2)	Spike recovery (%)	
					0.5 mg/L	1.0 mg/L
Cu	327.396	0.0013	0.0042	0.9962	111	112
Zn	213.856	0.0004	0.0014	0.9960	92	93
Mn	257.610	0.0002	0.0005	0.9999	112	114
Fe	239.562	0.0011	0.0036	0.8900	91	89
Cr	283.563	0.0011	0.0035	0.9997	110	113
Al	308.215	0.0045	0.0151	0.9763	90	93
Co	228.616	0.0005	0.0016	0.9999	103	106

2.3. Land use and cover

Land use and land cover ratios at the sampling sites were measured in June 2016 using high-resolution aerial images obtained from Google Earth Pro®, with a pixel size of 1 m. For the study limit, buffers of 2.0 km were generated around each sampling site (18 sites), and 10 classes of land use and land cover were categorized: an agricultural area, pasture, anthropic occupation, forest fragments, dense forest, planted forest, water bodies, wetlands, fish farming, and exposed soil, according to the Brazilian recommendations (IBGE, 2013). For the interpretation of the images, a visual classification was performed using the scanning tools provided by ArcGIS® 10.4 in its test version (ESRI, 2015), and the areas and percentages of each land cover category were calculated.

2.4. Risk assessment for aquatic biota preservation

A preliminary risk assessment was conducted for aquatic biota preservation. We calculated the risk quotient (RQ) as the ratio between the individual concentrations of each metal detected in the water samples and their respective Class II freshwater quality standard, provided by Brazilian legislation (Conselho Nacional do Meio Ambiente, 357/2005) (Conama, 2005). The DR and BR waters were classified as Class II, a category that aims to guarantee the preservation of aquatic life. An RQ value ≥ 1 indicated a possible ecological risk (Godoy *et al.*, 2015). For the risk index (IR) the sum of the RQ values was obtained for each metal individually. Higher IR values indicated a high potential risk of harmful effects to aquatic biota (Evans *et al.*, 2015; Gustavsson *et al.*, 2017). RQ and IR were calculated according to the Equation 1 below:

$$RQ = \frac{Water}{RfD} \quad (1)$$

Where RQ = risk quotient,

Water: concentrations of each metal detected in the water samples and

RfD = Reference value for the contaminant of interest (mg L^{-1}) (Conama, 2005).

2.5. Water quality criteria and risk assessment for human consumption

Risk assessments were used to estimate the probability of a selected factor adversely affecting human health. The water quality criteria (WQC) for human consumption based on health protection were calculated considering the exposure scenario proposed by the World Health Organization (WHO, 2006) for metals.

The reference doses (RfD) were obtained from the U.S. Environmental Protection Agency's Integrated Risk Information System (IRIS) and the Agency for Toxic Substances and Disease Registry (ATSDR). The Water Quality Criteria (WQC) were calculated according to the Equation 2 below:

$$WQC = \frac{RfD \times AF \times BW}{DWC} \quad (2)$$

Where RfD is the reference dose for each compound, AF is the allocation factor (10%), BW is the body weight of a human (60 kg) and DWC is the daily water consumption (2 L per day).

2.6. Literature review about high Fe concentrations found in the study region

A search was conducted in the following online databases: SciELO, ScienceDirect, Capes periodicals portal and Google Scholar. The keywords used in the search were: water quality, metals, Fe, Ivinhema River Basin and Dourados River Basin. All studies in which the identification of metals in water bodies was performed were considered. The inclusion criteria was selected as: scientific articles that presented Fe concentration results in water bodies situated in the sub-basin of the Ivinhema River, that is, the Dourados River, Ivinhema River and tributaries of both rivers, were selected.

3. RESULTS AND DISCUSSION

3.1. Metal concentrations in water

Concentrations of Cu, Zn, Mn, Fe, Cr, Al and Co were present in both the DR and BR. However, Zn was quantified at only one site in the BR. The Fe concentrations recorded for all the sites exceeded the water threshold values specified by Resolution 357/2005 of the National Environmental Council (Conama, 2005) for Class II freshwater (Table 3).

Site DR1, located in the headwaters, recorded the highest Fe concentrations for the DR sample set, followed by sites DR6, DR7 and DR8 located in the lower portion of the river (Table 3). For the BR analysis, BR6, situated in the lowest portion of the river, displayed higher Fe concentrations than the other BR samples (Table 3). For the remaining metals, only Al at site BR9 showed a value above what is considered safe for aquatic biota by the legislation mentioned above (Table 3). High Fe concentrations were detected in the samples collected from the DR and BR, with values above the limit considered safe for aquatic life according to the Brazilian Legislation Conama (357/2005). Our results were corroborated by previous research conducted on these two rivers, which also indicated high Fe concentrations for the Ivinhema River sub-basin (Figure 2).

Table 3. Metal concentrations (mg L⁻¹) in the water samples from the Dourados and Brilhante Rivers.

Sites	Cu	Zn	Mn	Fe	Cr	Al	Co	
Dourados River (DR)	DR1	<LOD	<LOD	0.0280±0.0001	3.6838±0.0003	0.0067±0.0002	0.0256±0.0065	<LOD
	DR2	<LOD	<LOD	<LOD	0.9768±0.0038	0.0066±0.0227	0.1035±0.0004	<LOD
	DR3	<LOD	0.0067±0.3720	0.0160±0.0001	1.8030±0.0008	0.0067±0.0004	<LOD	<LOD
	DR4	<LOD	<LOD	0.0320±0.0001	2.4951±0.0041	0.0068±0.4938	<LOD	<LOD
	DR5	<LOD	0.0019±0.6572	0.0397±0.0004	1.8874±0.0163	0.0063±0.0003	0.0376±0.0064	<LOD
	DR6	<LOD	<LOD	0.0465±0.0002	2.8249±0.0055	0.0064±0.0008	<LOD	<LOD
	DR7	<LOD	<LOD	0.0488±0.0005	3.0837±0.0192	0.0071±0.0006	<LOD	<LOD
	DR8	<LOD	<LOD	0.0373±0.3494	2.6860±0.0048	0.0065±0.0004	<LOD	<LOD
	DR9	<LOD	<LOD	0.0265±0.0003	2.2479±0.0199	0.0070±0.0006	<LOD	<LOD
Brilhante River (BR)	BR1	<LOD	<LOD	0.0325±0.6144	2.0509±0.0014	0.0075±0.0006	<LOD	<LOD
	BR2	<LOD	<LOD	0.0427±0.0003	2.7166±0.0092	0.0078±0.0003	<LOD	<LOD
	BR3	<LOD	<LOD	0.0383±0.0002	2.7398±0.0247	0.0070±0.0005	<LOD	<LOD
	BR4	<LOD	<LOD	0.0380±0.2870	2.7615±0.0059	0.0073±0.0005	<LOD	<LOD
	BR5	<LOD	<LOD	0.0230±0.0003	2.0902±0.0051	0.0073±0.0005	<LOD	<LOD
	BR6	<LOD	0.0019±0.5190	0.0425±0.0022	3.0414±0.0935	0.0068±0.0004	<LOD	<LOD
	BR7	<LOD	<LOD	0.0311±0.3732	2.5054±0.0181	0.0074±0.4503	<LOD	<LOD
	BR8	<LOD	<LOD	0.0356±0.0013	2.8408±0.0475	0.0067±0.0006	0.0642±0.0039	<LOD
	BR9	<LOD	<LOD	0.0056±0.0032	1.4280±0.0475	0.0075±0.0004	0.4128±0.0037	<LOD
Conama	0.009	0.18	0.1	0.3	0.05	0.1	0.05	

Maximum permitted value by Brazilian law, in accordance with Resolution 357 (Conama, 2005), for Class II fresh water; <LOD – Analyte concentrations were below the limits of detection.

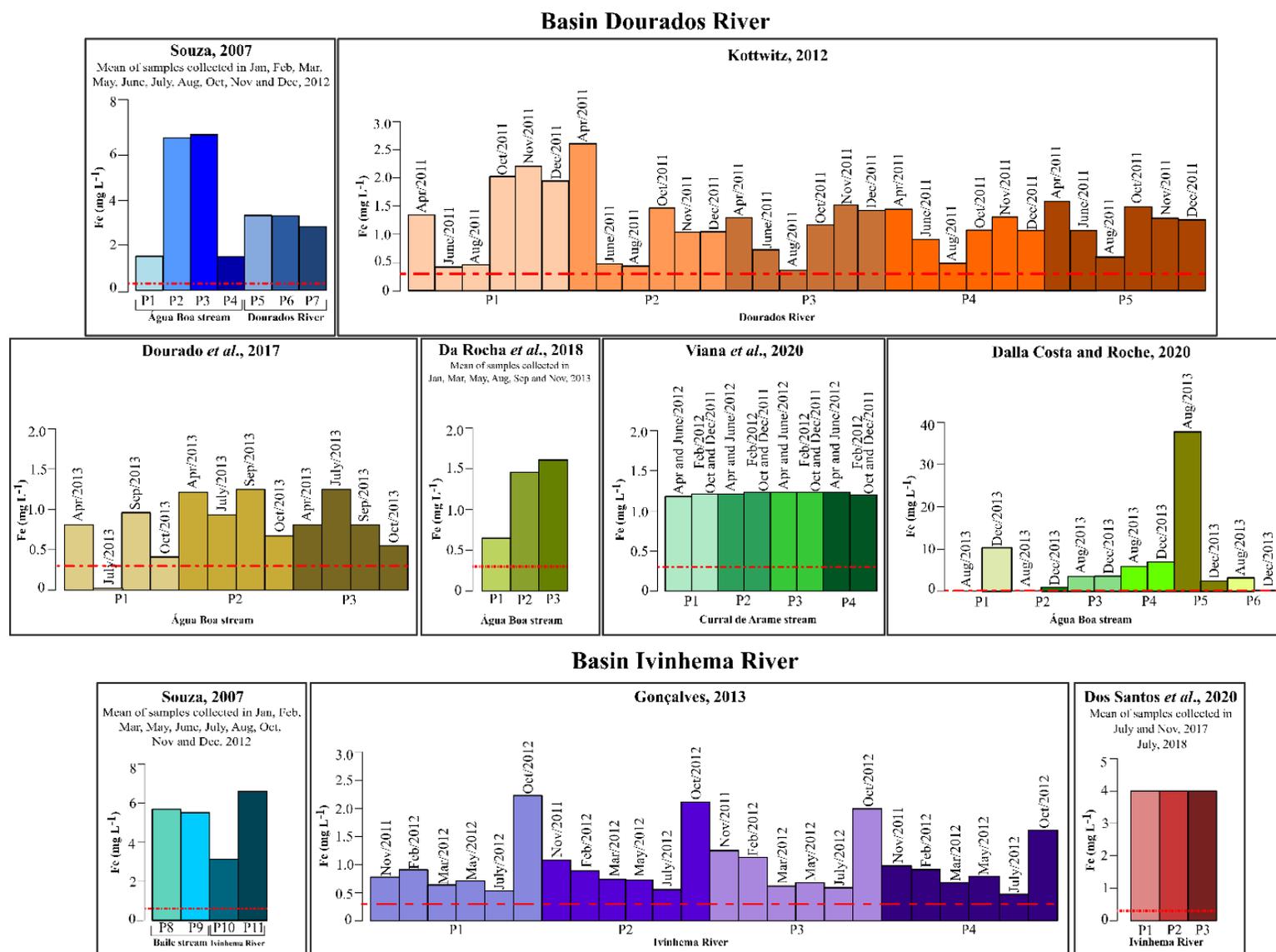


Figure 2. Fe concentrations based on previous studies exceed the limit (red line) specified by the Resolution Conama 357/2005 in rivers of the Ivinhema river sub-basin.

Excess Fe may be attributed to runoff from agricultural processes such as the application of fertilizers to the soil during land preparation and the spraying of pesticides (Kortei *et al.*, 2020).

Only one of the BR sites, located further downstream, recorded an Al value above the threshold value considered safe for aquatic life according to the Brazilian Legislation Conama (357/2005). This metal is a non-essential element for aquatic life, and high Al concentrations may lead to mutagenic and genotoxic changes and the promotion of bone diseases in vertebrates (Francisco *et al.*, 2018; Rahmani *et al.*, 2018; Chandrapalan and Kwong, 2020). Sources of Al are related to industrial and domestic applications as Al is typically used in antiperspirants, food preservatives and automobile structures (Callewaert *et al.*, 2014; Gebara *et al.*, 2020).

A comparison of the DR and BR samples with the values established by the Conama 357/2005 legislation revealed a seven-fold ($>2.0 \text{ mg L}^{-1}$) increase in the threshold value (0.3 mg L^{-1}) for the river water samples (Figure 3).

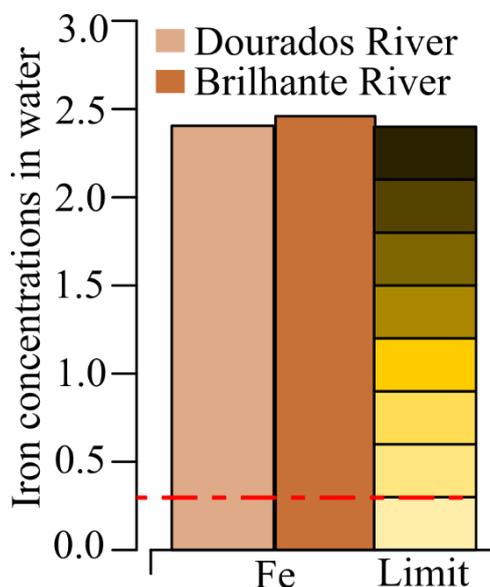
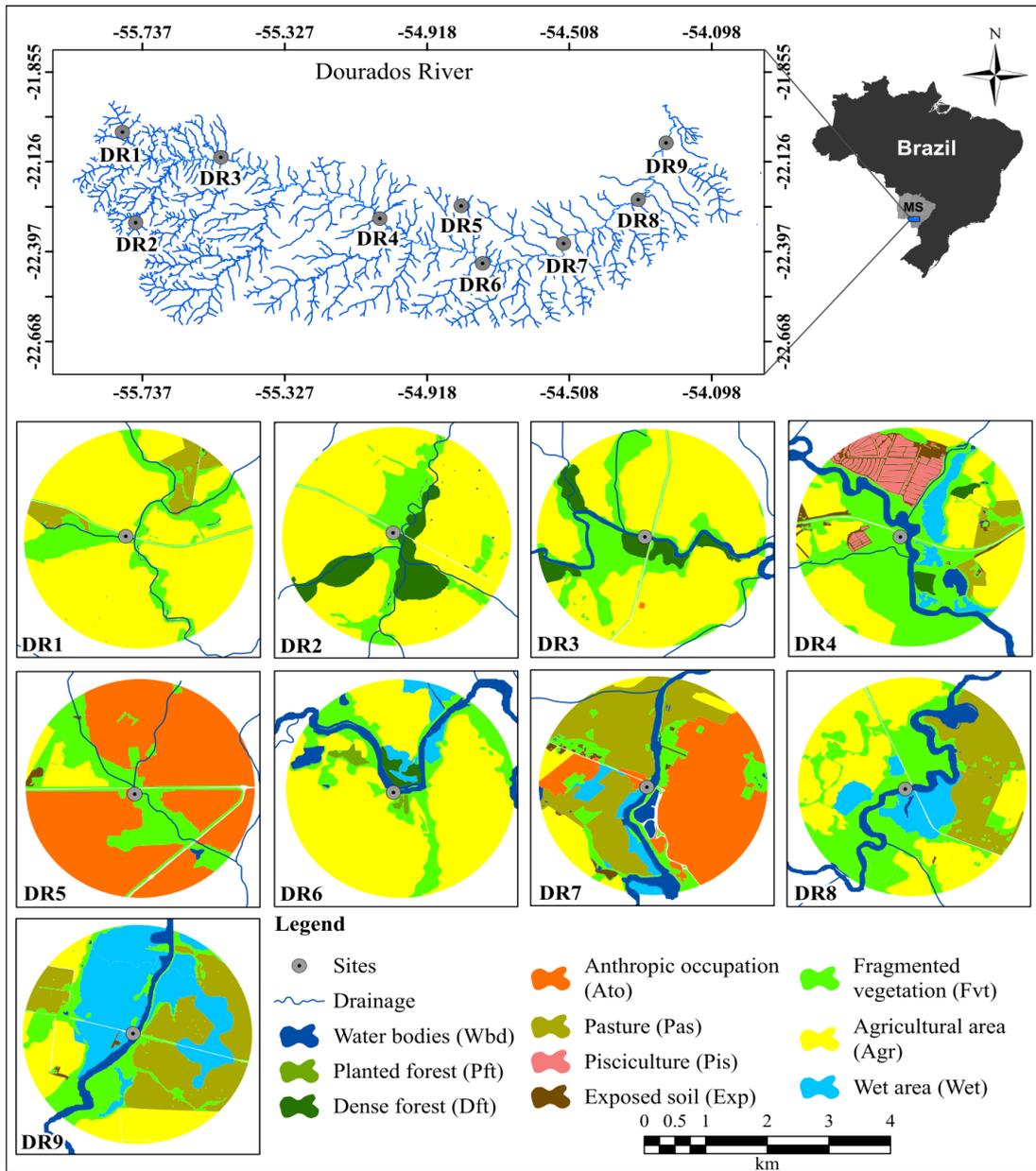


Figure 3. Fe concentrations in the river water samples compared to the limit (red line) specified by the Resolution Conama 357/2005.

The high Fe concentrations detected in the river water pose a severe threat to the aquatic biota of the hydrological systems in the sub-basin and humans reliant on this water for drinking (Bianchi *et al.*, 2019). Fe concentrations in aquatic ecosystems, particularly freshwater systems, have increased significantly in recent years, highlighting a serious environmental concern (Sarkkola *et al.*, 2013; Bjorneras *et al.*, 2017; Chandrapalan and Kwong, 2020).

3.2. Characterization of land use and land cover

Agricultural intensity in the vicinity of the samples obtained from the DR decreased consecutively (DR1 > DR2 > DR6 > DR3) (Figure 4). Moreover, the occurrence of forest fragments decreased in the following order: DR4 > DR8 > DR3 > DR5 (Figure 4). The most significant anthropogenic activity occurred in the proximity of DR5 and DR7. DR7 > DR9 > DR8 > DR1 had the most significant pasture areas, while DR9 > DR8 > DR4 > DR7 contained the most significant flood plains. DR2, followed by DR3, were situated in more densely vegetated areas (Figure 4). DR4, followed by DR7 and DR5, contained large areas of exposed soil. Fish farming occurred in the vicinity of DR4 and DR7. Only DR6 presented areas with planted forests.

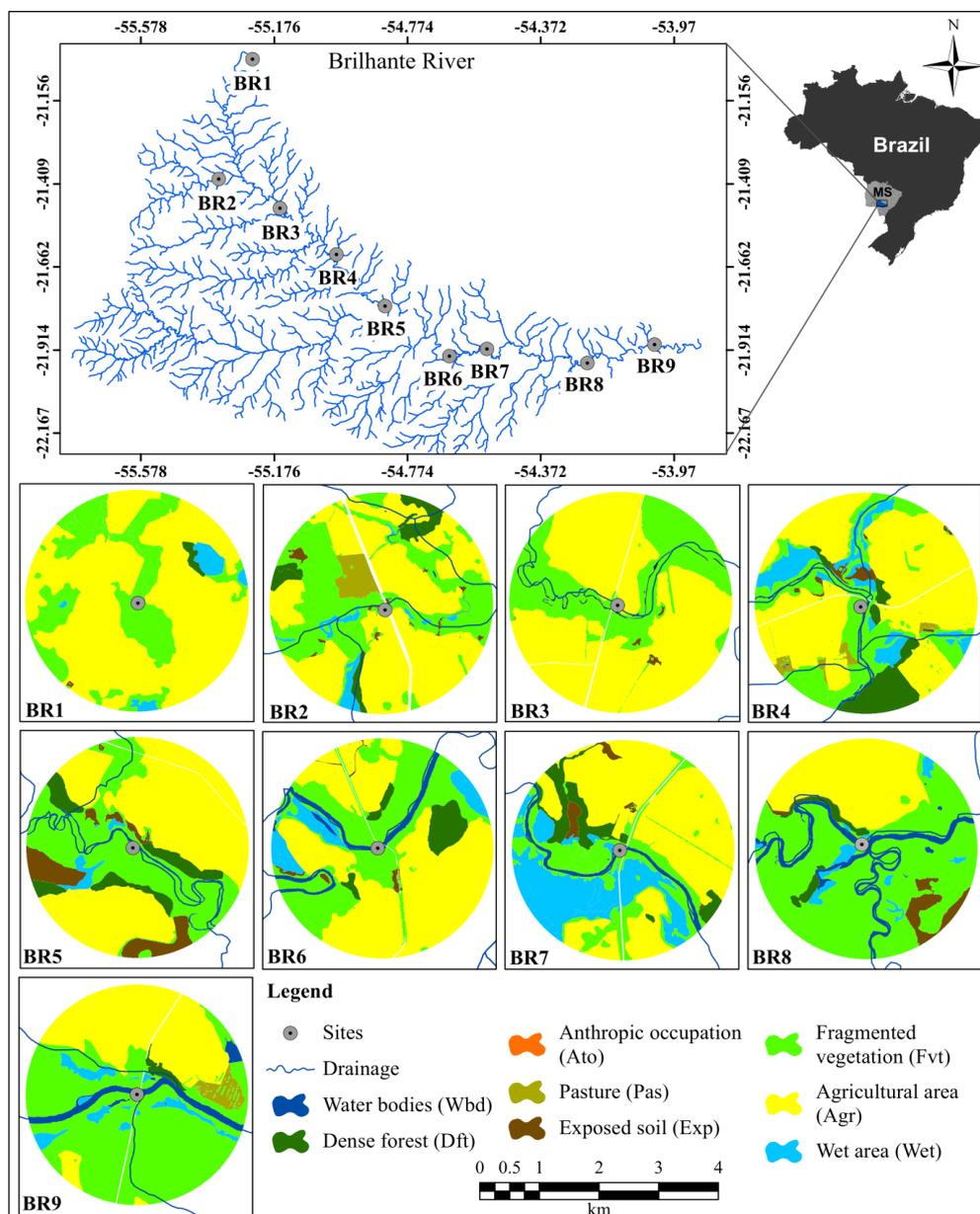


River	Sites	Land use and cover									
		Agr	Wet	Ato	Wbd	Dft	Pas	Pis	Pft	Exp	Fvt
Dourados River	DR 1	74.284	0.000	0.046	0.144	0.000	6.494	0.000	0.000	0.040	18.571
	DR 2	73.499	0.000	0.008	0.167	11.349	0.000	0.000	0.000	0.000	14.565
	DR 3	68.081	0.000	0.093	1.088	7.083	0.000	0.000	0.000	0.000	23.111
	DR 4	28.832	5.758	0.088	2.801	1.607	4.050	8.840	0.000	6.136	41.334
	DR 5	4.820	0.000	72.253	0.199	0.000	0.000	0.000	0.000	0.464	21.084
	DR 6	70.277	4.617	0.000	3.552	1.699	0.000	0.000	1.441	0.000	18.414
	DR 7	7.588	5.007	36.948	4.071	0.000	31.388	0.307	0.000	1.129	12.500
	DR 8	34.560	9.493	0.064	3.463	0.000	19.451	0.000	0.000	0.036	32.479
	DR 9	17.374	32.876	0.047	2.304	0.000	29.624	0.000	0.000	0.290	16.889

Figure 4. Land use and cover at selected sampling sites along the Dourados River (DR), Mato Grosso do Sul, Brazil.

Agricultural activities were also dominant along the BR and the size of the farming areas adjacent to the sampling sites decreased in the following order: BR1 > BR3 > BR4 > BR2 > BR5 > BR6 (Figure 5). BR8 > BR9 > BR2 > BR3 > BR6 > BR5 were the locations with the largest forested areas. Site BR4 was most significantly affected by anthropogenic activity and

BR2, BR9, and BR4 had the largest adjacent pastures of the sample set (Figure 5). BR4 >BR5 > BR7 >BR6 >BR2 were the sampling sites comprising significant areas of dense vegetation and BR8 >BR9 > BR6 >BR7 were situated in extensive areas of the river (Figure 5). The most significant areas of proposed soil were observed for BR5 > BR8 > BR7 (Figure 5).



River	Sites	Land use and cover									
		Agr	Wet	Ato	Wbd	Dft	Pas	Pis	Pft	Exp	Fvt
Brilhante River	BR 1	69.902	2.752	0.007	0.000	0.735	0.000	0.000	0.000	0.065	26.539
	BR 2	52.459	2.616	0.005	0.162	4.871	3.551	0.000	0.000	0.953	33.690
	BR 3	66.887	0.000	0.012	0.941	0.000	0.000	0.000	0.000	0.351	31.019
	BR 4	55.764	8.808	0.038	1.277	7.820	1.655	0.000	0.000	1.414	22.597
	BR 5	51.602	1.454	0.006	1.749	7.038	0.000	0.000	0.000	7.415	30.394
	BR 6	51.229	5.977	0.001	4.152	5.214	0.000	0.000	0.000	0.847	32.212
	BR 7	48.562	20.961	0.004	2.641	6.800	0.000	0.000	0.000	1.595	18.748
	BR 8	24.227	2.886	0.000	7.005	2.232	0.000	0.000	0.000	3.782	59.869
	BR 9	30.913	4.442	0.016	4.852	1.037	2.437	0.000	0.000	0.000	55.669

Figure 5. Land use and cover at selected sampling sites along the Brillhante River (BR), Mato Grosso do Sul, Brazil.

An evaluation of the average land use and land cover for all the sites along each river revealed more significant agricultural activity along the BR with fragmented vegetation areas, and more significant pasture and fish farming activity along the DR (Figure 6).

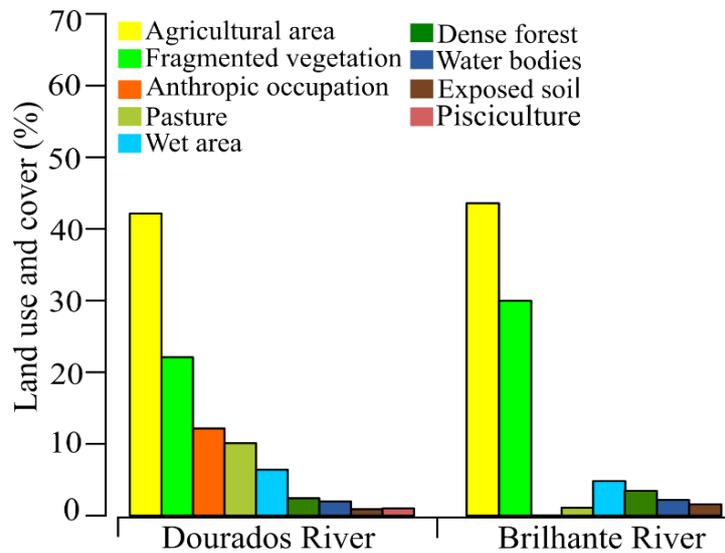


Figure 6. Total percentage of land use and cover in the sampled locations along the Dourados (DR) and Brilhante (BR) Rivers, Mato Grosso do Sul, Brazil.

The land use and coverage data revealed that the DR and BR surroundings are predominantly occupied by agricultural activities, particularly the DR headwater areas. Expansions of agricultural areas combined with deforestation near riverbanks pose severe environmental risks, predominantly related to environmental safety, the integrity of aquatic ecosystems and local biodiversity (Ezemonye *et al.*, 2019). River headwaters directly influence basin hydrology. Moreover, these areas are affected by anthropogenic activity due to their proximity to the watercourse. For this reason, riparian forests are likely to be replaced by agricultural activities, causing vegetation scarcity along the watercourses. Thus, intensive agricultural practices are an essential source of contamination and surface rainwater runoff draining directly into river systems may transport agrochemicals applied to agricultural fields (Bartley *et al.*, 2006).

The forested areas adjacent to both rivers, classified as semi-deciduous seasonal forest, were significantly reduced, further indicating the adverse effects of agriculture on natural vegetation. In Brazil, the Brazilian Forestry Code regulates the protection of indigenous vegetation and defines Permanent Preservation Areas (PPAs) to preserve riverbanks and protect headwaters (Brasil, 2012). Therefore, the reduction in riparian forest areas observed in this study indicated an infringement of the regulations established by the Brazilian Forestry Code. Moreover, numerous areas in the study area comprised fragmented and fragile vegetation remains, possibly indicating the vulnerability of the watercourse to anthropogenic disturbances. In addition, increased agricultural and anthropogenic malpractices result in habitat loss for a significant number of diverse terrestrial animals.

Dystrophic Red Latosol (FDRL) was the dominant soil type for both DR and BR. However, in several stretches of the basins, Dystrophic Red Latosol (DRL) was detected (Figure 7).

Both hydrographic basins were predominantly composed of Dystrophic Red Latosol, which is a type of soil with high levels of Fe oxide (Amaral *et al.*, 2000). Therefore, Fe enrichment in the DR and BR may be related to the dominant soil type in the region in addition to contamination generated by agricultural activity, and urban and industrial effluents in the vicinity of these water bodies (Bonnail *et al.*, 2017; Viana *et al.*, 2020). Viana *et al.* (2020)

reported that the combination of soil type in the DR region and the effects of urban waste and agricultural activities lead to a significant increase in Fe levels in aquatic environments. This may be indicative of environmental disturbances, as excess Fe concentrations are toxic to aquatic biota.

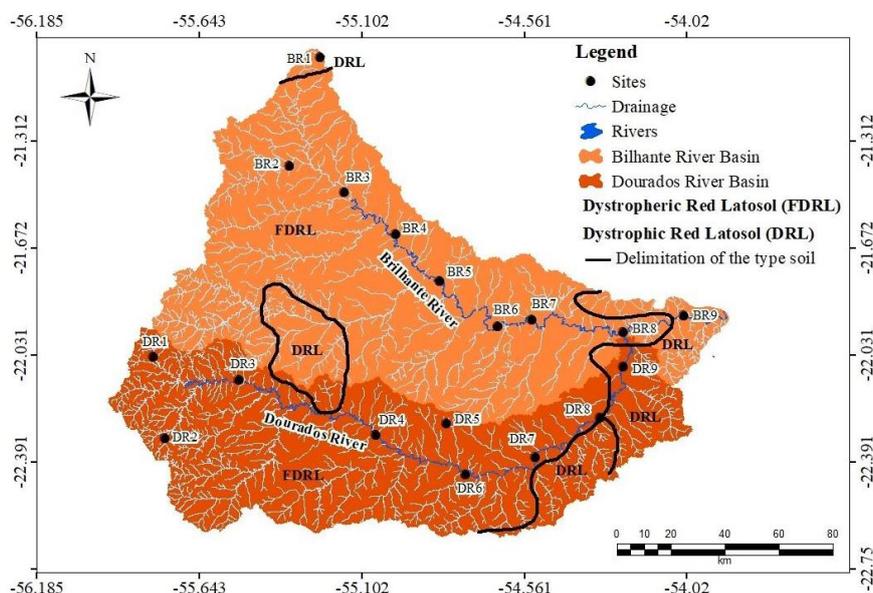


Figure 7. Type of soil surrounding the Dourados (DR) and Brilhante (BR) Rivers, Mato Grosso do Sul, Brazil.

The headwaters for the DR and BR are located at high altitude plateaus exceeding heights of 490 m and the rivers flow down to minimum depths ranging from 258-371 m (Figure 8).

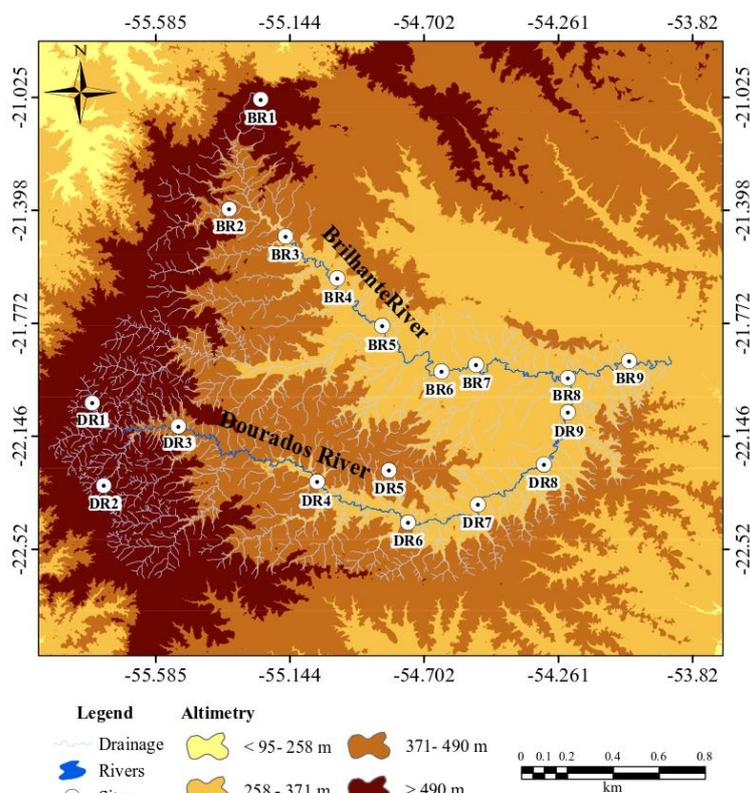


Figure 8. Altimetry of the Dourados (DR) and Brilhante (BR) Rivers, Mato Grosso do Sul, Brazil.

Another process that may be associated with the release of Fe in the DR and BR is the weathering of rocks, since the headwaters of both rivers are located in rocky areas, and the weathering of Fe-rich rocks releases significant amounts of Fe into the water. Latosols are usually strongly acidic, susceptible to erosion, and represent an advanced stage of weathering as a result of energetic transformations in their composition. Thus, the quality of water can be altered if sediments are carried to water bodies, as a high acidity increases the solubility of several chemical compounds, thus increasing their concentrations in the environment (Embrapa, 2006).

3.3. Risk assessment for aquatic biota preservation

The RQ in the rivers indicated that Fe was the metal that exceeded the threshold, posing a health risk for the aquatic biota (Figure 9a). Moreover, an evaluation of the total metal concentration in the samples from both rivers significantly exceeded the threshold value and indicated a risk of metal contamination (Figure 9b).

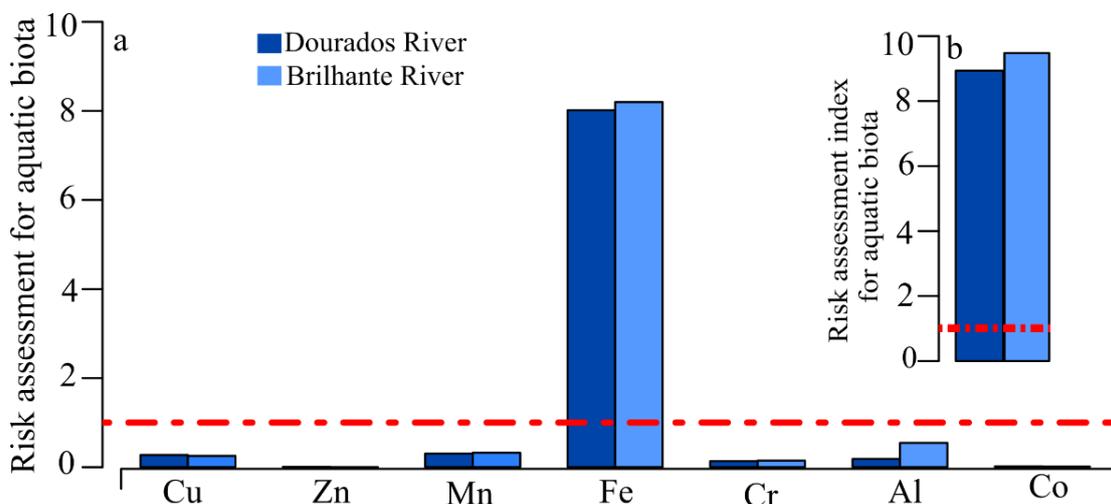


Figure 9. Risk quotient (RQ) (a) for individual metals and risk index (RI) (b) for the sum of individual RQs of average concentrations of metals present in waters in the Dourados and Brilhante Rivers, Mato Grosso do Sul, Brazil. RQ/RI above the red dotted line represents values > 1 and, consequently, risk to aquatic biota.

The RI in the DR and BR indicated Fe concentrations >1, posing a severe threat to the aquatic biota. These threats include genetic and metabolic diseases and mutagenic and genotoxic impacts. Fe toxicity will most likely adversely affect sensitive aquatic species and favor the selection of more tolerant species (Rahmani *et al.*, 2018; Viana *et al.*, 2020). Assessing the total metal concentration in these rivers revealed a value >1, indicating risks for aquatic biota preservation. Therefore, most of the metals analyzed originate from similar sources and may have the same sources and sinks in aquatic environments, thus generating pollutants in water bodies (Bianchi *et al.*, 2019).

3.4. Water quality criteria for human consumption and risk assessment

Based on an evaluation of the water quality criterion, Fe was the only metal detected above the threshold value specified for human consumption (Figure 10 a–b).

An analysis of the Water Quality Criteria (WQC) indicated the possibility of Fe adversely affecting human health at most of the sampling sites, as the concentrations exceeded the QC threshold value (Umbuzeiro *et al.*, 2010). In addition, Fe concentrations also exceeded the maximum limit indicated by legislation (Conama 357/2005) at all the sampling sites (Table 3). Although it is an essential metal for human health, high Fe concentrations are harmful to humans, affecting several physiological processes (Huang *et al.*, 2015). When ingested in

excess, Fe has been associated with diabetes, cirrhosis, heart alteration, gastrointestinal effects and DNA damage (Gurzau *et al.*, 2003; Jaishankar *et al.*, 2014; Izah *et al.*, 2016; Edokpayi *et al.*, 2018). Therefore, this water is not suitable for human consumption.

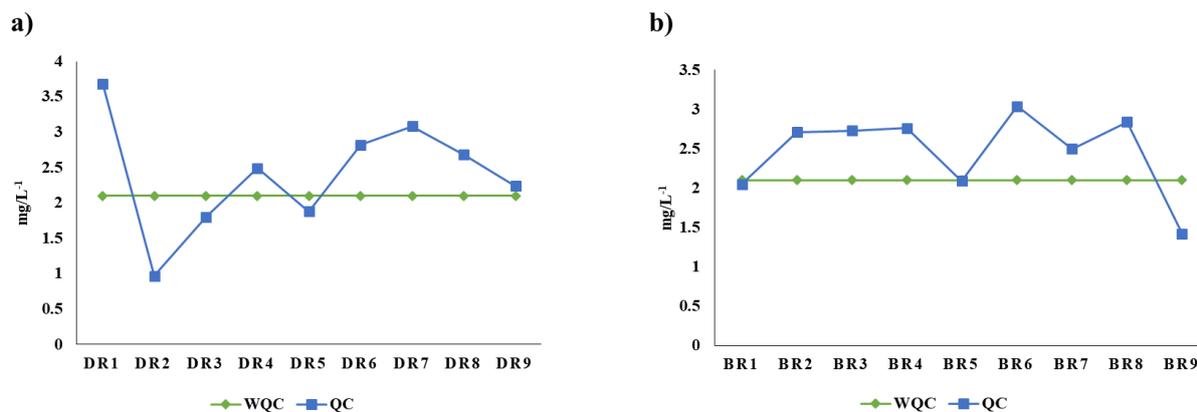


Figure 10. Potential human health risks associated with Fe contamination detected at the sampling sites along the (a) DR and (b) BR. The green line represents the water quality criterion (WQC), and points plotted above the QC (quantified concentration) represent potential risks for human health.

4. CONCLUSION

The decline in quality of the DR and BR waters due to excess Fe can be attributed to the reduction of indigenous forests, intense agriculture adjacent to the watercourse, and soil characteristics in the region. Moreover, sparse and fragile vegetation cover detected in the study area was attributed to agricultural malpractice. Fe concentrations in the DR and BR waters indicated risks for the aquatic biota. Considering the importance of river basins and the local soil structure, the adoption of more rigorous agricultural practices by farmers and the application of stringent conservation policies for indigenous forests are essential. Moreover, improved infrastructure for effluent treatment is required to prevent the contamination of water resources and control local pollution and the risks associated with human health.

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