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ORIGINAL PAPER

Assessment of risk to human health associated with the consumption of contaminated groundwater in the Western Brazilian Amazon

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Abstract The present study evaluates the risk to human health associated with the consumption of groundwater in municipalities in the Western Brazilian Amazon (Jaru, Ouro Preto do Oeste, Ji-Paraná and Presidente Médici, all in the state of Rondônia). Water was collected directly from wells with an underground collector and PET bottles between 2017 and 2019, in periods (low water, high water, Transition high water/low water). Nitrite and nitrate analyses were carried out using spectrophotometry (APHA, Standard methods for the examination of water and wastewater, Washington, 2017; EPA, Technical Resource Document, EPA/600/4-79/020 Disponívelem, 1971). Trace elements were detected by inductively coupled plasma-optical emission spectrometry. The hazard quotient was obtained from the ratio between the exposure level and the acceptable level for each substance present in the samples, and the hazard index resulted from the sum of the hazard quotients found for each substance. We found that the groundwater in the study areas is improper for human consumption in accordance with Brazilian regulations. Concentrations were found above the maximum values permitted by the Edict on Potability of Water for Human Consumption (PRC Edict 5/2017, as amended by GM/MS Edict 888/2021), and the World health organization standard for 2017 for Al (< 200 μg L^{-1}), As (< 10 μg L^{-1}), Ba (< 700 μg L^{-1}), Fe (< 300 μg L^{-1}), Mn (< 100 μg L^{-1}), Pb (< 10 μg L^{-1}), Zn (< 5,000 μg L^{-1}), and nitrate (< 10,000 μg L^{-1}). The results of the risk assessment indicated that the values were above the recommended levels (< 1) in 75.3%

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of the samples analyzed, meaning that people in the areas studied are highly exposed to contaminants that are harmful to human health.

Keywords Trace elements · Hazard quotient · Hazard index · Amazônia

Introduction

Water is essential for all aspects of human development, and the supply of clean water is a global priority (Sharma et al., 2021). In this context, groundwater plays an important role, especially in regions where rainwater and/or surface water are insufficient or unreliable to meet human needs, such as in various areas of the United States (Baris et al., 2016; Ward et al., 2005), Jordan (Wedyan et al., 2021), China (Chen et al., 2021; Zhang et al., 2025), Iran (Bazeli et al., 2020; Golak et al., 2022), Nepal (Ghimire, et al., 2025), Romania (Senila et al., 2017), Türkiye (Yazman et al., 2024) and India (Sharma et al., 2021).

In Brazil, the management of groundwater faces multiple challenges, but it is fundamental to guarantee national water security. Despite its natural and social invisibility, it is essential to maintain the base flow in rivers and various ecosystems, besides assuring the supply of water for multiple uses, especially in places where there is no access to a treated water system (ANA, 2022).

In general, the scarcity and low quality of water resources has been increasing in recent years due to factors such as water pollution and contamination, and the growth in demand due to urban expansion and industrial and agricultural development (Ribeiro et al., 2019).

Nitrate is the most common inorganic contaminant in aquifers in the world. Due to its high mobility and persistence, it has been used globally as an indicator of contamination, and it can affect large areas (Varnier et al., 2010). Its frequent presence in groundwater has worried water resource managers, given the growing number of cases of excessive pollution reported in urban and rural areas in several countries, including Brazil (Varnier, 2019). Fertilizer is the main source of nitrogen in agricultural areas, while human waste is the most important source of the element in urban areas lacking treated water and sanitation systems (Ward et al., 2005). A significant amount of this nitrogen is converted into nitrate in the surface and groundwater sources that supply communities that depend on it as a source of drinking water (Temkin et al., 2019).

Drinking water high in nitrate can have a major impact on human health (Wedyan et al., 2021). In the body, igested nitrate is reduced to nitrite, which binds to hemoglobin to form methemoglobin (MetHb). Methemoglobinemia occurs when elevated levels of MetHb interfere with the blood's ability to transport oxygen. Its presence is considered hazardous when exceeding about 10% (Ward et al., 2005). In particular, it can cause blue baby syndrome, a condition that can kill newborns due to oxygen deprivation (Temkin et al., 2019). Newborns are particlulary susceptible to developing it due to their greater ability to convert nitrate to nitrite and their lower levels of the cytochrome b5 enzyme (Ward et al., 2005).

Epidemiological studies provide evidence of an association between nitrate ingestion from drinking water and adverse health outcomes. Besides methemoglobinemia, these include colorectal cancer, thyroid disease, and neural tube defects (Ward et al., 2005, 2018). For example, higher nitrate intake in drinking water was found to be related to increased risk of renal cell carcinomas in the American state of Iowa (Ward et al., 2007). The potentially harmful influence of nitrate and the association between exposure and the occurrence of numerous health problems makes nitrate pollution an urgent public health problem (Bazeli et al., 2020).

Another group of contaminants of great concern is trace elements, which are present in different chemical forms in the main compartments of the environment (Mortatti et al., 2002). Trace elements are chemical elements that occur in nature in small concentrations, not exceeding 0.1% (Esteves, 2011). They are also known as heavy metals, trace metals, micronutrients, essential elements, etc.), but the name "trace element" is the most widely accepted, due to the lack of distinction between metal and non-metal elements and its reference to low concentrations (Esteves, 2011). Elements such as arsenic (As), silicon (Si) and germanium (Ge) are classified as metalloids or semimetals since they are elements with metallic or non-metallic properties (Csuros & Csuros, 2002).

Some trace elements, such iron (Fe), zinc (Zn), manganese (Mn) Copper (Cu) are essential to living beings with positive effects on human health (Albals et al., 2021; Ryan-Harshman & Aldoori, 2005), while others, such lead (Pb), mercury (Hg), e arsenic (As), have no known biological function, being potentially toxic elements and representing a risk to human health, even in low concentrations (Senila et al., 2024). Even elements with a defined biological function can in large concentrations be highly toxic to plants and animals (Esteves, 2011). Toxicity poses a risk to living beings, whether through consumption of polluted water and food, or intermediately through trophic chains (Mortatti et al., 2002).

The trace elements with the leading rates of poisoning reports and the most notable effects are Pb, Hg, Cd, aluminum (Al), Cu, Mn and Fe, among others. Each one presents a specific symptomatic and functional clinical picture (Moschem & Gonçalves, 2020).

The presence of trace elements in groundwater in the Amazon region was reported by Meyer et al. (2017) in the Western Peruvian Amazon; by Meyer et al. (2023) in the Amazonian Plain of Peru; and by Santos et al. (2024) and Carvalho et al. (2015), respectively, in the Brazilian cities of Parintins (Amazonas State) and Belém (Pará). In the state of Rondônia, studies were conducted by Nascimento (2022), Ramos (2022), Martins (2011) and Cremonese (2014) in the municipality of Ji-Paraná; by Laureano et al. (2018) in the municipality of Presidente Médici; and by Pavanello (2018) in the municipality of Ouro Preto do Oeste. In all cases, the authors reported concentrations above what Brazilian legislation considers safe for human consumption according to PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021), which establishes the potability standard for human consumption.

Groundwater contamination can have serious effects on human health, mainly through two routes, ingestion (oral) and physical contact (dermal) (Wedyan et al., 2021). Adverse health effects to humans who are exposed to environmental contaminants can be determined through a risk assessment approach (Bazeli et al., 2020; Wedyan et al., 2021).

According to Freitas (2002), risk assessment has become an important tool to support decisions on efforts to control and prevent human exposure to health-threatening agents that are present in the environment. It also acts as a tool for the sustainable management of underground water resources (Castilhos et al., 2014). Finally, it plays a significant role in quantifying the risk of exposure to chemicals, by defining allowable limits in programs to clean up contaminated sites (Mohan & Sruthy, 2022). The possibility of relating environmental and health data is fundamental for understanding the interrelationships of levels of exposure to agents and the effects on health (Freitas, 2002).

The use of shallow wells has long historical roots, and the tapping of groundwater for supply is an ancient alternative (Moreira et al., 2021). This practice is not restricted to cities with easy access to high-yield aquifers. It also occurs in areas where the public water supply comes from distant, unreliable and/or expensive surface water sources (Foster, 2020). In these situations, the private construction of wells for self-supply from groundwater represents a significant proportion of the water "actually received" by global users (generally 20–30% of total water supply, and well over 50% in extreme cases) (Foster, 2020).

In the Amazon region, such as the state of Rondônia, it is common to rely on groundwater as the only alternative for domestic supply (Barros et al., 2016; Ferreira et al., 2014; Lauthartte et al., 2016; Leite et al., 2011), or to complement supply from the piped water system (Rodriguez et al., 2014), due to the low cost of water collection and the population's lack of confidence in the quality of the water offered by collective supply systems (Silva et al., 2009).

Although several studies have investigated the quality of groundwater in the Amazon region (Carvalho et al., 2015; Meyer et al., 2017, 2023; Santos et al., 2024) including the state of Rondônia (Nascimento, 2022; Ramos, 2022; Martins, 2011; Cremonese, 2014; Leite et al., 2011; Laureano et al., 2018), little is known about the possible risks that contaminants pose to human health.

In this context, the present study was carried out in order to determine the contamination of groundwater by nitrite, nitrate and trace elements, as well as assess the risk to human health from the use of these waters as a source of water for human consumption, using as hazard quotient (HQ) and the hazard index (HI) as indicators. Considering the importance of the Amazon region in terms of water resources, and the gap that exists in this area, this study's findings can serve as a basis for establishing sustainable management strategies and for the protection of groundwater and public health.

Materials and methods

Study area

The study area comprised the municipalities of Jaru, Ouro Preto do Oeste, Ji-Paraná and Presidente Médici, all located in the central-eastern region of the state of Rondônia (Fig. 1), one of the nine states composing the so-called "Legal Amazon" in Brazil.

We used data on the concentration of nitrite, nitrate and trace elements in groundwater intended for human consumption in the four municipalities, totaling 77 wells, evaluated between 2017 and 2019.

The contamination assessment was carried out by comparing the concentrations found with the benchmark values defined in PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021) (Brasil, 2021), and the World Health Organization (WHO, 2017), considering potability values for human consumption, as shown in (Table S1).

We collected groundwater samples from shallow wells with diameter of 1 to 1.5 m and a depth of less than 30 m, and tubular wells, with greater depth (between 100 and 200 m), and diameter of 10 to 50 cm, along with two springs (Iritani & Ezaki, 2012).

Figure 1 shows the location of the municipalities studied and the distribution of the points sampled.

Table S2 reports the types of groundwater exploitation, number of samples in each municipality, month and year of collection, and the corresponding hydrological period. With the aim of sampling the region's seasonal periods, different months were selected according to the local rainfall regime, low

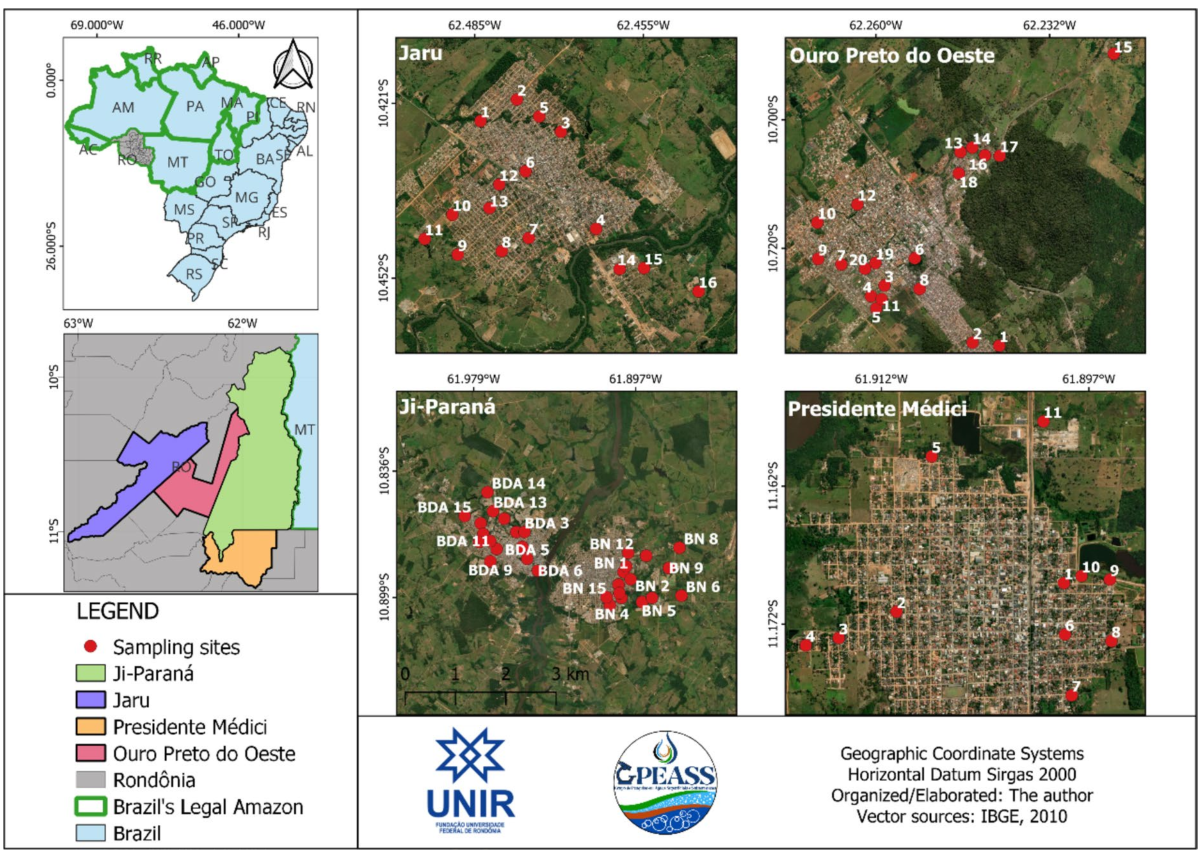

Fig. 1 Area of the municipalities of Jaru, Ouro Preto do Oeste, Ji-Paraná and Presidente Médici, indicating the points sampled

water (September e August), high water (December, February, March e April) and the month of June classified as transition from high water to low water.

Collection

Water was collected directly from each well using a collector adapted for groundwater sampling (CETESB, 2011). The water samples were transferred to 500 mL PET bottles used for sale of mineral water, which were opened and emptied for replacement by the well or spring water. Afterwards, the samples were placed in refrigerated isothermal boxes and transported to the Limnology and Microbiology Laboratory of Federal University of Rondônia (UNIR), in Ji-Paraná.

Analysis of nitrite, nitrate and trace elements

To determine the nitrite and nitrate concentrations, a volume of 100 mL of each water sample was filtered through a 0.45 μm cellulose membrane. Concentrations were measured by spectrophotometry (Kasuaki model IL-226-NM) as described in the Standard Methods for the Examination of Water and Wastewater (APHA, 2017; EPA, 1971). These analyses were also carried out at the Limnology and Microbiology Laboratory of Federal University of Rondônia in Ji-Paraná.

With regard to trace elements, the concentrations of Al, As, Cd, Cr, Mn, Pb, Zn, Co, Cu, Ag, Mo, Sn, Ni, barium (Ba), beryllium (Be), antimony (Sb), strontium (Sr), and vanadium (V) were analyzed in the total fractions.

From each sample we removed 15 mL of raw water, which was placed in a Falcon tube and acidified with 100 μL of nitric acid (1% v/v HNO_3 p.a) in order to maintain its preservation, keeping the pH below 2. The tubes were then stored in thermal boxes with ice and transported to the Environmental Biogeochemistry Laboratory of Federal University of Rondônia in Porto Velho, samples were filtered through a syringe filter (hydrophilic PTFE, 25 mm, 0.45 μm), where they were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES Optima 8300/Perkim Elmer), with S10 autosampler. Using Perkin Elmer WinLab 32 software for ICP version 5.5.0.0174. The standard solution used to prepare the calibration curves for all elements was Instrument Calibration Standard 2 from Perkin Elmer. In this standard solution, all trace elements are at a concentration of 100 mg L^{-1}. The calibration curve was obtained at the following concentrations: 0, 20, 40, 80, 200, 400, 800, 1200 μg L^{-1}, the calibration curves for all elements had the same range and the same concentrations at the points. Two blank controls were used to control the analytical quality of the results. The limits of detection-LOD, limit of quantification-LOQ and correlation coefficient are presented in Table S1, the calculation for the LOD was obtained using equation S1 and the LOQ using equation S2 in the supplementary material. The nebulizer used was the concentric model (meinhard type) and the nebulization chamber had a cyclone effect. According to Costa Jr., (2017) the following operating conditions were adopted for the equipment, as shown in table S3 in the supplementary material.

Risk assessment

We evaluated the risk by calculating the Hazard index *(HI)*, according to the formula described by Evans et al. (2015):

$$HI = \sum_{i=1}^{n} \frac{EL_i}{AL_i} \quad (1)$$

where *EL* is the exposure level, *AL* is the acceptable level, and n is the number of chemical substances in the mixture. We also calculated a hazard quotient *(HQ)* for each chemical substance, by dividing *EL* by *AL*. And the *HQs* are summed to give the hazard index-*HI*. The $HI > 1$ indicates that the total exposure exceeds the level considered acceptable.

For the points where the concentration of the contaminant was below the limit of detection, we attributed a value of zero.

Statistical analysis

Since the assumption of normal data distribution was not was not satisfied, we used nonparametric tests for the statistical analysis of the hazard index (HI). In order to identify significant relationships between the hydrological periods analyzed, the paired Wilcoxon test was applied, which checks whether two means differ significantly, where a p-value < 0.05 indicates a significant difference between two means.

To identify significant relationships between municipalities, we employed the unpaired Kruskal–Wallis test. This test checks whether three or more populations have distributions that differ significantly from each other, where a p-value < 0.05 indicates that not all populations have equal distributions.

Results

Nitrite, nitrate and trace elements

Table 1 summarizes the main results (minimum–maximum, mean and standard deviation) found in each municipality in the representative period of low water (LW) and the transition period between high water and low water (HW-LW) for Presidente Médici.

In the municipality of Jaru (Table 1), during the LW period, Al concentrations were found to be above the limit recommended by the corresponding Brazilian and WHO standards, with a maximum value of 5,425 μg L^{-1} and with 100% of the wells above the maximum permitted value -MPV (200 μg L^{-1}) of both standards, Fe was found with a maximum of 2,450 μg L^{-1} and 68.75% of wells above the MPV according to Brazilian legislation (300 μg L^{-1}), Mn with 56.25% above the MPV (100 μg L^{-1}) of

Table 1 Minimum and maximum values, mean and standard deviation of concentrations of trace elements, nitrite and nitrate (μg L^{-1}) found in each municipality, in the period of low water and transition between high and low water

Parameters	Jaru LW	OPO LW	BDA LW	BNZ LW	PM HW/LW
Ag	–	< LOD	–	–	< LOD
Al	2,574–5,425 3,390/606	35.4–10,310 1,158/3,216	16.2–506 127/121	18.6–6,602 597/1,730	< LOD-2,236 334/692
As	–	< LOD-227 23.0/72	–	–	< LOD-26.3 3.43/8.1
Ba	11.6–421 111/105	52.6–1,476 372/523	26.9–1,131 192/283	8.68–194 51.1/55	36.3–873 229/254
Be	–	< LOD-4.30 0.49/1.4	–	–	< LOD-0.86 0.13/0.28
Cd	< LOD-0.80 0.08/0.24	–	–	–	–
Cr	6.14–18.4 10.6/2.8	< LOD-1.13 0.15/0.35	–	–	–
Cu	< LOD-16.0 1.76/4.2	0.91–38.7 7.10/12	< LOD-96.8 8.09/25	< LOD-32.8 4.51/9.6	0.64–3.83 1.79/0.93
Fe	122–2,450 705/612	–	< LOD-387 66.3/97	< LOD-119 48.4/40	–
Mn	17.9–427 150/110	< LOD-2,673 360/825	7.40–209 65.4/54	5.20–205 45.4/54	< LOD-1,963 258/602
Mo	–	< LOD	–	–	< LOD
Ni	1.09–3.12 1.85/0.56	4.12–7.79 5.05/1.1	< LOD-2.06 0.19/0.53	< LOD-0.92 0.11/0.26	3.05–5.48 4.05/0.81
Pb	< LOD-16.2 2.52/4.2	< LOD-52.2 5.21/ 16	< LOD-6.90 0.64/1.8	< LOD-5.07 1.04/1.8	< LOD-32.0 3.20/10
Se	–	–	–	–	–
V	8.50–11.6 9.62/0.85	< LOD-1.45 0.53/0.42	8.00–11.5 9.02/0.92	7.64–8.98 8.50/0.38	–
Zn	4,514–9,773 6,244/1,096	276–507 364/70	31.9–285 83.6/65	< 14.3–875 159/227	< 18.0–49.7 30.9/8.4
NO_2	< LOD-126 15.4/31	< LOD-45.6 7.79/10	< LOD-11.5 1.10/3.2	< LOD-13.6 1.42/3.9	< LOD-79.8 13.5/23
NO_3	1,659–6,163 3,630/1,659	< LOD-5,125 1,737/1,380	< LOD-1,693 5,580/5,074	< LOD-26,807 9,457/8,288	< LOD-48,450 12,108/13,260

Brazilian legislation (maximum of 427 μg L^{-1}), and Pb level greater than the MPV (10 μg L^{-1}) of both standards in only one well (maximum 16.2 μg L^{-1}), while in 93.7% of the wells, Zn was above the MPV (5,000 μg L^{-1}), and the maximum value found was 9,773 μg L^{-1} (Table S1). The WHO does not establish a reference value for Fe and Zn, whereas the MPV for Mn is more restrictive (80 μg L^{-1}) than in Brazilian legislation.

In the municipality of Ouro Preto do Oeste (Table 1), 20 wells were sampled, with trace elements found in 10 of them. During low water, only one point presented concentrations above the MPV for As (227 μg L^{-1}), MPV = 10 μg L^{-1}, and Pb (52.2 μg L^{-1}) MPV = 10 μg L^{-1} according to both Brazilian and WHO standards (Table S1). In 30% of the wells, Al concentrations were greater than the MPV (200 μg L^{-1}) in both standards, with a maximum of 10,310 μg L^{-1}, 20% for Ba (MPV = 700 μg L^{-1}), with maximum of 1,476 μg L^{-1}, and 40% for Mn, MPV = 100 μg L^{-1} and maximum concentration of 2,673 μg L^{-1}, approximately 26.7 × greater than the MPV according to Brazilian standards. For the WHO standard in relation to Mn, the MPV is more restrictive (80 μg L^{-1}) than in Brazilian legislation, and for Ba the MPV is 1,300 μg L^{-1} (Table S1).

In the municipality of Ji-Paraná, in the area of Stream Dois de Abril (Table 1), the elements Ba, Fe, and NO_3 were above the MPV (700 μg L^{-1}, 300 μg L^{-1}, 10,000 μg L^{-1}) in a single point, with values of 1,131 μg L^{-1}, 387 μg L^{-1} and 21,693 μg L^{-1} respectively. In 13.3% of the points, Al was above the MPV and in 20% manganese was greater than the MPV (200 μg L^{-1} and 100 μg L^{-1}) according to PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021) (Table S1). The maximum values found for both were 506 μg L^{-1} and 209 μg L^{-1}, while according to the WHO standard, the values are 200 μg L^{-1} and 80 μg L^{-1}, respectively, while for nitrate the MPV is 50,000 μg L^{-1}.

In Stream Nazaré (Table 1), the elements with concentrations above the MPV of the standards in the low-water period were: Al, with maximum value of 6,602 μg L^{-1} and 33.3% of the wellsbeing greater than the MPV (200 μg L^{-1}) according to both standards; NO_3, for which 40% of the wells had water with concentration above the MPV (10,000 μg L^{-1}) according to Brazilian legislation (Table S1), with maximum value of 26,807 μg L^{-1}; and Mn, for which one point had a reading of 205 μg L^{-1}, about 2 × MPV (100 μg L^{-1}).

In the municipality of Presidente Médici in the transition period between high and low water (HW-LW) (Table 1), the levels of As, Ba and Pb were greater than the MPV at 1 collection point, with values of 26.3 μg L^{-1}, 873 μg L^{-1} and 32.0 μg L^{-1}, respectively. In 27.3% of the collection points, the concentrations of Al and Mn were above the MPV, with maximum values of 2,236 μg L^{-1} and 1,963 μg L^{-1}. The concentrations of nitrate were also above the MPV in 45.4% of the wells, with the highest value being 48,450 μg L^{-1}.

Table 2 reports the summarized data on the concentrations found for each element (minimum–maximum, mean and standard deviation) in the high water period (HW) and transition from high to low water (HW-LW) in the area corresponding to Stream Nazaré in the municipality of Ji-Paraná.

In the municipality of Jaru (Table 2), the level of Al was above the MPV (200 μg L^{-1}) in only one well, with value of 1,420 μg L^{-1}. For Mn, two wells (12.5%) were above the maximum value of 465 μg L^{-1}, finally, for nitrate, the level in six of the wells (31.25%) extrapolated the MPV (10,000 μg L^{-1}) set by Brazilian legislation, and the maximum found was 16,436 μg L^{-1}.

In the municipality of Ouro Preto do Oeste during the high water period, trace element concentrations were only measured in 10 wells, for Al and Zn, All of those wells had concentrations of the two elements greater than the MPV considered safe for human consumption. The maximum values were 10,080 μg L^{-1} for Al and 6,472 μg L^{-1} for Zn. The elements Ba, Mn and Pb had maximum values of 1,150 μg L^{-1}, 1,993 μg L^{-1} and 97 μg L^{-1} respectively, and were above the MPV in two wells (20%), while concentrations of As above the MPV were found in one well (172 μg L^{-1}) (Table 2).

In the area of Stream Dois de Abril (Table 2), the elements Al, Fe and Mn were higher than permissible (200 μg L^{-1}, 300 μg L^{-1} and 100 μg L^{-1}) according to PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021), according to the WHO, the values of Al and Mn are 200 μg L^{-1} and 80 μg L^{-1}, respectively (Table S1), in 20% of the wells, with respective maximum levels of 681 μg L^{-1}, 3,492 μg L^{-1} and 195 μg L^{-1}. In turn, NO_3 was above the MPV in 26.6% of the wells, with maximum of 21,327 μg L^{-1},

Table 2 Minimum, maximum, mean and standard deviation of concentrations of the trace elements, nitrite and nitrated, in the high-water period (HW) and transition from high to low water period (HW-LW), measured in µg L^{-1}

Parameters	Jaru HW	OPO HW	BDA HW	BNZ HW-LW	PM HW
Ag	–	< LOD-35.6 3.70/11	–	–	–
Al	24.0–1,420 154/341	2,270–10,080 3,295/2,400	< LOD-681 163/178	18.9–9,750 1,314/3,070	–
As	–	< LOD-172 18.1/54	< LOD-2.56 0.78/1.0	< LOD-1.01 0.105/0.29	–
Ba	4.56–483 118/130	58.3–1,150 347/385	8.50–163 75.7/48	9.00–273 61.4/71	–
Be	–	–	–	–	–
Cd	–	0.13–0.24 0.17/0.030	0.33–0.62 0.45/0.10	–	–
Cr	< LOD-5.72 0.35/1.4	7.26–9.06 8.18/0.50	< LOD-2.38 0.22/0.65	–	–
Cu	< LOD-11.3 1.06/3.1	9.71–36.0 13.5/8.4	< LOD-4.48 0.55/1.4	–	–
Fe	< LOD-201 23.8/50	–	< LOD-3,492 538/1,036	< LOD-130 58.9/30	–
Mn	1.02–465 71.3/111	11.0–1,993 260/616	4.72–195 69.6/50	2.91–335 55.5/89	–
Mo	–	< LOD	–	–	–
Ni	< LOD-1.66 0.49/0.53	< LOD-24.8 2.65/7.8	< LOD-19.0 2.52/5.1	–	–
Pb	< LOD-2.33 0.28/0.64	1.34–97.0 16.9/32	< LOD-13.2 2.80/ 4.3	< LOD-42.6 3.13/11	–
Se	–	< LOD	–	–	–
V	7.98–10.7 8.71/0.65	–	–	8.13–9.33 8.84/0.40	–
Zn	26.4–418 170/89	5,329–6,472 5,927/298	< LOD-214 49.2/61	18.2–52.4 37.5/11	–
NO_2	< LOD-37.2 3.58/9.4	–	< LOD-93.2 12.8/23	< LOD-9.46 1.43/3.1	6.80–16.4 9.74/3.8
NO_3	3.0–16,436 7,812/4,560	< LOD-5,803 1,744/1,706	< LOD-21,327 6,784/5,824	< LOD-34,640 10,815/9,687	2,018–27,540 16,508/8,765

while Pb was higher than the MPV in only one well, with concentration of 13.2 µg L^{-1}.

The values of Al measured in the wells in the area of Stream Nazaré (Table 2) in the period of transition from high to low water (HW-LW) were above the MPV in 33.3% of the wells, with maximum of 9,750 µg L^{-1}, while for Mn, two wells (20%) were above the MPV, with maximum of 335 µg L^{-1}, and for Pb, one well had concentration higher than the MPV, at 42.6 µg L^{-1}. The concentrations of nitrate were greater than the MPV in 46.6% of the wells (seven wells), with maximum value of 34,640 µg L^{-1}.

In the municipality of Presidente Médici in the HW period (Table 2), we only analyzed NO_2 and NO_3. The nitrite concentrations in the 11 wells evaluated were all below the MPV (1,000 µg L^{-1}). With regard to nitrate in the same period, 72.7% of the wells were above the MPV established by the Brazilian standard (10,000 µg L^{-1}) (Table S1), with a maximum level of 27,540 µg L^{-1}.

Assessment of risk to human health

The hazard quotient *(HQ)* was calculated for each chemical substance, by dividing *EL* is the exposure level (Table 1 and 2), *AL* is the acceptable level (Table S1, supplementary material).

In the municipality of Jaru in the LW period, the hazard quotient (HQ) was greater than 1 for Al in 100% of the wells evaluated, Fe in 68.7% of the wells (11 wells), Mn in 56.3% (9 wells), Pb in one well (6.25%), and for Zn in 15 wells (93.7%). The HQ was greater than 1 in the HW period for Al in one well (6.25%), Mn in two wells (12.5%), and NO_3 in five wells (31.3%).

The hazard index (HI) obtained from the sum of the HQ values found for each element, as shown in Fig. 2a, exceeded the value of 1 in 100% of the wells in the LW period, varying from 15.6 in well 13 to 32.9 in well 14.

In the HW period, 93.8% of the wells presented HI above 1 (Fig. 2b). The minimum value found was 0.70 in well 14 (the only point that did not present risk), and the maximum was 10.7 in well 13.

In the municipality of Ouro Preto do Oeste in the LW period, the HQ was above 1 for Al in three wells (15%), Ba in two wells (10%), Mn in four wells (20%) and As and Pb in one well each (5%). In the HW period, 10 wells (50%) showed high HQ for Al and Zn, one well for As, while for the parameters Ba, Mn and Pb, two wells (10%) had HQ > 1.

The HI for the low water period (Fig. 3a) was greater than 1 in seven wells (35%). The minimum value of the index was 0.16 (P6) and the maximum was 110 (P9).

In the HW period (Fig. 3b), 10 wells (50%) had HI above 1, ranging from 0 in (P10, P11) to 96.4 in (P9). The high HI found in well 9 in both periods was due to the presence of elements such as Al, As, Ba, Mn, Pb, Zn in that well's water.

In the municipality of Ji-Paraná, in the area corresponding to Stream Dois de Abril, the HQ was higher than 1 for Al, Fe and Mn in the HW period in three wells (20%), while nitrate presented HQ above 1 in four wells (26.6%), and Pb in one well. In the LW period, Mn presented HQ greater than 1 in three wells (20%), Al in two wells (13.3%), and Fe, Ba and NO_3 in one well each.

The calculation of the HI of the wells located in the Stream Dois de Abril area (Fig. 4a) showed that in the HW period, 14 wells (93.3%) were above 1. Of the 15 wells evaluated, only well 9 did not exceed the established limit (1), with vales ranging from 0.24 (P9) to 14.5 (P4).

According to the results obtained for the Stream Nazaré area, the assessment of HQ indicated a risk of Al concentration in five wells (33.3%) in the HW-LW and LW periods. In turn, the Mn concentration showed HQ above 1 in two wells (13.3%) in the HW-LW period, and one well during the LW period. Lead concentration had HQ greater than 1 only in HW-LW in one well. The results obtained for nitrate showed HQ above 1 in the HW-LW period in seven wells (46.6%), while in the LW period, six wells (40%) had HQ above 1.

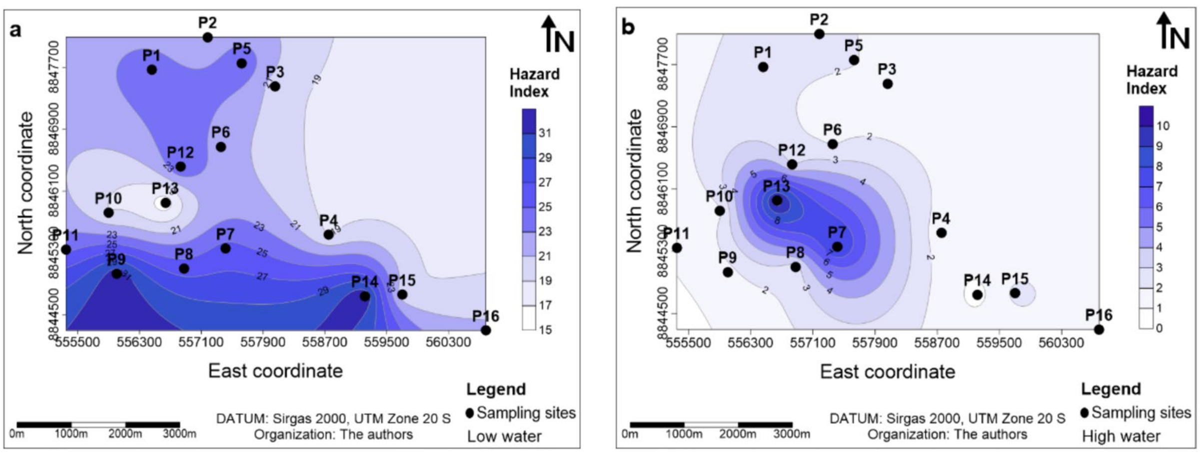

Fig. 2 Risk assessment cartogram in points sampled in the municipality of Jaru in the hydrological periods: **a** Low water-LW and; **b**) high water-HW

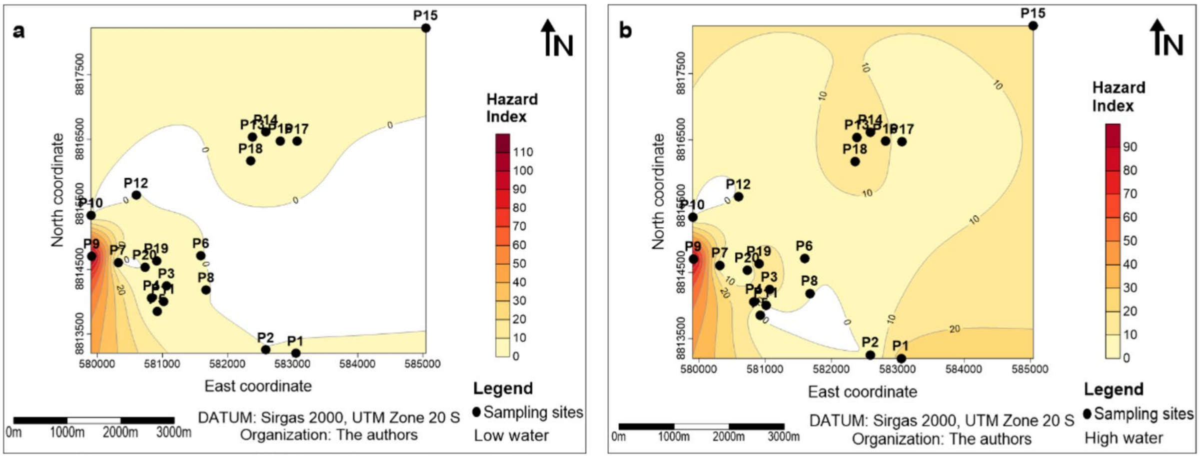

Fig. 3 Risk assessment cartogram in points sampled in the municipality of Ouro Preto do Oeste in the hydrological periods: **a** Low water-LW; and **b**) high water-HW

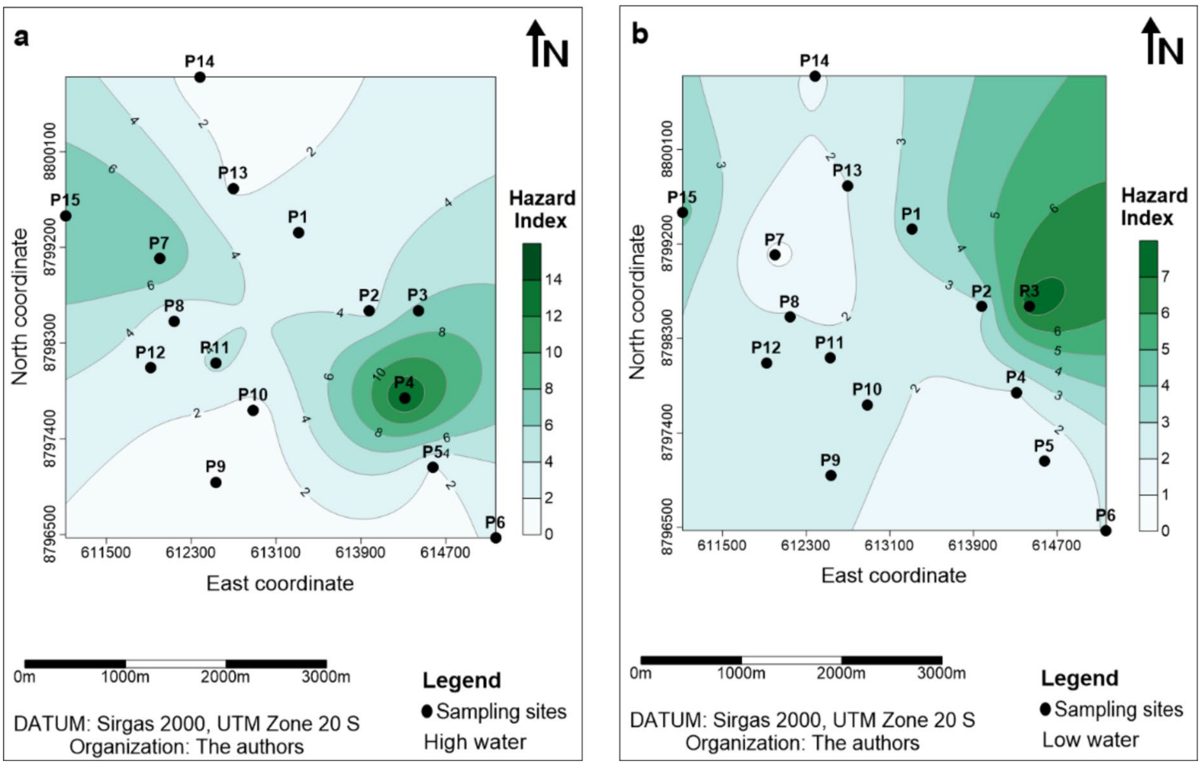

Fig. 4 Risk assessment cartogram in points sampled in the Stream Dois de Abril basin in the municipality of Ji-Paraná in the hydrological periods: **a** High water-HW; and **b**) low water-LW

In the HW-LW transition period (Fig. 5a), 12 wells (80%) presented HI above 1, the minimum value was 0.72, which occurred in wells (P5 and P6), and the maximum value was 58.4, in P15.

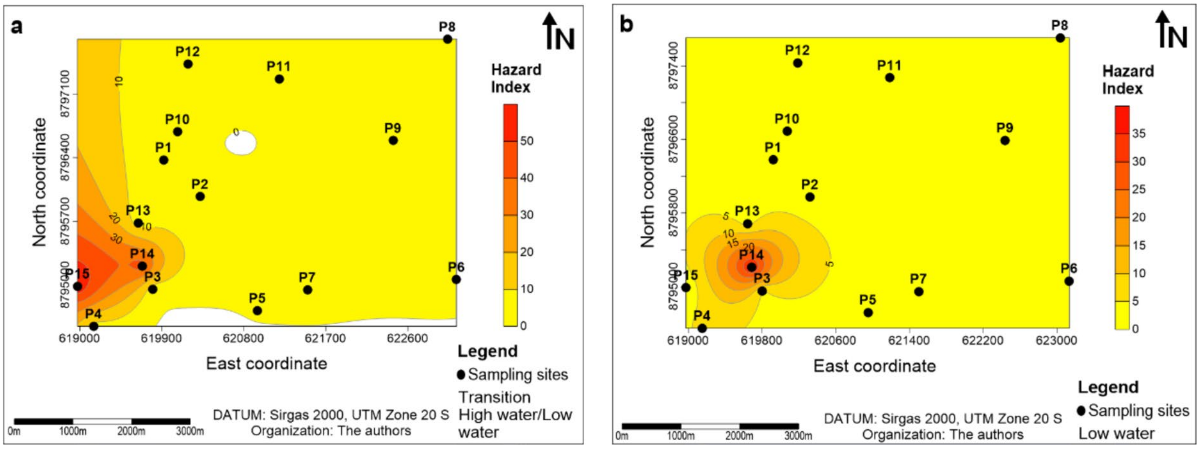

Fig. 5 Risk assessment cartogram in points sampled in the Stream Nazaré area, in the municipality of Ji-Paraná in the hydrological periods: **a**) Transition from high to low water -HW-LW; and **b**) Low water-LW

In the LW period (Fig. 5b), again 80% of the wells presented HI above 1, and the values were between 0.88 (P7) and 37.2 (P14).

In the municipality of Presidente Médici, the results of the hazard quotient (HQ) analysis in the HW period were above 1 for NO_3 in eight wells (72.7%). In the HW-LW transition period, the HQ values for Al and Mn were above the limit in three wells (27.2%). The elements As, Ba and Pb presented HQ above 1 in one well, while nitrate had HQ above 1 in five wells (45.5%).

The HI value was above 1 in the HW period (Fig. 6a) in eight wells (72.7%). All told, the values were between 0.21 (P2) and 2.76 (P6). It is noteworthy that in the HW period, the hazard index was measured only regarding the NO_2 and NO_3 concentrations of the wells.

In the HW-LW period (Fig. 6b), the HI exceeded 1 in 8 wells (72,7%), ranging from 0.32 (P10) to 43.0 (P6).

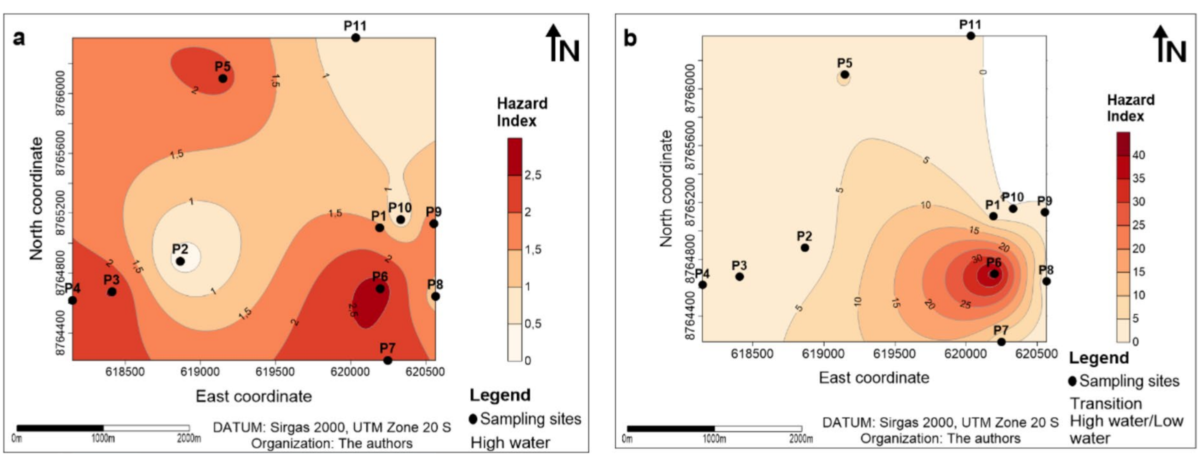

Fig. 6 Risk assessment cartogram in points sampled in the municipality of Presidente Médici in the hydrological periods: **a**) High water-HW; and **b**) transition from high to low water –HW-LW

Discussion

Nitrite and nitrate contamination

No nitrite concentrations were observed above the MPV (1,000 μg L^{-1}) according to PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021) and the standard of the WHO (2011) (3,000 μg L^{-1}) in any wells in any of the municipalities studied. The highest concentration occurred in well 5 in the municipality of Jaru during LW (126 μg L^{-1}).

Regarding nitrate, the percentage of wells above the MPV in the legislation during the high water period was higher than in the other periods evaluated, demonstrating that this parameter is influenced by local rainfall variations. This situation occurs due to the overflow of inadequate sewage systems used as a destination for domestic sewage, the main source of nitrate contamination in urban areas.

As for nitrate, concentrations above the MPV (10,000 μg L^{-1}) of PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021) were found in Jaru (HW-31.5%), in the wells in the Stream Dois de Abril area (HW-26.6%, LW-6.6%), Stream Nazaré area (HW-LW-46.6%, LW-40%), and Presidente Médici (HW-72.7%, HW-LW-45.4%). The highest concentration was 48,450 μg L^{-1} in Presidente Médici, while in Ouro Preto do Oeste, no concentrations higher than recommended by the Brazilian standard were found (Table 2). The WHO MPV standard (2011) for nitrate is 50,000 μg L^{-1}.

In a study carried out by Silva et al. (2009) in the urban area of Ji-Paraná (Table 3), a maximum nitrate concentration of 239 mg L^{-1} was found, while Leite et al. (2011), studying rural wells, found a maximum

Table 3 Minimum, maximum and mean values of the concentration of nitrate (mg L^{-1}) found in Rondônia, in the Amazon region and in other studies

References	Site	Period	Min–Max	Mean
Present study	Jaru	HW	0.003–16.4	7.81
		LW	1.65–6.16	3.63
	Ouro Preto do Oeste	HW	Nd-5.80	1.74
		LW	Nd-5.12	1.73
	Ji-Paraná BDA	HW	Nd-21.3	6.78
		LW	Nd-21.7	5.58
	Ji-Paraná BNZ	HW/LW	Nd-34.6	10.8
		LW	Nd-26.8	9.45
	Presidente Médici	HW	2.0–27.5	16.5
		HW/LW	Nd-48.4	12.1
Silva et al. (2009)	Ji-Paraná (RO)	–	Nd-239	–
Leite et al. (2011)	Ji-Paraná (RO)	Rainy season	0.04–11.5	3.62
		Dry season	0.20–25.8	4.54
Cremonese (2014)	Ji-Paraná (RO)	Rainy season	2.17–21.0	11.1
		Dry season	0.44–23.2	11.7
Nascimento (2022)	Ji-Paraná (RO)	Dry season	0.10–26.8	9.00
		Rainy season	1.0–27.0	9.40
Oliveira et al. (2015)	Vilhena (RO)	Dry season	0.06–13.9	3.48
		Rainy season	0.10–25.8	10.9
Meschede et al. (2018)	Santarém (PA)	Dry season	5.70–6.00	5.80
		Rainy season	7.10–8.70	8.00
Santos et al., 2024	Parintins (AM)	flood	1.10–15.1	6.36
		Ebb	1.10–20.9	8.14
Sharma et al. (2021)	Iha do rio Majuli (Índia)	–	26.1–74.1	39.6
Chen et al. (2021)	Província de Shanxi (China)	–	1.00–43.6	12.9
Bazeli et al. (2020)	Condado de Khaf (Irã)	–	1.54–83.0	16.7
Golak et al. (2022)	Kazerun também ((Irã)	–	3.70–25.5	13.5

value of 25.8 mg L^{-1}, Nascimento (2022) found a maximum value of 27 mg L^{-1}, and Cremonese (2014) found a maximum value of 23.2 mg L^{-1}. Oliveira et al. (2015), studying the municipality of Vilhena (Rondônia) found a maximum of 25.8 mg $L^{-1.}$ A nearby value was found by Santos et al. (2024), of 20.9 mg L^{-1}, in Parintins (Amazonas in the North Region). In Santarém (Pará), also in Brazil's North region, Meschede et al. (2018) found a maximum value of 8.70 mg L^{-1}. The authors attributed these results to the lack of an adequate sewage system, inadequate well installations, and the influence of pastures.

Through endogenous nitrosation, nitrate is a precursor in the formation of N-nitroso compounds (NOC), most of which are carcinogens and teratogens (Ward et al., 2018). The development of cancer after ingestion of nitrate is a complex process. In the body, nitrate can be reduced to nitrite and subsequently metabolized to produce nitrosating agents, capable of reacting with dietary amines to form such compounds (Temkin et al., 2019), resulting in adverse effects on human health (Ward et al., 2018).

Individual nitrate exposure was calculated for 2.7 million adults based on data from analysis of drinking water quality in public water supply systems and private wells between 1978 and 2011, along with data from health records in Denmark. The data revealed a high risk of colorectal cancer associated with nitrate concentrations above 3.87 mg L^{-1} (Schullehner et al., 2018). Espejo-Herrera et al. (2016a) carried out a case study in Spain and Italy during 2008–2013, and found a positive association between the risk of colorectal cancer and nitrate ingested via water (surface/underground), mainly among subgroups with other risk factors. The associations were higher among men with high red meat consumption. In another study, between 2008 and 2013 in eight Spanish provinces, nitrate ingested in drinking water (surface/underground) was found to be a risk factor for breast cancer. The researchers observed that breast cancer was more common among postmenopausal women with higher levels of nitrate intake (>6 mg/day), associated with greater consumption of red meat (>20 g/day) (Espejo-Herrera et al., 2016b).

Concentrations above 2.5 mg L^{-1} of nitrate in drinking water were associated with an increased risk of thyroid cancer and a higher prevalence of hypothyroidism in elderly women in Iowa, United States (Ward et al., 2010). Temkin et al. (2019), evaluating data from all 50 US states, linked exposure to nitrate in drinking water to cases of low birth weight, premature birth and neural tube defects, in addition to a higher risk of cancer (colorectal, ovarian, thyroid, renal and bladder). The authors stated that existing levels of nitrate in drinking water in the United States can generate negative impacts on health and the economy. Approximately 81 million people are exposed to concentrations ≥ 1 mg L^{-1}, while 6 million people receive water with average concentrations ≥ 5 mg L^{-1}. Considering medical costs alone, this cancer burden corresponds to an annual economic cost of \$250 million to \$1.5 billion, along with a potential impact of \$1.3 to \$6.5 billion due to lost productivity (Temkin et al., 2019).

In the studies cited (Temkin et al., 2019; Ward et al., 2018; Schullehner et al., 2018; Espejo-Herrera et al., 2016a, 2016b; Ward et al., 2010; Ward et al., 2005), the adverse health effects were observed at nitrate concentrations lower than the Al threshold concentrations established by the respective countries for drinking water. Another worrying factor was that private wells generally had higher nitrate levels than wells used for public supply. Hence, these wells are unregulated, infrequently monitored, often shallower and constructed outside of the relevant standards (Ward et al., 2007; Ward et al., 2005). Profiles such as those are found in very small communities, which are often unserved by sanitation services and obtain most of their domestic supply from groundwater (Temkin et al., 2019). This situation is similar to our findings.

According to the Brazilian Potability Edict (PRC 5/2017, as amended by GM/MS Edict 888/2021), all water for human consumption obtained from an individual alternative source is subject to monitoring, through the National Program for Quality Surveillance of Water for Human Consumption (Vigiágua). However, because this program is based on sampling, many wells end up not being monitored.

According to Temkin et al. (2019), exposure to nitrate in drinking water in the United States may be responsible for 1–8% of total colorectal cancer cases, which translates into 1,233 to 10,379 cases annually. Of these cases, 12–24% are due to nitrate exposure in water from private wells, especially for people whose well water contains nitrate concentrations ≥ 5 mg L^{-1}. The authors stated that the epidemiological evidence linking nitrate in drinking water with harm to health casts doubt on whether the nitrate limit of 10 mg L^{-1} recommended by the WHO and adopted by many countries adequately protects the general population against adverse health outcomes.

Contamination by trace elements

Among the trace elements studied, the only one with concentrations higher than the Brazilian and WHO standards was aluminum, found in Jaru (LW-100%, HW-6.25%), Ouro Preto do Oeste (LW-30%, HW-100%), Stream Dois de Abril (LW-13.3%, HW-20%), Stream Nazaré (LW-33.3%, HW-LW-33.3%) and Presidente Médici (HW-LW-27.3%). The maximum value of aluminum in the analyzed samples was 10,310 µg L^{-1}, approximately 51 × higher than the MPV (200 µg L^{-1}), found in the municipality of Ouro Preto do Oeste. The percentage of wells with aluminum concentrations higher than the MPV was higher in the AA period in the areas of Ouro Preto do Oeste and in the Stream Dois de Abril, in the municipality of Jaru. The rainy season caused a reduction in the presence of the contaminant, which may be the result of the dilution of the concentration of aluminum present in the water due to the rise in the water table.

The wide distribution of aluminum in the region can be explained by soil formation. In the state of Rondônia (Western Brazilian Amazon), Oxisols (58%), Argisols (11%), Neosols (11%), Cambisols (10%) and Gleisols (9%) predominate, Most of these soils have a pH lower than 5.5, which is considered low. High levels of aluminum can cause toxicity to roots and nutrient uptake, thus impairing plant growth (Schlindwein et al., 2012).

Human exposure to aluminum occurs mainly through food and drinking water. Most cases of aluminum toxicity in humans are observed in patients with chronic kidney failure. It can also affect the lungs, bones and central nervous system, causing developmental problems (Klaassen & Watkins, 2012). Some research suggests a possible association between Alzheimer's disease and aluminum concentrations in water, (Mirza et al., 2017). Al can also affect immune functions in patients suffering from aplastic anemia (Zuo et al., 2021).

Since the predominant soils in Rondônia are Lattosols and Argisols, classified as acidic, the presence of iron and manganese, besides aluminum, is common (Barbosa et al., 2011; Shinzado et al., 2010). In the present study, we found iron in concentrations greater than the MPV established by the previously mentioned Brazilian and WHO standard (300 µg L^{-1}) in two municipalities, Jaru during the LW period in 68.75% of the wells (maximum 2,450 µg L^{-1} in P9), and in the municipality of Ji-Paraná, in the igarapé Dois de Abril area (HW-20%, LW-6.6%) (maximum 3,492 µg L^{-1} in P4). The WHO does not establish a reference value for Fe.

Iron is an essential metal for erythropoiesis (production of red blood cells) and a key component of hemoglobin, myoglobin, heme group enzymes, metalloflavoproteins and mitochondrial enzymes (Klaassen & Watkins, 2012). Toxicological investigation is important both to detect iron deficiency and acute exposure, which can be toxic to the central nervous system, digestive tract, lungs, liver and blood (Klaassen & Watkins, 2012).

Manganese is an essential element for living beings, albeit in small concentrations (Esteves, 2011). However, it can cause toxicity to the central nervous system and lungs (Klaassen & Watkins, 2012). Levels in freshwater vary in the range 1–200 µg.L^{-1}. Higher levels are generally associated with groundwater, lakes and reservoirs under acidic or reducing conditions, or in aerobic water with industrial pollution (WHO, 2017). The MPV established in PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021) is 100 µg L^{-1}. The WHO (2017) is more restrictive, establishing a limit of 80 µg L^{-1}. Manganese, like aluminum, was present in all municipalities and areas studied in concentrations above that permitted for drinking water: Jaru (LW-56.25%, HW-12.5%); Ouro Preto do Oeste (LW-40%, HW-20%); Stream Dois de Abril 20% in both periods; Stream Nazaré (LW-6.6%, HW-LW, 20%); and Presidente Médici (HW-LW, 27.3%). The highest level found was 2,673 µg L^{-1} in Ouro Preto do Oeste (P9). Manganese concentrations showed a higher percentage of wells above the MPV in the AB period for Jaru and Ouro Preto do Oeste, with a reduction in contaminants occurring in these areas during the rainy season, consequently increasing the water level in the well.

We found As concentrations above the Brazilian and WHO MPV standards (10 µg L^{-1}) in two wells (2.60%), P6 in the municipality of Presidente Medici

(26.3 μg L^{-1}), and P9 in Ouro Preto do Oeste (227 μg L^{-1}), around 22.7 × the MPV.

Meyer et al. (2017) reported the presence of geogenic contaminants in the groundwater of the Western Peruvian Amazon. According to the authors, most of the wells studied presented high concentrations of aluminum, arsenic or manganese, at levels harmful to human health. Aquifers with anoxic groundwater, with almost neutral pH, contained high concentrations of arsenic (up to 700 μg.L^{-1}) and manganese (up to 4 mg L^{-1}). Around the city of Iquitos, acidic groundwater ($4.2 \leq pH \leq 5.5$) was found in unconfined aquifers with aluminum concentrations of up to 3.3 mg L^{-1} (Meyer et al., 2017).

In the present study, the average pH values were close to those reported by Meyer et al. (2017). In Jaru, average pH values were found for the LW periods of 6.07 and HW of 5.78. In Ouro Preto do Oeste, the average pH during LW was 5.85 while in HW it was 5.41. In Ji-Paraná, wells located in the Stream Dois de Abril areahad average pH of 5.18 in HW and 4.60 in LW, while in Stream Nazaré the average pH values were 5.2 in HW-LW and 5.4 in LW. Finally, in Presidente Médici, the average during the HW period was 5.64 while in HW-LW it was 4.94.

In another study, Meyer et al. (2023) also found contamination of natural origin by arsenic (maximum value 430 μg L^{-1}) and manganese (6.6 mg L^{-1}) in groundwater in the Amazonian Plain of Peru and Brazil. The maximum concentrations found in the present study of 227 μg L^{-1} for As and 2,673 μg L^{-1} for Mn (both in P9 in Ouro Preto do Oeste), are below the concentrations found by Meyer et al. (2023) in the Amazonian Region of Peru and Brazil. The maximum concentration of aluminum (10,310 μg L^{-1} in well 9 in Ouro Preto do Oeste) were 3 × higher (3.3 mg L^{-1}) than those reported by Meyer et al. (2017).

According to Berg et al. (2016), approximately one-third of the world's population depends on groundwater, and it is estimated that 10% of wells are contaminated with natural geogenic contaminants such as arsenic (As) and/or fluoride. In the human body, ingestion of high doses (70 to 180 mg) of inorganic arsenic can be fatal. Symptoms of acute poisoning include fever, anorexia, hepatomegaly, melanosis and cardiac arrhythmia, along with fatal heart failure. Ingestion can damage the digestive tract, while sensory loss in the peripheral nervous system is the most common neurological effect (Klaassen & Watkins, 2012).

Arsenic contamination of water threatens the health of millions of people around the world. Numerous cases of skin lesions were correlated with high arsenic content in groundwater (greater than the MPV indicated by the WHO of 50 μgL^{-1}) in West Bengal (India) and in Bangladesh (Chakraborti et al., 2003; Chowdhury et al., 2000). Of 10,991 water samples collected in Bangladesh and 58,166 in West Bengal, 59% and 34% respectively contained arsenic levels above 50 μgL^{-1}. According to the authors, water samples containing concentrations > 1,000 μgL^{-1} of As are more abundant in Bangladesh (2.1%) than in West Bengal (0.06%) (Chowdhury et al., 2000).

Other regions with high concentrations of As in drinking water include Argentina, Cambodia, Chile, China, Ghana, Hungary, India, Inner Mongolia, Mexico, Nepal, New Zealand, Philippines, Romania, Slovakia, Taiwan and Vietnam (McCarty et al., 2011).

In a study conducted in Romania, As concentrations were measured in twenty water samples from public and private wells in thirteen villages in the Timis-Bega area. As concentrations were in the range of 0.1–168 μg L^{-1}, thus exceeding the reference value (10 μg L^{-1}) in 75% of the samples analyzed. Hazard indices for As exposure were calculated, and HI values > 1 were found in most villages, indicating a risk to the health of the population (Senila et al., 2017).

Arsenic is a human carcinogen, associated with skin cancer, lung cancer, bladder cancer, and possibly kidney, liver and prostate cancer (Klaassen & Watkins, 2012). Signs of chronic arsenicism, including dermal lesions, peripheral neuropathy, skin cancer, bladder and lung cancer, and peripheral vascular disease, have been observed in people ingesting arsenic from contaminated drinking water (WHO, 2017). Baris et al. (2016) studied groundwater in the New England region (United States) and correlated arsenic concentrations (< 3.8–124.8 mg L^{-1} <) from shallow wells with an increased risk of bladder cancer.

Lead was found above the MPV (10 μg L^{-1}) of the Brazilian and WHO standards at a lower frequency, with only one well in the municipality of Jaru (P9/16.2 μg L^{-1}); two in Ouro Preto do Oeste, P9 (LW/52.2 μg L^{-1}, HW/49.9 μg L^{-1})

and P1 (97 μg L^{-1}); one well in Stream Nazaré (P15/42.6 μg L^{-1}); one well in Stream Dois de Abril (P12/13.22 μg L^{-1}); and one well in Presidente Médici (P6/32.0 μg L^{-1}). The MPV for lead established by PRC Edict 5/2017(as amended by GM/MS Edict 888/2021) and the WHO (2017) standard is 10 μg L^{-1}.

Lead is a toxic metal detectable in practically all phases of the inert environment and in all biological systems. The main route of exposure for the general population is through food and water (Klaassen & Watkins, 2012). Lead exposure is associated neurodevelopmental problems, impaired renal function, hypertension, impaired fertility, adverse pregnancy outcomes, impaired neurodevelopment of children, and even mortality (due to cardiovascular disease) (WHO, 2017). Children are more vulnerable to the neurological, metabolic and behavioral effects of lead (Moreira & Moreira, 2004). The lead is carcinogenic and induces tumors of the respiratory and digestive systems, epidemiological studies suggest a relationship between occupational exposure to the metal and lung, brain and bladder cancer (Klaassen & Watkins, 2012).

In isolated cases, Ba concentrations were also found that exceeded the MPV of the Brazilian (700 μg L^{-1}) and WHO standards (1,300 μg L^{-1}), in two wells in Ouro Preto do Oeste (LW -P9/1,476 μg L^{-1} and P19/1,223 μg L^{-1}, and HW—P9/1,150 μg L^{-1} and P19/940 μg L^{-1}); one well in the Dois de Abril basin (LW, P3/1,131 μg. L^{-1}); and one in Presidente Médici (LW-P6/873 μg L^{-1}).

Barium compounds are present in nature as ore deposits. Their presence in water comes from natural sources, industrial emissions and other anthropogenic practices. Food is the main source of intake, but when barium concentrations in drinking water are high, it can contribute significantly to total intake (WHO, 2017). There is no evidence that barium is carcinogenic or genotoxic. Acute hypertension has been observed in case reports, but this effect may be secondary to hypokalemia (low blood potassium levels) (WHO, 2017). Studies to establish guideline values have several limitations (small study size, short duration of exposure). Nevertheless, barium has been shown to cause nephropathy in laboratory animals, and this was selected as the toxicological endpoint of concern in the current guidelines (WHO, 2017).

According to Moreira and Moreira (2004), trace elements can damage all biological activity. However, the varied accesses to biological components causes certain types of responses to predominate. For example, all enzyme systems are potentially susceptible to trace elements, but in living organisms, access may be limited by anatomical structures. In addition, inert binding sites can compete for the metal ions, explaining the differences in sensitivity among organs and tissues.

Risk assessment

Due to the consumption of groundwater outside potability standards, 75.3% of the people in the study area are highly exposed to elements harmful to human health. The human health risk assessment indicated that the four municipalities studied had wells with hazard indices above 1. The municipality with the highest percentage (100%) of wells that presented risk was Jaru in the LW period. Al was the element responsible for the increase in the value of the index in the period. During HW, 93.7% of the wells presented risk, with nitrate as the main problematic element.

In Ouro Preto do Oeste, the hazard index for well 9 stood out in the periods of LW (110) and HW (96.4). This well's water contained concentrations of trace elements above the MPV of PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021) in the LW period of Al, As, Ba, Be, Mn and Pb, while during HW the elements above the hazard index threshold were Al, As, Ba, Mn, Pb and Zn. These results suggest punctuated contamination. However, it is noteworthy that Al in both periods studied had a contribution of more than 46% in the formation of the hazard index.

The paired Wilcoxon test indicated that the means of the hazard index (HI) of Jaru (Fig. 2a e 2b) during LW (23.3) and HW (2.8) (p-value $= 3.05 \times 10^{-5}$) and of Ouro Preto do Oeste (Fig. 3a e 3b) in the LW (6.71) and HW (12.5) periods (p-value $= 0.019$) differed significantly. No significant differences were found between the HI averages obtained for the hydrological periods studied in the municipality of Ji-Paraná (in the area of Stream Dois de Abril, Fig. 4a e 4b), during HW (4.13) and LW (2.61), in Stream Nazaré (Fig. 5a e 5b) during HW-LW (9.0) and LW (4.7), and in the municipality of Presidente Médici

(Fig. 6a e 6b) during HW (2.76) and HW-LW (6.08) (p-values of 0.30, 0.84 and 0.12) respectively.

The unpaired Kruskal–Wallis test indicated that the average HI values of Jaru (Fig. 2a) during LW (23.3) was significantly different (p-value 1.26×10^{-7}) than the averages of Ouro Preto do Oeste (Fig. 3a) during LW (6.71), Stream Dois de Abril (Fig. 4b) during LW (2.61), Stream Nazaré (Fig. 5b) during LW (4.70) and Presidente Médici (Fig. 6b) during HW-LW (6.08). No significant differences were found (p-value of 0.60) between the average HI values in the municipalities of Jaru (Fig. 2b) during HW (2.8), Ouro Preto do Oeste (Fig. 3b) during HW (12.5), Stream Dois de Abril (Fig. 4a) during HW (4.13), Stream Nazaré (Fig. 5a) during HW-LW (9.0), and Presidente Médici (Fig. 6a) during HW (2.76).

Castilhos et al. (2014), evaluated the quality of groundwater and potential risks to human health in the municipality of Capitão Gervásio de Oliveira (Piauí/Northeast Brazil) and found that Ni and Hg were the most important elements in the human health risk assessment index in 8 of the 12 wells studied, with values up to 10×times higher for children than those obtained for adults. Sharma et al. (2021) evaluated exposure to iron and manganese along with the non-carcinogenic risks to human health linked to the ingestion of groundwater by the population of Majuli River Island in India, corroborating the results of greater risk in children than in adults.

Regarding the presence of nitrate, PRC Edict 5/2017 (as amended by GM/MS Edict 888/2021) establishes that the sum of the ratios of nitrite and nitrate and their respective MPVs must not exceed unity. In the areas studied, the nitrite levels were below the MPV (1,000 μg L^{-1}) in all the samples, thus not being very representative in the sum of the HI. However, nitrate in 23.3% of the wells analyzed proved to be a risk factor for human health, exceptin Ouro Preto do Oeste, where in 100% of the sampling points, nitrate values were below the MPV (10,000 μg L^{-1}).

In the municipality of Ji-Paraná, Nascimento (2022) calculated the risk coefficient for the consumption of groundwater involving 12 chemical variables (metals, metalloids, nitrite and nitrate). In the dry season, 80% of the wells posed risks, ranging from (0.88–4.52), while in the rainy season the percentage was 90% (0.22–3.39). Nitrate was the variable with the greatest contribution to the risk calculation. This result was due to the high concentrations detected in groundwater, ranging from 100 to 2,680 μg L^{-1} (dry season) and 1,000 to 27,000 μg L^{-1} (rainy season).

Studies of nitrate contamination and risk assessment to human health have been conducted in several countries. Chen et al. (2021) evaluated the quality of groundwater and its potential risks to human health in the Xinzhou Basin, Shanxi Province (China), an agricultural area where fertilizers and pesticides are widely used. The results indicated that fluoride, nitrate and nitrite were the main elements ($F^- > NO_3^- > NO_2^-$), threatening the health of residents, who had suffered from fluorosis arising from the interaction between water and rocks that increases the dissolution of minerals containing fluorine. According to the authors, the risk levels for children and women were respectively 2.18 and 1.71 times greater than that for men. The study of Bazeli et al. (2020) in Khaf County (Iran) demonstrated that nitrate and fluoride had a non-carcinogenic risk to the population assessed, while nitrite presented no risk, and babies were more vulnerable to the non-carcinogenic risk (for nitrate in groundwater), with body weight being inversely related to the sensitivity of the age groups analyzed.

Golak et al. (2022) studied the Iranian city of Kazerun, calculating the risk for four age groups (infants, children, adolescents and adults), and demonstrated that children at 56% of the sampling points were at greatest risk. Similar results were reported by Wedyan et al. (2021) when examining nitrate concentrations in groundwater in Al Duliel (Jordan) and its likely effects on the health of local in habitants. The authors concluded that in 86% of the sampled sites, both children and infants were more vulnerable to non-cancer human health risks compared to adults. These results may have been related to the lower body weight of the infants and children, as also noted by Chen et al., (2021 and Bazeli et al., 2020). According to Wedyan et al. (2021) similar results serve as a warning to consumers that groundwater is not safe, especially for children under 1 year of age.

In the present study, the hazard index (HI) used demonstrated that drinking groundwater poses a risk to the health of the population (75.3%). The results indicated that aluminum (42.2%), nitrate (35.3%) and manganese (16.3%) were the main elements in the samples that threaten the health of residents.

We found no significant differences between the hydrological periods regarding the substances contained in the well water in the areas of Stream Dois de Abril and Stream Nazaré and the municipality of Presidente Médici. However, the water in the municipalities of Jaru (LW, 23.3) and Ouro Preto do Oeste (HW, 12.5) presented the highest average HI among the periods evaluated. The municipality with the highest average HI was Jaru during LW (23.3).

The human health risk assessment methodology is a widely used approach worldwide. There are several methodologies proposed for forming the harzard index that were not the focus of this research. Some, for example, consider the sex and age group of the exposed population (Sharma et al., 2021; Chen et al., 2021; Bazeli et al., 2020; Golak et al., 2022; Wedyan et al., 2021). Others consider carcinogenic risk in the assessment (Mohan & Sruthy, 2022; Yazman et al., 2024). Some studies associate health risk indices with ecological indices (Yasman et al., 2024; Chen et al., 2021). However, the methodology used in the present research described by Evans et al. (2015), despite having a simplified structure, is consistent and applicable, meeting the objectives proposed here. Finally, the presence of substances in concentrations that exceed the limits established in potability standards indicates that there is a high risk of adverse effects on human health associated with the consumption of groundwater from wells as a source for human supply in the study area, therefore these are considered inadequate as alternative sources for the supply of drinking water.

Conclusions

In the Western Brazilian Amazon region, specifically the central region of the state of Rondônia where the studied municipalities are located (Jaru, Ouro Preto do Oeste, Ji-Paraná and Presidente Médici), we analyzed the levels of metals and trace elements in groundwater and their effect on the residents' health, due to the presence of substances that exceed regulatory limits for drinking water. In some wells, the contamination exceeded the value established by around 100x.

The risk assessment method is an essential tool for studying environmental contamination, and is widely used around the world. Even though some elements, such as aluminum, arsenic, iron and manganese, have been associated with local geology, since evidence of geogenic contamination of large areas by them exists in the literature, their high values and the damage caused by their human consumption must be taken into account.

Some substances found here are considered potentially toxic (Al, As, Ba, Fe, Mn, Pb) and carcinogenic (As, Pb, NO_3^-). It is thus necessary to consider, in addition to their concentrations, individuals' exposure period, which can worsen the contamination situation.

The results found contribute to guiding the creation of public politics aimed at protecting and preserving human health and the region's water resources. They also guide government intervention actions with regard to the lack of basic sanitation, which, in addition to exposing the local population to water supplies from sources of questionable quality (such as water from underground well), also contribute to the degradation of underground resources. It is also important to highlight the importance of actions to raise awareness among the local population about the importance of using safe drinking water sources, as well as the implementation of a sewage and solid waste collection and treatment system.

A broad study is needed to survey and identify potential sources of contamination for the groundwater in the area under study, as well as continuous monitoring in order to understand future changes, such as changes in land use and occupation, and the efficiency of government actions in these areas, in order to reduce the population's exposure to elements that are harmful to health.

Although the present study includes data from 77 underground wells distributed in four municipalities in the state of Rondônia (Western Amazon), the number of samples is still too limited to accurately determine the degree of contamination of groundwater in the region. However, the results presented here are relevant due to the gap that exists on this topic. Finally, it is necessary to expand studies of underground water resources throughout the region in order to better understand the distribution of these contaminants and identify safe levels of the human supply of drinking water, in addition to shedding more light on the characteristics of the groundwater of the world's largest river basin.

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Author contributions Josilena de Jesus Laureano, wrote the main manuscript text, carried out the research in the municipalities of Presidente Médici and Ji-Paraná (basin stream Nazaré). Caryne Ferreira Ramos carried out the research in the municipality of Ji-Paraná (basin stream Dois de Abril), and revision of the manuscript. Daíse da Silva Lopes carried out the research in the municipality of Jaru, and revision of the manuscript. Luiza Fernanda Silva Pavanello carried out the research in the municipality of Ouro Preto do Oeste, and revision of the manuscript. Tiago de Oliveira Lima carried out the research in the municipality of Ji-Paraná (basin stream Nazaré e Dois de Abril), and revision of the manuscript. Alan Gomes Mendonça carried out the research in the municipality of Ji-Paraná (basin stream Nazaré), and revision of the manuscript. Ana Lúcia Denardin da Rosa coordinated all research, and overall revision of the manuscript. Walkimar Aleixo da Costa Junior carried data analysis and interpretation, and revision of the manuscript. Maria Cristina N. do N. Recktenvald carried data analysis and interpretation, and revision of the manuscript. Wanderley Rodrigues Bastos carried overall revision of the manuscript. Elisabete Lourdes do Nascimento coordinated all research, wrote the main manuscript text, and overall revision of the manuscript.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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