

## Hydrochemistry and Contamination in Sedimentary and Fractured-Rock Aquifers of The Upper Rio Negro Basin – Amazonas/Brazil

*Hidroquímica e Contaminação em Aquíferos Sedimentares e Rochosos Fraturados da Bacia do Alto Rio Negro – Amazonas/Brasil*

Lucindo Antunes Fernandes Neto  & Ingo Daniel Wahnfried 

Universidade Federal do Amazonas, Instituto de Ciências Exatas, Departamento de Geociências, Manaus, AM, Brasil

E-mails: [lucindofernandes@gmail.com](mailto:lucindofernandes@gmail.com); [iwahnfried@ufam.edu.br](mailto:iwahnfried@ufam.edu.br)

**Corresponding author:** Lucindo Antunes Fernandes Neto; [lucindofernandes@gmail.com](mailto:lucindofernandes@gmail.com)

### Abstract

The Amazon region has the largest hydrographic network on the planet. However, cities and communities along rivers obtain water from tube wells without studying the chemical quality and, consequently, the potability of their water. In specific geological contexts, there is a significant probability of natural contamination by arsenic in groundwater in the region, already attested in previous works in the Solimões, Madeira and Amazonas rivers basins, but not yet found in the Negro river basin. As the Negro is the second largest river in the Amazon Basin, it has become necessary to study the chemical quality of its groundwater, relating it to the geology of the region. In this work, water samples were collected from 21 wells and 4 water springs used for human consumption, following the protocols proposed by the US – EPA. In the field, the physicochemical parameters of the in-situ water were measured, and alkalinity tests were carried out on the samples. The cations were analyzed at INPA and the anions at the Geological Survey of Brazil (SGB). From the 25 samples, 16 had analyses results within acceptable ionic balance values, and 12 of the 16 had at least one of the following elements in concentration above World Health Organization and Brazilian Guideline Values: Al, As, Fe, Mn and Pb. The presence of values below the GV, but above what is considered natural, of  $\text{NO}_3^-$  in 66% of the contaminated points, associated with the shallow depth of most of the wells, installed in areas of recent sedimentary deposits and that do not show any or few signs of care demonstrate that the contamination in these localities is of anthropic origin. Two samples (16% of the contaminated samples) are from deep wells installed in fractured aquifers, which in this case indicate contamination of geogenic origin. Arsenic was found in association with iron and aluminum in a well installed in alluvial sediments, which indicates that more studies are needed for this specific geologic formation to know the quality of this water. For other locations and cities, short, medium and long-term measures are needed to prevent anthropogenic contamination of aquifers.

**Keywords:** Groundwater aquifer; Anthropic contamination; Amazon

### Resumo

A região Amazônica possui a maior rede hidrográfica do Planeta. Entretanto, as cidades e comunidades ao longo dos rios obtêm água a partir de poços tubulares sem o estudo da qualidade química e, conseqüentemente, da potabilidade de suas águas. Em contextos geológicos específicos, existe probabilidade significativa de contaminação natural por arsênio em águas subterrâneas da região, já atestada em trabalhos anteriores nas calhas dos rios Solimões, Madeira e Amazonas, mas ainda não testemunhou na bacia do rio Negro. Sendo o rio Negro o segundo maior rio da Bacia Amazônica, tornou-se necessário o estudo da qualidade química das suas águas subterrâneas relacionando-a com a geologia da região. Neste trabalho, foram coletadas amostras de água de 21 poços e 4 nascentes, todos utilizados como fontes de água para consumo humano, seguindo os protocolos propostos pela US – EPA. Em campo, foram medidos os parâmetros físico-químicos das águas in-situ e foram feitos os testes de alcalinidade nas amostras. Os cátions foram analisados no Instituto Nacional de Pesquisas da Amazônia, e os ânions no LAMIN, do Serviço Geológico do Brasil. Das 25 amostras, 16 tiveram resultados dentro dos limites aceitáveis de pelo menos um cálculo de balanço iônico, das quais 12 tiveram um ou mais dos seguintes elementos em concentrações superiores aos valores de referência estabelecidos pela Organização Mundial da Saúde e pelo Ministério da Saúde do Brasil: Al, As, Fe, Mn and Pb. A presença de valores abaixo do permitido, mas acima do considerado natural, de  $\text{NO}_3^-$  em 66% dos pontos contaminados, associados profundidade rasa da maioria dos poços, instalados em áreas de depósitos sedimentares recentes e que não apresentam nenhum ou poucos sinais de cuidado evidenciam que a contaminação nestas localidades

é de origem antrópica. Duas amostras (16% das amostras contaminadas) são de poços profundos instalados em aquíferos fraturados, que nesse caso indicam contaminação de origem geogênica. O arsênio foi encontrado em associação com ferro e alumínio em um poço instalado em reservatórios aluvionares o que indica para esta formação geológica são necessários mais estudos para saber a qualidade dessa água. Para as demais localidades e cidades, são necessárias medidas de curto, médio e longo prazo para impedir o avanço de contaminação antrópica de aquíferos.

**Palavras-chave:** Aquífero subterrâneo; Contaminação antrópica; Amazônia

## 1 Introduction

The state of Amazonas is the largest in northern Brazil. It has a high rate of preservation of its forest. Two of the main rivers in the world flow through the state, the Negro and Solimões. Despite the vast surface water availability, the population of the Amazon region mostly uses tubular wells as an alternative for the supply of drinking water.

In big cities, there is still a control of the chemical quality of the water carried out by companies that exploit water resources, but in the interior of the state, in smaller cities and riverside communities, the exposure to possible anthropic or geogenic contaminants is very high due to lack of inspection, sanitation and poor construction of wells. The interaction of groundwater with the environment around it influences its composition, defining its chemical characteristics. To be considered potable water, the dissolved chemical elements must be within the Guidance Value (GV) defined by the Brazilian Health Ministry Ordinance nr. 888/2021 (Brasil 2021), so that it is not harmful to human health. Among the main potentially harmful contaminants of water are arsenic, mercury, lead, cadmium, barium, copper, fluorine, chromium and zinc. If water contamination is caused by human activities, it is called anthropogenic contamination. If it is not originated by human activities, it is considered a natural or geogenic contamination.

The fact that the chemical quality of aquifers in the Amazon region is not well studied is worrying because of scientific indications that show that groundwater in the region may present geogenic contamination by arsenic in a reducing environment (Amini et al. 2008). Arsenic has four oxidation states (-3, 0, +3, +5), and can be of organic and inorganic origin. For many regions, arsenic can be found in low concentrations, but contaminations of human origin such as mining tailings, chemical industries and lack of sanitation can generate anomalous concentrations that can be harmful to health.

Arsenic can become mobile in extreme pH and Eh environments, whether acidic or basic, reducing or oxidizing, in association with oxides of iron, aluminum, zinc and manganese, and contamination can occur together. When arsenic adsorbed on minerals present in the hydrogeological environment is released by this set of characteristics, it

can cause contamination of geogenic origin (Smedley & Kinniburgh 2002). According to Smedley and Kinniburgh (2002), geogenic arsenic contamination was first studied in 1989 in the river delta regions of Bangladesh and India, and in 1998 in Vietnam. It is estimated that millions of people use water contaminated by arsenic. Yoshida et al. (2004) show that, if consumed continuously and above the GV stipulated by the World Health Organization of 10 µg/L, arsenic is highly toxic and can cause from skin diseases to aggressive types of cancer.

Geogenic arsenic is adsorbed on weathered sediment surfaces, associated with iron oxides and hydroxides (Smedley & Kinniburgh 2002). The authors state that the element becomes mobile in water under pH conditions between 6.5-8.5, negative Eh values and an anoxic environment (rich in organic matter). Amini et al. (2008) constructed risk maps of arsenic contamination using statistical models, which indicated that the Amazon Basin is one of the areas with potential presence of arsenic in groundwater. Based on these results, the Swiss Federal Water Research Institute (Eidgenössische Anstalt für Wasserversorgung, Abwasserreinigung und Gewässerschutz – EAWAG) started its research on arsenic contamination in the Amazon, both in Peru, in cooperation with the National University of Ingenieria (UNI) in Lima, and in Brazil, with the Federal University of Amazonas (UFAM), in 2015.

The results were published by De Meyer et al. (2023), showing high levels of arsenic and manganese in recent sediments of the Brazilian and Peruvian Amazon, indicating the high risk of geogenic contamination in the region. Arsenic, iron, manganese and barium contaminants were found above the GV in the region of Careiro da Várzea – AM (Fernandes Neto 2018).

Among anthropogenic groundwater contaminants, Varnier et al. (2019) state that nitrate is the most frequent contaminant, both in Brazil and abroad, making it used worldwide as an indicator of groundwater contamination.

The objectives of the present work are to compare the geology with the hydrogeochemistry of the region; to investigate factors that influence the chemical characteristics of the water; and to verify the contamination of groundwater and once the existence of contamination is confirmed, verify the possible factors that generate them.

## 2 Geological Framework

The Negro River passes through several geological units until it meets the Solimões River, passing through the rocks of the rocky basement of the state of Amazonas and through the Paleozoic sedimentary basins of the Solimões and Amazonas.

It is in the NW portion of the Amazonian Craton and Amazonas state, it is limited to the east and south by the Provinces of Tapajós – Parima and Rondônia – Juruena, respectively. The Rio Negro Province makes up one of the largest areas of rocky basement in the state of Amazonas and comprises two tectono-stratigraphic domains, Imeri to the east and Uaupés to the west (Reis et al. 2006). Mapping work carried out by the Geological Survey of Brazil resulted in 2006 in a geological map for the state of Amazonas. According to this proposal, granite genesis in the Rio Negro Province was intense and varied, with Paleo and Mesoproterozoic ages (Veras 2012).

The Paleozoic Solimões sedimentary basin occupies an area of approximately 948,600 km<sup>2</sup> (Souza et al. 2013). Of this total, about 576,300 km<sup>2</sup> of sediments belonging to the Içá Formation surface, while the remaining 372,300 km<sup>2</sup> of sediments of the Solimões Formation appear. This basin developed in Proterozoic crystalline and sedimentary rocks of the Central Amazon Province. The boundary with the Amazon basin is made through the Purus Arch (Eiras et al. 1994).

The stratigraphic framework of the Solimões basin is divided into six sequences: Ordovician, Silurian-Devonian, Devonian-Carboniferous, Carboniferous-Permian, Cretaceous and Tertiary-Quaternary, in which the sedimentation in this basin ends. Regarding the depositional environments of the formations under study, the Cretaceous sequence is characterized by a high energy fluvial system, responsible for the deposition of the Alter do Chão Formation, under humid climate, while the Tertiary-Quaternary sequence, discordant over the Alter do Chão Formation, and represented by the Solimões and Içá formations, forms a sedimentary wedge from the Purus Arch to the sub-Andean basins (Souza et al. 2013). The deposition environments of these two formations were interpreted as meandering fluvial and deltaic fluvial, respectively (Silveira 2005).

The Paleozoic Amazonas sedimentary basin occupies a total area of approximately 615,600 km<sup>2</sup>. Alter do Chão and Içá Formations are at the surface of the sedimentary sequence, with an area of respectively 410,000 and 205,000 km<sup>2</sup>. Souza et al. (2013) describe its geological limits as the Purus Arch to the west, the Gurupá Arch to the east, the Guiana Shield to the north and the Central Brazil Shield to the south. According to these authors, the evolution of the Amazonas Basin comprises the Ordovician-Devonian, Devonian-Carboniferous, Permo-Carboniferous depositional sequences and, finally, the Cretaceous-Tertiary sequence, which ends the sedimentation in this basin; the Cretaceous-Tertiary sequence is initially characterized by the deposition of the Alter do Chão Formation, under humid climatic conditions and a high energy sandy fluvial system. With the uplift of the Andean Chain, the Cretaceous rivers became shallow freshwater lakes, fed by low-energy rivers, responsible for the deposition of the Solimões Formation, which grades towards the top of the Alter do Chão Formation. The Penatecaua Magmatism (Santos & Araújo 1978), represented by the intrusion of diabase sills, occurred during the Triassic.

## 3 Hydrogeological Framework

The principal constituents of the fractured-rock aquifers are granitoids, gneisses, granulites, migmatites, basic and ultrabasic rocks. These aquifers are discontinuous, rendering low water production is mostly saline. Due to the extension of the lithotypes, this is the aquifer that presents the least possibility of water accumulation (CPRM 2007).

The Içá Formation consists of fine to medium sandstones and siltstones, locally with reddish yellow clayey conglomerates (Nogueira et al. 2003). According to Galvão et al. (2012), in the region of Urucu/AM, the aquifer thickness reaches 50 m and is considered hydraulically connected with the Solimões Aquifer. The waters are classified as bicarbonate-sodic, with low ion concentration, which reflects in the average electrical conductivity of 12 µS/cm.

According to Maia and Marmos (2010) the Alluvial Aquifer System is formed by recent fluvial sedimentary deposits that are at the river channel margins. Alluvial deposits are made up of sediments with granulometries ranging from clay, sand, to pebbles, in addition to containing organic matter. These are local, shallow phreatic aquifers (Pereira & Cajazeiras 2012).

## 4 Materials and Methods

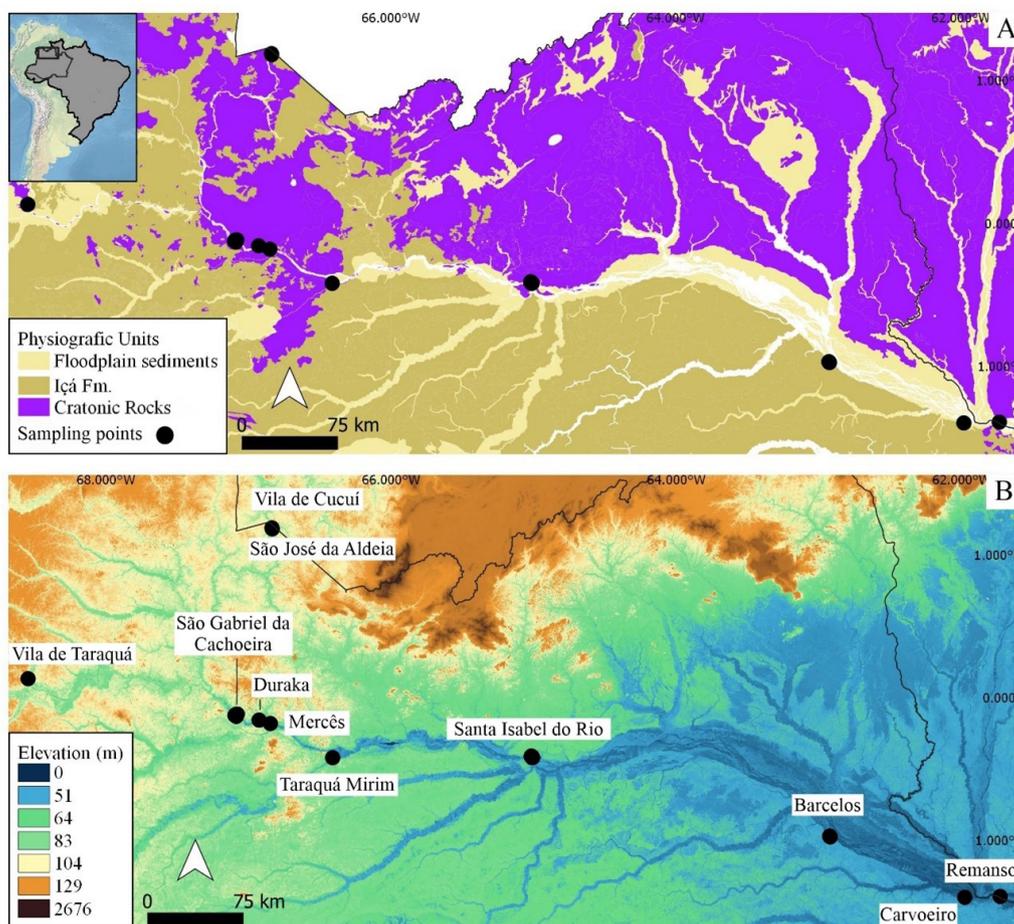
### 4.1 Data Acquisition in GIS and Survey of Wells for Sampling

Areas with greater probability for the occurrence of geogenic contamination where the initial focus of this work. Therefore, the model by Amini et al. (2008) was used to select sampling priorities. The Brazilian Geological Survey's (SGB) Groundwater Information System (SIAGAS) was used to find information on the location and constructive characteristics of wells in the upper Negro River region. Geological, geomorphological, and geographic information that would help in the production of maps, regional context and in the field work, were obtained from geoSBG, also from SGB (Figure 1). In addition to this information, the fieldwork logistics were selected the main wells that had the appropriate characteristics for the study, in the end there were 21 wells and 4 sampled springs.

### 4.2 Groundwater Sampling

Water sampling was carried out following USEPA protocols (US-EPA 2015). The point of collection was usually at the wellhead, and always during pumping, thus avoiding water that was stored in reservoir or tubes. A small diameter flexible PVC tube was used to divert part of the water from the pumping well to an open container, where the pH, Eh, temperature, electric conductivity and dissolved oxygen probes were inserted. The multi-parametric probes used were the YSI 30, HANNA HI 9146 and JANWEY. To avoid collecting water that was stagnant in the well, the parameters were measured at 5-minute intervals during pumping, and the samples were collected when readings became stable.

For chemical analysis of cations and anions, different 50 mL bottles were collected, intended for water analysis using disposable syringes with 45 µm filters, thus avoiding the passage of solid particles, and 200 mL of unfiltered water were also collected for the determination of alkalinity



**Figure 1** A. Geological map of the upper Rio Negro region, highlighting the areas of the floodplain sediments, Içá Formation and cratonic rocks. B. Digital elevation model of the study area and collecti points.

in suitable and numbered containers. For the conservation of the samples in which the cation analyzes were carried out, 6 drops of nitric acid were added to reduce the pH to 2, in order to avoid its oxidation and precipitation of the elements and keep them in solution. At the end, the samples that were previously numbered were stored in a freezer on the boat and upon arrival in Manaus they were stored in the refrigerator of the UFAM geochemistry laboratory.

### 4.3 Chemical Analyses

Alkalinity was measured in the field, the same day the samples were collected, to avoid changes caused by contact with air. Titration with methyl red acid-base indicator ( $C_{15}H_{15}N_3O_2$ ) was used, since all samples had a pH below 5.5. Six drops were added to 50 mL of water sample. Total alkalinity is calculated using Equation (1).

$$[\text{alkalinity}] = (\text{Vac} * \text{M} * \text{MM}) / \text{Vam} \quad (1)$$

where Vac: volume of added acid; M: molarity of the acid; MM: molar mass of the element in which the alkalinity will be expressed; Vam: sample volume.

Cations were analyzed at Instituto de Pesquisas da Amazônia in an optical plasma emission spectrometer (ICP-OES) from Thermo Scientific, model iCAP 7000 SERIES. The analyzed elements were As, Mn, Na, Al, Ba, Cu, K, Mg, Ca, Cr, Ni, Co, B, Zn, Pb, Sr, Ti, Be, Sb, Tl, V, Mo, W, Cd, Fe, Li.

The anions were analyzed by ion chromatography on the Dionex ICS-5000 chromatograph in the LAMIN lab, from SGB in Manaus. The analyzed anions were  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{F}^-$ ,  $\text{Br}^-$  and  $\text{Cl}^-$ .

Analytical results were checked by ionic balance error. The equations from Custodio and Llamas (1983, *apud* Mobus 2014) (Equation 2) and Logan (1965, *apud* Mobus 2014) (Equation 3) were used, based on the sum of bicarbonate, carbonate, chloride, sulfate anions and the sum of Ca, K, Na and Mg cations.

$$\text{Ep}(\%) = (|\sum \text{anions} - \sum \text{cations}|) / (|\sum \text{anions} + \sum \text{cations}|) * 200 \quad (2)$$

$$\text{Ep}(\%) = (|\sum \text{anions} - \sum \text{cations}|) / (|\sum \text{anions} + \sum \text{cations}|) * 100 \quad (3)$$

The results were compared with the Guidance Values (GV) proposed by the WHO (2017) and Brazilian Health Ministry Consolidation Ordinance no. 888/2021 (Brasil 2021).

For the chemical classification of the waters, the Qualigraf freeware was used. It was developed by the Ceará Foundation for Meteorology and Water Resources (Mobus 2014). Piper, Stiff and Schoeller diagrams were constructed to classify the samples according to the content of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  previously analyzed and visualize the variation of the concentration of these ions in the wells visited in the work.

## 5 Results and Discussion

From the total 25 collected samples, 32% came from shallow wells (up to 30 m), 8% came from intermediate depth wells (31 to 60 m), and 20% came from deep wells (deeper than 60 m). Three wells had no depth information, and four samples came from natural springs (16%). Temperature, pH, Eh, electrical conductivity and dissolved oxygen were measured in the field. Temperatures ranged from 26.9 to 29.2 °C. Values for pH varied between 3.47 and 5.46 Eh ranged from -74 mV to 41 mV. Electrical conductivity ranged from 6.9  $\mu\text{S}/\text{cm}$  to 239.9  $\mu\text{S}/\text{cm}$  and we did not have reliable readings for dissolved oxygen (Table 1).

In groundwater, nitrate is commonly present in low concentrations. In the State of São Paulo, a survey was carried out by the Environmental Company of the State of São Paulo (CETESB) in which reference values for groundwater quality in the main aquifers were defined. The highest concentration used as a reference is from the Bauru Aquifer System, with a quality reference value of 1.5 mg/L of  $\text{NO}_3^-$  as N, or 6.7 mg/L of  $\text{NO}_3^-$  as  $\text{NO}_3^-$  (CETESB 2022, p. 31). Bertolo et al. (2007) used a reference value of 5 mg/L of  $\text{NO}_3^-$  (as  $\text{NO}_3^-$ ) for a countrywide evaluation of groundwater quality to indicate possible anthropogenic contamination. This value will be used in the present work as a Prevention Value (PV), indicating locations where an anthropogenic contamination is likely, and attention should be paid despite the water being considered potable by WHO and Brazilian Health Ministry standards. The limit for potability, called Guidance Value (GV), is 44 mg/L for the Brazilian Health Ministry (Brasil 2021) and 50 mg/L for World Health Organization (WHO 2021), both as concentration of  $\text{NO}_3^-$ . The results for  $\text{NO}_3^-$ , As, Al, Mn, Fe and Pb are shown in Table 2.

From the 25 samples, 16 had the ionic balance within the limits defined by either Custodio and Llamas (1983, *apud* Mobus 2014) or Logan (1965, *apud* Mobus 2014) (Appendix 1). These were used for hydrochemical interpretations, and for considerations about contaminations.

**Table 1** Location data and measurements of physical-chemical parameters measured in the field. Wells without depth values had no information on the construction aspects defined. São Gabriel da Cachoeira was abbreviated as SGC.

Sample ID	City/ Community	Unit of origin	Depth (m)	pH	Eh (mV)	Electrical conductivity ( $\mu\text{s}/\text{cm}$ )	Temperature ( $^{\circ}\text{C}$ )
18-RN-001	Vila de Cucuí	Tarsira	99	4.32	-12	50.2	28.9
18-RN-002	Cucuí	Tarsira	94	5.46	-74	100.3	28
18-RN-003	Comunidade Taraquá	Depositos Aluvionares	0	4.22	10	6.9	26.9
18-RN-004	SGC	Rio Uaupés		5.31	-64	239.4	28
18-RN-005	SGC	Rio Uaupés	86	4.12	5	35.3	29.2
18-RN-006	SGC	Rio Uaupés	45	4.71	-35	51.9	26.6
18-RN-007	SGC	Rio Uaupés	76	5.41	-70	155.2	27.7
18-RN-008	SGC	Rio Uaupés	18-20	3.81	21	58.7	28.6
18-RN-009	SGC	Rio Uaupés	18-20	3.74	27	140.6	27.2
18-RN-010	SGC	Rio Uaupés		4.98	-44	151.6	28.6
18-RN-011	SGC	Rio Uaupés		3.81	21	170.1	27.1
18-RN-012	Camanaus	Rio Uaupés	80	3.67	30	15.7	27.8
18-RN-013	Merces	Santa Isabel do Rio Negro	0	4.13	2	22.2	27.5
18-RN-014	Taraquá Mirim	Santa Isabel do Rio Negro	0	3.73	29	18.1	27.1
18-RN-015	Santa Isabel	Formação Içá	28	3.68	31	66.1	27.4
18-RN-016	Santa Isabel	Formação Içá	30	3.47	41	38.3	27.2
18-RN-017	Santa Isabel	Formação Içá	28	3.54	36	12.2	27.7
18-RN-018	Santa Isabel	Formação Içá	18	3.77	24	45.1	27.2
18-RN-019	Santa Isabel	Formação Içá	24	3.62	33	25	28.2
18-RN-020	Santa Isabel	Formação Içá	18	3.57	26	49.6	28.1
18-RN-021	Barcelos	Depositos Aluvionares	60	3.93	16	120	28
18-RN-022	Barcelos	Depositos Aluvionares	60	3.86	20	128.9	28.5
18-RN-023	Barcelos	Depositos Aluvionares	42	3.82	21	33.8	27.7
18-RN-024	Carvoeiro – Barcelos	Depositos Aluvionares	30	3.97	12	35.0	28
18-RN-025	Remanso – Rorainópolis	Depositos Aluvionares	0	4.76	-30	17.5	27.5

To visualize the distribution of the collected waters in relation to the oxidation/reduction potential and its contaminants, a pH x Eh graph was constructed (Figure 2).

With it, it is possible to identify that there is a negative correlation between the values of pH and Eh, which means that the increase in the value of one of the parameters results in a decrease in the value of the other. In this case, 15 of the 16 samples were in the first quadrant, indicating that the contaminants are, in their entirety, in aquifers with a reducing environment.

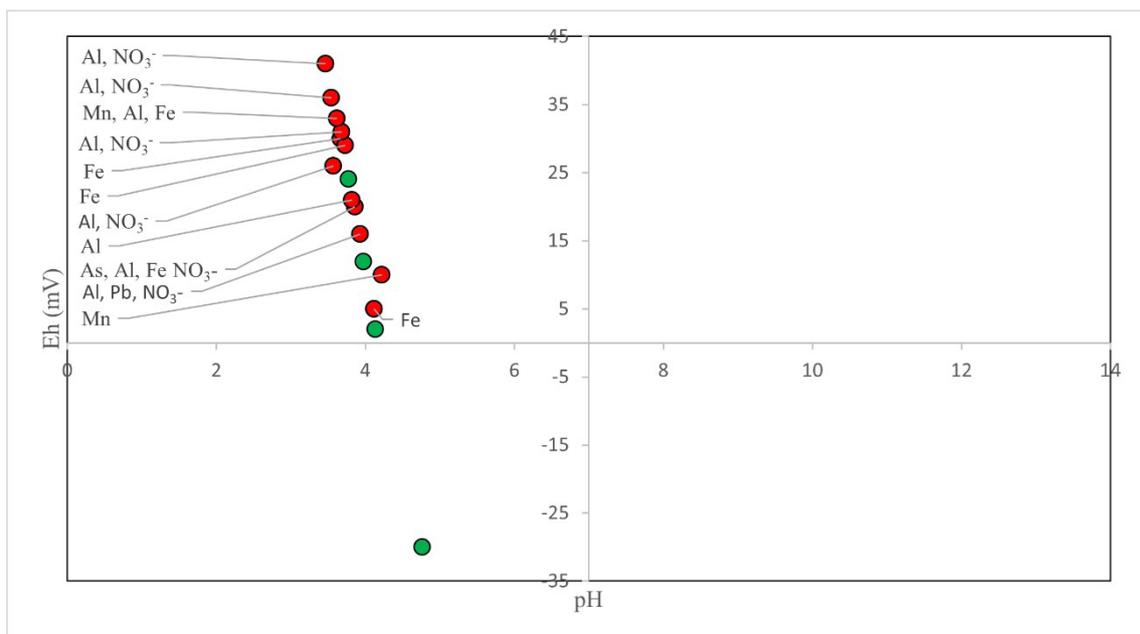
The hydrochemical classification using Piper diagrams indicate the arrangement of the grouped samples according to the probable aquifer they represent (Figure 3). Of the 16 samples collected, two were classified as sodium

chloride type, four as magnesium bicarbonate type and ten as sodium bicarbonate type, totaling three distinct classifications for the samples.

As for the grouping of samples into types of aquifers, the arrangement of the samples failed to show any pattern. Spatial water type distribution is presented by the Stiff diagrams in Figure 4. With the mosaic it is possible to visualize in plan the different characteristics of groundwater in the region. The red figures indicate the presence of geogenic contaminants, and the green figures indicate the absence of these contaminants. The yellow outline in the figures indicates the presence of nitrate in concentrations above PV, which indicates a possible source of anthropic contamination, but its values are still within the GV.

**Table 2** Results for all analyses with at least one adequate ionic balance. Guideline Values (GV) (Brazil 2021; WHO 2017) and Prevention Values (PV) (Bertolo et al 2007) are indicated at the bottom of the table. Bold numbers indicate results above GV or PV.

Sample ID	As (mg/L)	Mn (mg/L)	Al (mg/L)	Pb (mg/L)	Fe (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)
18-RN-003	0.000497	<b>0.22466</b>	0.05367	0.00215	0.1034	1.0694
18-RN-005	0.000708	0.0216	0.02642	0.00029	<b>0.3123</b>	1.7629
18-RN-012	8.68E-05	0.00824	0.09908	0.00312	<b>0.7217</b>	1.5662
18-RN-013	0.000834	0.02028	0.08053	0.00039	0.0181	2.5257
18-RN-014	0.002305	0.01389	0.10345	0.00036	<b>0.3747</b>	2.2806
18-RN-015	0.000278	0.00351	<b>0.72329</b>	0.00179	0.0159	<b>19.5432</b>
18-RN-016	-2.7E-06	0.00268	<b>0.37372</b>	0.00109	0.0087	<b>10.1291</b>
18-RN-017	0.002334	0.00232	<b>0.25699</b>	0.00152	0.0337	<b>18.412</b>
18-RN-018	0.000754	0.0034	0.16908	0.00126	0.0151	<b>8.9033</b>
18-RN-019	0.001236	<b>0.19533</b>	<b>0.28217</b>	0.00153	<b>1.7666</b>	<b>5.83595</b>
18-RN-020	0.002922	0.00644	<b>0.44501</b>	0.00207	0.0141	<b>14.1328</b>
18-RN-021	0.005324	0.04669	<b>1.45643</b>	<b>0.02504</b>	0.0809	<b>27.7267</b>
18-RN-022	<b>0.025578</b>	0.05459	<b>1.06603</b>	0.00669	<b>0.7024</b>	<b>28.2461</b>
18-RN-023	0.000348	0.01596	<b>0.26059</b>	0.00106	0.0382	<b>7.7041</b>
18-RN-024	0.000375	0.02384	0.07128	0.00126	0.0507	3.38465
18-RN-025	-5.8E-06	0.02023	0.03346	0.0006	0.0408	<b>15.9929</b>
<b>GV (mg/L)</b>	0.01	0.1	0.2	0.2	0.3	44
<b>PV (mg/L)</b>						5



**Figure 2** A pH x Eh plot indicating the characteristics of the waters where values in excess of were found (red dots) and the green dots represent samples that do not have contaminants.

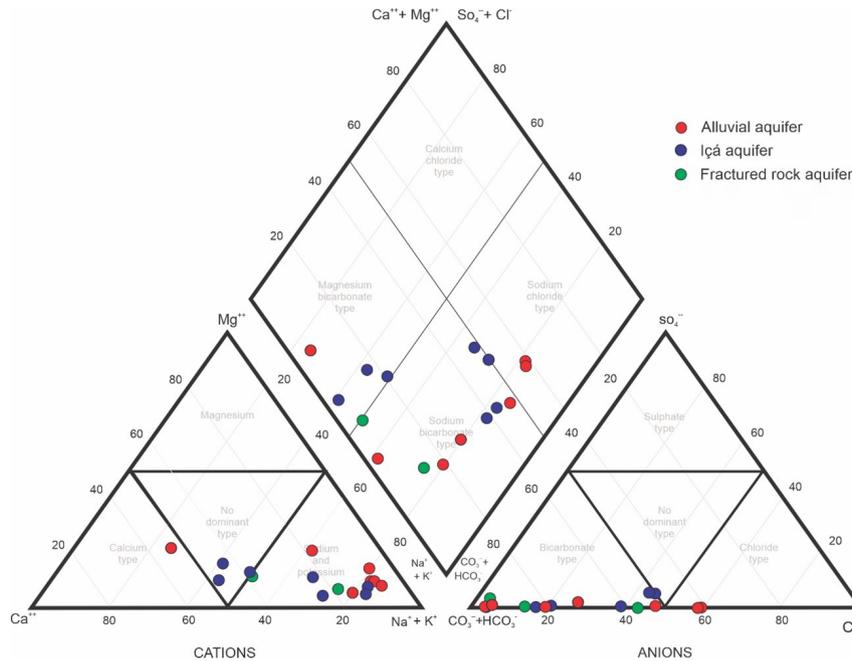


Figure 3 Piper diagram with indication of the aquifer.

Of the 16 samples, only four (25%) are within the concentration limits allowed for human consumption. Ten samples had  $\text{NO}_3^-$  concentrations higher than PV, what can be expected in an unspoiled environment, but still below the GV. The remaining samples have concentrations above GV for Mn, Fe, Al, Pb and As. The contaminants are presented in groups of As+Al+Fe (one sample), Al (five samples), Al+Mn+Fe (one sample), Al+Pb (one sample), Fe (three samples) and Mn (one sample), of which 80% appear in association with nitrate values above PV.

Of the four samples collected from the springs, two were considered suitable for consumption, with one presenting  $\text{NO}_3^-$  values above PV, but still within GV.

Of the 16 samples analyzed only 4 were classified as potable, this represents 75% of the waters as unfit for human consumption, presenting at least one contaminant and one of the samples, located in the city of Barcelos-AM, presented As one of its contaminants (Table 2).

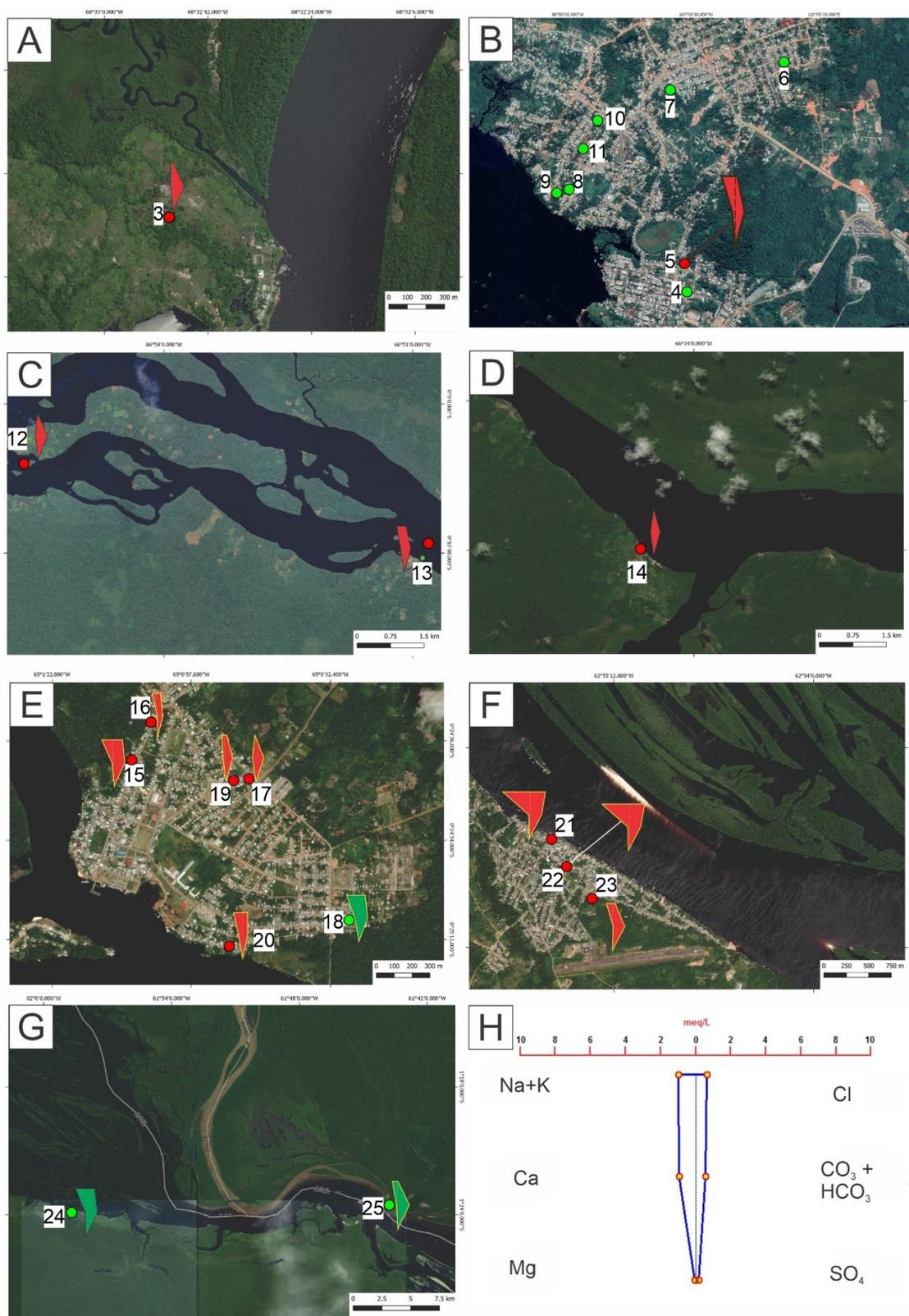
Of the 12 contaminated samples, 7 were collected from wells or springs in sedimentary units and only 2 samples were collected in wells built in crystalline units. Of the 10 samples with nitrate values above PV, 70% were collected from shallow wells (depths of up to 30 m) or from springs. These characteristics, together with the geological setting of sedimentary environments, make them zones of greater probability of contamination by anthropic influence.

The observation of the surroundings of the wells indicated a significant presence of sources of anthropic contamination. Evidence such as the location of wells

near septic tanks, garbage thrown in the vicinity of wells, lack of protection areas or structures around all sampled wells indicate possible reasons for altered  $\text{NO}_3^-$  concentrations. Interpretation of possible sources of anthropic contamination. Precisely because the  $\text{NO}_3^-$  anion is, like the above observations, an indicator of anthropic contamination, its separation from the other contaminant elements was necessary (Figure 5). When the value found is between PV and GV, Varnier et.al, 2019 suggest that points with suspected contamination should be targets for water collection and analysis every three months, to check for increased concentration. Another Piper graph was constructed where the samples were grouped using the geology of the area along with the chemical quality of the waters (Figure 6).

Arsenic, an element that has a GV of  $10 \mu\text{g/L}$ , was found as a contaminant only at point 18-RN-022. This is a well approximately 60 meters deep, which is in apparent good condition and is used by the city of Barcelos for public supply.

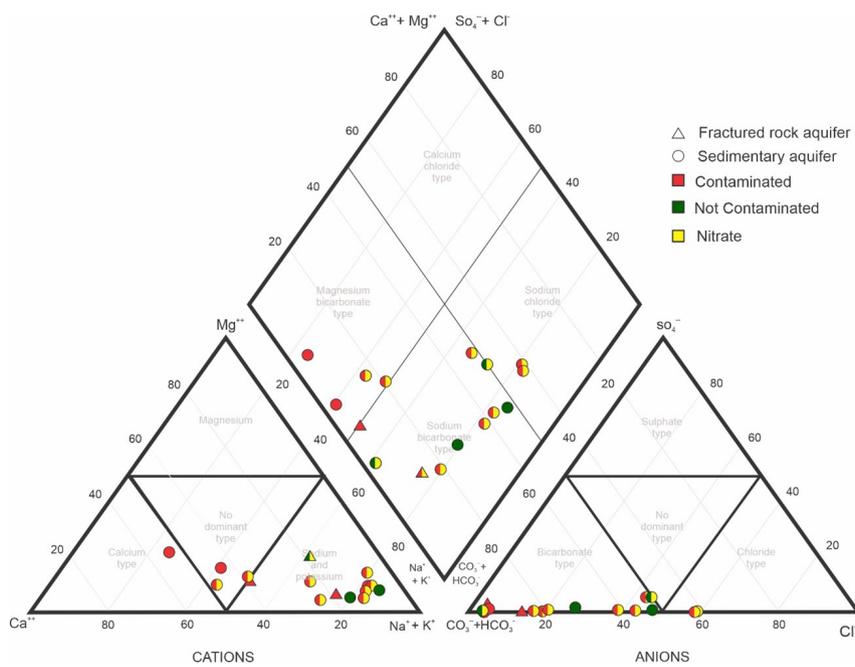
Fractured aquifer samples are classified as sodium and potassium bicarbonate. Samples from sedimentary aquifers are mixed, with a higher concentration of calcium and chloride. The chloride ion can be, as well as the nitrate, derived from septic tanks, forming another indication of anthropic contamination, associated with shallow wells and water sources in sedimentary aquifers and close to sources of anthropic contamination.



**Figure 4** Stiff diagrams distributed in plan in the locations of collection of the samples: **A.** Taraquá Community; **B.** São Gabriel da Cachoeira; **C.** Duraka and Mercês communities (left to right); **D.** Taracua Mirim; **E.** Santa Isabel do Rio Negro; **F.** Barcelos; **G.** Carvoeiro and Rorainópolis (from left to right); **H.** Stiff diagram used as a model for image production.



**Figure 5** Examples of some of the sampled wells: **A.** Private well in São Gabriel da Cachoeira; **B.** Well without protections in SGC; **C.** Water spring used by a community with garbage around (diapers, plastic bags, batteries, beverage bottles and tires); **D.** Well without protections in Santa Isabel do Rio Negro.



**Figure 6** Piper diagram with samples divided into sedimentary, fractured rock aquifer and contaminated and uncontaminated aquifers.

## 6 Conclusion

In the present work, 12 of 16 water samples had at least one of the contaminants As, Fe, Mn, Al and Pb in concentrations above the Guideline Values (GV). 75% of the contaminants were investigated from supply wells or water sources that serve for consumption by riverside communities. 2 samples (16% of the contaminated samples) come from deep wells installed in fractured rock aquifers.  $\text{NO}_3^-$  with values above what is expected in unspoiled environments, called prevention value (PV), but below the guidance value, appears together with contaminated samples in sedimentary environments, but shows values below PV in deeper wells. This should draw attention to the quality of groundwater used for human consumption in all cities and communities along the Negro River, most of which depend exclusively on groundwater as a source of drinking water and especially in communities that do not have deep wells to collect water.

Nitrate is an indicator of anthropogenic contamination of groundwater. Its presence in anomalous concentration in 10 of the 16 points of evolution indicates that there is an evident failure in the care with the protection around the wells (Figure 5), with a record in this work of the lack of cleaning in most of the wells and springs studied.

Cleaning of the wells and surrounding areas, creation of a protection zone around wells, with a fence that avoids access and littering, and regular water quality monitoring for nitrate and bacteria, should be done at all wells to reduce probability of water contaminated by anthropogenic sources being used by the population. Water springs should be substituted by adequately constructed wells, as safer waters sources.

The geogenic arsenic present in one of the sampled wells fits the description by Amini et al. (2008), located in a 60-meter well, characteristics of recent alluvial deposits, presenting acidic pH and positive Eh and in association with Al and Fe as contaminants. Thus, because it contains a contaminant such as As, more studies must be carried out regarding the quality of its water, which, since it is used for public supply, must be potable, otherwise it can pose serious health risks.

## 7 References

- Amini, M., Abbaspour, K., Berg, M., Winkel, L., Hug, S.J., Hoehn, E., Yang, H. & Johnson, C.A. 2008, 'Statistical modeling of global geogenic arsenic contamination in groundwater', *Environmental Science & Technology*, vol. 42, no. 10, pp. 3669-75, DOI:10.1021/es702859e.
- Bertolo, R. A., Hirata, R., & Fernandes, A. 2007, *Hidrogeoquímica das águas minerais emvasadas no Brasil*, Revista Brasileira de Geociências, 37(3), 515-529.
- Brasil, Ministério da Saúde 2021, *Portaria GM/MS nº 888, de 4 de maio de 2021*, viewed 31 January 2023, <[https://bvsvms.saude.gov.br/bvsvms/saudelegis/gm/2021/prt0888\\_07\\_05\\_2021.html](https://bvsvms.saude.gov.br/bvsvms/saudelegis/gm/2021/prt0888_07_05_2021.html)>.
- CETESB 2022, *Qualidade das águas subterrâneas do estado de São Paulo*, CETESB, São Paulo, <<https://cetesb.sp.gov.br/aguas-subterraneas/wp-content/uploads/sites/13/2023/10/Qualidade-das-Aguas-Subterraneas-no-Estado-de-Sao-Paulo-2022.pdf>>.
- CPRM. 2007, *Mapa de domínios/subdomínios hidrogeológicos do Brasil*, CPRM.
- De Meyer, C. M., Wahnfried, I., Rodriguez, J. M. R., Kipfer, R., Avelino, P. A. G., Deza, E. A. C., & Berg, M. 2023, *Hotspots of geogenic arsenic and manganese contamination in groundwater of the floodplains in lowland Amazonia (South America)*, *Science of the Total Environment*, 860, DOI 10.1016/j.scitotenv.2022.160407
- Eiras, J., Becker, C., Souza, E., Gonzago, F., Da Silva, J., Daniel, L., Matsuda, N. & Feijo, F. 1994, 'Bacia do Solimões', *Boletim de Geociências da Petrobras*, vol. 8, no. 1, pp. 17-45.
- Fernandes Neto, L.A. 2018, 'Análise de contaminações geogênicas sazonais em águas subterrâneas na região do Careiro da Várzea - AM', Bachelor Thesis, Universidade Federal do Amazonas.
- Galvão, P., Demétrio, J., Souza, E.L. de, Pinheiro, C.S.S. & Baessa, M.P.M. 2012, 'Hidrogeologia e geometria dos aquíferos das formações cretáceas Içá e Solimões, Bacia Paleozoica do Solimões, na região de Urucu, Amazonas', *Revista Brasileira de Geociências*, vol. 42, pp. 142-53, DOI:10.5327/Z0375-75362012000500012.
- Maia, M. & Marmos, J. 2010, *Geodiversidade do estado do Amazonas*, CPRM, Manaus.
- Mobus, G. 2014, *Qualigraf - Software para auxiliar na análise e interpretação gráfica de dados hidroquímicos*. Funceme-Fundação Cearense de Meteorologia e Recursos Hídricos, versão 10, viewed 31 January 2023, <<https://qualigraf.funceme.br/>>.
- Nogueira, A.C.R., Arai, M., Horbe, A.M.C., Horbe, M.A., Silveira, R.R., Silva, J.S. & Motta, M.B.A. 2003, 'Influência Marinha nos Depósitos da Formação Solimões na Região de Coari (Amazonas): Registro da Transgressão Miocênica na Amazônia Ocidental', *VIII Simpósio de Geologia da Amazônia, sessão temática: Sedimentologia e Estratigrafia*, Amazonas, pp 468-73.
- Pereira, L.A.D.A.C. & Cajazeiras, C.C.A. 2012, 'Caracterização dos principais aquíferos da região sudoeste da Amazônia Ocidental', *Águas Subterrâneas*, pp. 1-4.
- Reis, N., Almeida, M., Riker, S. & Ferreira, A. 2006, *Geologia e recursos minerais do estado do Amazonas*, CPRM, Manaus.
- Santos, J.O.S. & Araújo, H. de. 1978, 'Algumas características químicas do magmatismo Parima/Tapuruquara', *Acta Amazon*, vol. 8, no. 4, pp. 639-56, DOI:10.1590/1809-43921978084639.
- Silveira, R.R. da. 2005, 'Cronoestratigrafia e interpretação paleoambiental de depósitos Miocenos da Formação Solimões, região de Coari, AM', PhD thesis, Universidade Federal do Amazonas, Manaus.
- Smedley, P. & Kinniburgh, D. 2002, 'A review of the source, behaviour and distribution of arsenic in natural waters', *Applied Geochemistry*, vol. 17, no. 5, pp. 517-68, DOI:10.1016/S0883-2927(02)00018-5.

- Souza, E., Galvão, P., Pinheiro, C., Baessa, M.P.M., Demétrio, J.G.A. & Brito, W.R.R. 2013, 'Síntese da hidrogeologia nas bacias sedimentares do Amazonas e do Solimões: Sistemas Aquíferos Içá-Solimões e Alter do Chão', *Geologia USP*, vol. 13, no. 1, pp. 107-117, DOI:10.5327/Z1519-874X2013000100007.
- US-EPA. 2015, *Groundwater Sampling*, SESD Operating Procedure.
- Varnier, C., Rocha, G.A., Campos, J. E., Albuquerque Filho, J. L., Simonato, M. & Hirata, R. 2019, *Nitrato nas águas subterrâneas: desafios frente ao panorama atual*, SIMA/IG, São Paulo.
- Veras, R. 2012, 'Petrologia de granitóides dos arredores da Missão Tunuí, NW do Amazonas, Província Rio Negro, Cráton Amazônico', PhD thesis, Universidade Federal do Amazonas, Manaus.
- WHO – World Health Organization 2017, Guidelines for drinking-water quality. WHO chronicle, Fourth Edition 38(4), 104-8.
- Yoshida, T., Yamauchi, H. & Sun, G.F. 2004, 'Chronic health effects in people exposed to arsenic via the drinking water: Dose–response relationships in review', *Toxicology and Applied Pharmacology*, vol. 198, no. 3, pp. 243-52, DOI:10.1016/j.taap.2003.10.022.

#### Author contributions

**Lucindo Antunes Fernandes Neto:** conceptualization; formal analysis; methodology; validation; writing – original draft; writing review and editing; supervision; visualization. **Ingo Daniel Wahnfried:** conceptualization; formal analysis; methodology; validation; writing review and editing; funding acquisition; supervision; visualization.

#### Conflict of interest

The authors declare no conflict of interest.

#### Data availability statement

All data included in this study are publicly available in the literature.

#### Funding information

This project was funded by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES project PROCAD-Amazônia 2018, granted to the Geosciences Graduate Program - PPGGEO/UFAM named "Rio Negro TAR: Interação Tempo-Água-Rocha e a formação da bacia hidrográfica do rio Negro, Amazonas – Brasil." (Negro river Time-Water-Rock: formation of the Negro river basin, Amazonas, Brasil). Field activities had logistical support of the Brazilian Geological Survey (Serviço Geológico do Brasil - SGB). First author had a scholarship from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES.

#### Editor-in-chief

Dr. Claudine Dereczynski

#### Associate Editor

Dr. Gerson Cardoso da Silva Jr.

#### How to cite:

Fernandes Neto, L.A. & Wahnfried, I. D. 2024, 'Hydrochemistry and Contamination in Sedimentary and Fractured-Rock Aquifers of The Upper Rio Negro Basin – Amazonas/Brazil', *Anuário do Instituto de Geociências*, 47:57965. [https://doi.org/10.11137/1982-3908\\_2024\\_47\\_57965](https://doi.org/10.11137/1982-3908_2024_47_57965)

**Appendix 1:** Ionic Balance - Custódio and Llamas, 1983 (B.I.I) and Logan, 1965 (B.I.II), of all collected samples.

Sample ID	Na + K (meq/L)	Ca (meq/L)	Mg (meq/L)	Cl (meq/L)	CO <sub>3</sub> + HCO <sub>3</sub> <sup>-</sup> (meq/L)	SO <sub>4</sub> <sup>-</sup> (meq/L)	CE (μS/cm)	Σ Cations (meq/L)	Σ Anions (meq/L)	B.I. I (%)	B.I. II (%)	Comments
18-RN-001	0.2204	0.1545	0.0584	0.0781	0.1896	0.0033	50.2	0.4333	0.2711	46.04	23.02	Does not attend B.I. 1 and 2
18-RN002	0.3348	0.4674	0.1571	0.011	0.4545	0.0487	100.3	0.9593	0.5142	60.41	30.21	Does not attend B.I. 1 and 2
18-RN-003	0.0308	0.033	0.0123	0.0062	0.1755	0.0008	6.9	0.0762	0.1826	82.26	41.13	Does not attend B.I. 2
18-RN-004	0.9908	0.9578	0.0962	0.6164	0.5587	0.1678	239.4	2.0448	1.3429	41.44	20.72	Does not attend B.I. 1 and 2
18-RN-005	0.2136	0.0525	0.0197	0.0192	0.1239	0.0006	35.3	0.2859	0.1437	66.18	33.09	Does not attend B.I. 2
18-RN-006	0.2717	0.22	0.0296	0.046	0.2272	0.0025	51.9	0.5213	0.2756	61.64	30.82	Does not attend B.I. 1 and 2
18-RN-007	0.6067	0.9423	0.0691	0.0908	0.6817	0.031	155.2	1.6181	0.8035	67.27	33.64	Does not attend B.I. 1 and 2
18-RN-008	0.3521	0.041	0.0255	0.0922	0.1239	0.0002	58.7	0.4186	0.2164	63.69	31.85	Does not attend B.I. 1 and 2
18-RN-009	0.8457	0.097	0.0345	0.3526	0.1239	0.0004	140.6	0.9772	0.4769	68.8	34.4	Does not attend B.I. 1 and 2
18-RN-010	0.7356	0.4834	0.0584	0.3408	0.2478	0.1004	151.6	1.2774	0.6889	59.85	29.93	Does not attend B.I. 1 and 2
18-RN-011	0.7053	0.2849	0.0798	0.4799	0.1446	0.0452	170.1	1.07	0.6696	46.03	23.02	Does not attend B.I. 1 and 2
18-RN-012	0.043	0.0325	0.0099	0.0045	0.1446	0.0054	15.7	0.0853	0.1545	57.69	28.84	Does not attend B.I. 2
18-RN-013	0.1291	0.025	0.009	0.0378	0.1033	0.0029	22.2	0.1631	0.144	12.47	6.24	OK
18-RN-014	0.0166	0.0365	0.0148	0.0065	0.1342	0.0017	18.1	0.0679	0.1424	70.91	35.45	Does not attend B.I. 2
18-RN-015	0.2349	0.0345	0.0148	0.1461	0.1962	0.0025	66.1	0.2842	0.3448	19.26	9.63	OK
18-RN-016	0.0954	0.012	0.009	0.0702	0.1136	0.0015	38.3	0.1165	0.1853	45.62	22.81	Does not attend B.I. 2
18-RN-017	0.0444	0.0495	0.0107	0.0302	0.1549	0.0008	12.2	0.1046	0.1859	56	28	Does not attend B.I. 2
18-RN-018	0.2134	0.07	0.0132	0.1275	0.1446	0.0154	45.1	0.2966	0.2875	3.11	1.56	OK
18-RN-019	0.0644	0.05	0.0173	0.031	0.1239	0.0015	25	0.1317	0.1564	17.15	8.58	OK
18-RN-020	0.1918	0.066	0.0329	0.0767	0.0929	0.01	49.6	0.2907	0.1797	47.22	23.61	Does not attend B.I. 2
18-RN-021	0.465	0.0495	0.0551	0.2762	0.1927	0.001	120	0.5696	0.47	19.18	9.59	OK
18-RN-022	0.5581	0.052	0.0658	0.2858	0.2065	0.0004	128.9	0.6758	0.4927	31.35	15.67	Does not attend B.I. 1
18-RN-023	0.1133	0.0095	0.0206	0.0406	0.1755	0.001	33.8	0.1434	0.2172	40.95	20.47	Does not attend B.I. 2
18-RN-024	0.18	0.014	0.0173	0.1563	0.1755	0.0027	35	0.2113	0.3345	45.15	22.57	Does not attend B.I. 2
18-RN-025	0.1011	0.03	0.0345	0.0062	0.1962	0.001	17.5	0.1656	0.2034	20.49	10.24	OK