



A hydrogeological impact survey on the largest onshore oil field in Brazil: physicochemical and total petroleum hydrocarbon (TPH) analyses in the south of Japarutuba River Basin, Sergipe

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Abstract

The Japarutuba River Basin is one of the most important hydrogeological units in terms of water demand in the state of Sergipe, Brazil. Due to its poorly developed water supply plan, oil exploration and agricultural industries, the Japarutuba River Basin is susceptible to considerable environmental stress. Emphasis is given to the area of the Campo de Carmópolis which, being the largest onshore oil field in Brazil, represents the greatest agent of environmental pollution in the area. The aim of this study is to characterise the contaminants present in surface water and groundwater of the southern part of Japarutuba River Basin region which is proximal to Carmópolis Oil field. We performed physicochemical and total petroleum hydrocarbons (TPH) analyses in ten water samples from the southernmost part of the basin. To better characterise the hydrogeological systems, 27 physicochemical parameters were analysed: potential of hydrogen (pH), colour, turbidity, electrical conductivity (EC), hardness, acidity, alkalinity, iron (Fe), nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3), chloride (Cl^-), phosphorus (P), fluoride (F^-), sulphate (SO_4^{2-}), bromate (BrO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+) bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), aluminium (Al^{3+}), manganese (Mn^{2+}), total dissolved solids (TDS), chlorite (ClO_2^-) and glyphosate. The results identified concentrations above Brazil's maximum permitted value (MPV) for TPH in two samples, and at least four samples presented values that do not meet the potability standards established by Brazilian federal legislation (*Portaria de Consolidação N° 5, 2017*). This enforces the need for more robust remediation and mitigation methods on the contaminated sites, since the local population relies solely on these water resources and poor management would lead to health hazards and socioeconomic impacts. Continuous monitoring of sampled locations along with an increase in sampling mesh are also recommended.

Keywords Japarutuba river basin · Total petroleum hydrocarbons (TPH) · Physicochemical analyses · Onshore oil fields · Hydrogeology

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Introduction

Although contaminated groundwater systems are complex to remediate, assessments on the impact of industrial and anthropogenic activities in water systems are crucial for the development and application of novel environmental monitoring and conservation policies (Lovley 2001; Valinia et al. 2014; Freedman 2015).

As petroleum-derived contaminants tend to be transported as a dissolved phase in soil pore water, they can rapidly reach deep and shallow water systems, causing groundwater contamination (Maciel et al. 2015). This is one of the main concerns of oil spills due to environmental and social impacts related to them, especially when the affected resources are destined for human consumption.

The Japarutuba River Basin is particularly important because it houses the Carmópolis Oil Field, with the largest onshore oil reserves in Brazil (Petrobrás 2017). As one of the Sergipe's oldest fields (56 years of production), it has 1056 active oil wells, an accumulated production of 387 million barrels of oil and 14.73 million barrels of gas as of April 2017.

Based on the possible impact of industrial and oil activities on the quality of the water provided to the population in this region, the aim of this study was to: (1) characterise water quality in the southern part of the Japarutuba River Basin based on the physicochemical and total petroleum hydrocarbons (TPH) analyses of water collected from wells and surface water bodies; and (2) to analyse the relationship between water quality in Japarutuba River Basin in relation to organic and inorganic parameters and contaminants.

TPH is defined as a mixture of an extensive family of chemical compounds that originate from crude oil i.e. gasoline, kerosene, fuel oil, asphalt, mineral oil, etc. (Pawlark et al. 2008). When released into nature, most of the lower molecular weight TPH compounds can migrate through water and soil while undergoing oxidation, dissolution, and biotransformation processes (Teng et al. 2013). Due to the low vapour pressure, high octanol/water partition coefficient (K_{ow}) and low solubility in water, the heavier TPH molecules are slowly desorbed into the aqueous phase of the oil–soil matrix (Coulon et al. 2010). TPH compounds can then infiltrate groundwater, spread from the initial contamination spot, and become a suitable reservoir for hydrophobic contaminants (Adeniji et al. 2017).

Petroleum hydrocarbon (PH) pollutants present significant health risks to humans, both in the short and long term. Studies have shown a correlation between cancer risk rates and PH contaminants through their carcinogenic and mutagenic toxicity properties (Teng et al. 2013; Adeniji et al. 2019). Smaller TPH compounds such as benzene, toluene,

and xylene, for example, can affect the human central nervous system and high exposures can cause death (Todd et al. 1999). Furthermore, oil spills can cause severe damage to different ecosystems and natural resources (Wang et al. 2013).

This study presents an initial assessment on the environmental impact related to the activities of agricultural and oil industries and recurrent oil spills through TPH and physicochemical analyses of surface and groundwater.

Study site

The Carmópolis Oil Field is located in the Japarutuba River Basin (JRB) in Brazil (Fig. 1). The JRB is important to the State of Sergipe due to its regional well-developed economy which is supported by a range of extractive activities such as sugarcane cultivation which comprise a significant part of the JRB region. In addition, the JRB is home to about 18 municipalities in Sergipe and it is the main source of water supply to about 5.9% of the population of the State of Sergipe. Because of the public water supply deficit, many inhabitants rely on groundwater supply through private wells on their properties. During our field survey, we noted that most wells we mapped had never been tested for potability criteria.

This area attracted our attention due to the frequent oil spills that were reported to the local environmental authorities throughout 2017.

Geological and hydrogeological settings of the study area

Geology of Japarutuba River Basin

According to CPRM (2003), the Japarutuba River Basin is located in the tectonic–stratigraphic region of the Sergipe/Alagoas basin, Sergipano Fold Belt and part of the crystalline basement. The study area is situated within the Sergipe Alagoas basin represented by Cotinguiba (Sapucari and Aracaju Members), Riachuelo (Angico, Maruim and Taquari Members), Serraria and Bananeira formations. On top of the aforementioned formations lies the Barreiras Group and the recent alluvial deposits, which comprises the unconsolidated to loosely consolidated sediments present in our sampling area.

The Sergipe–Alagoas basin is divided into five stratigraphic supersequences: Paleozoic supersequence, Pre-Rift, Rift, Post-Rift and Drift (Campos Neto et al. 2007; Haeser 2015).

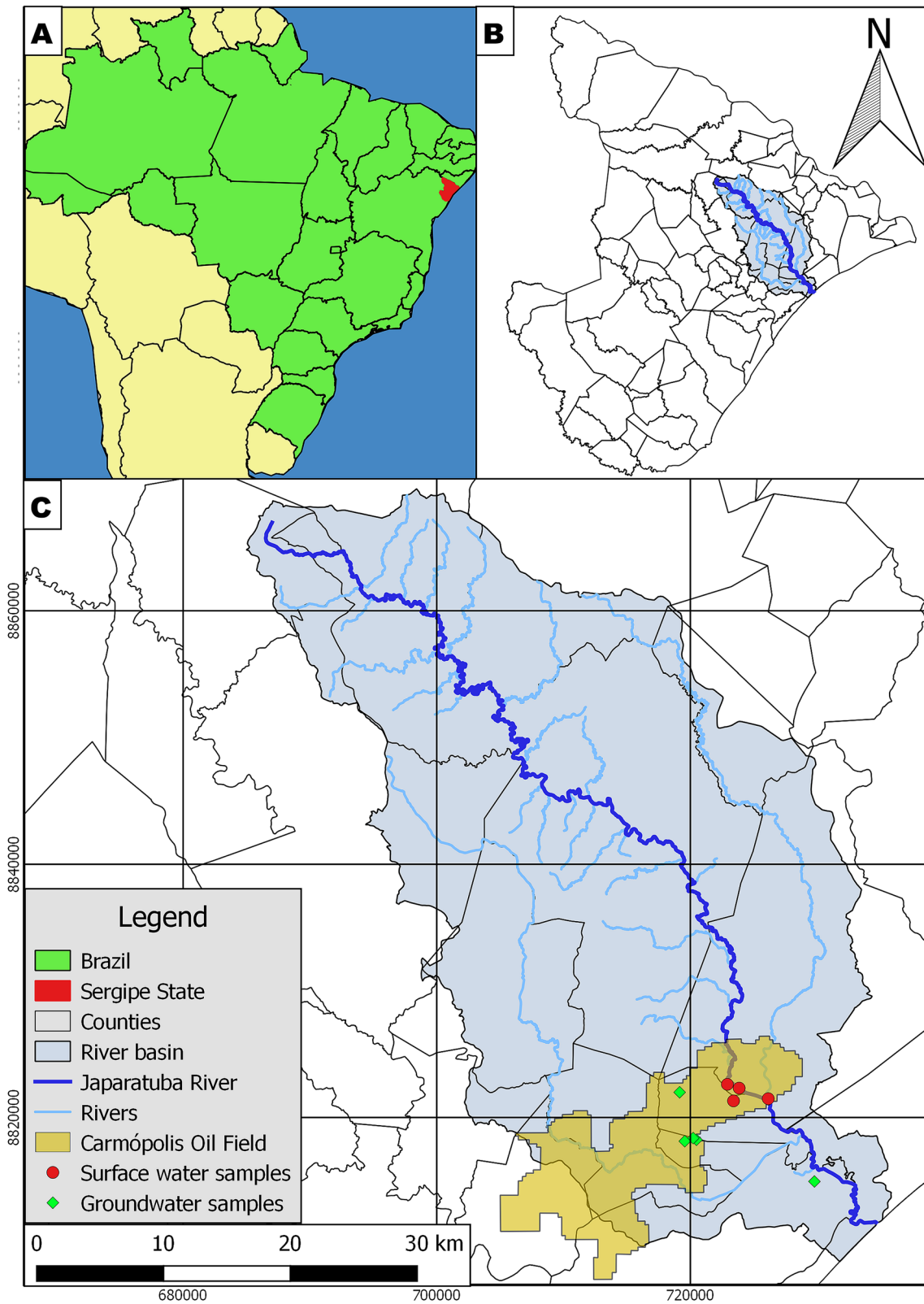


Fig. 1 a Brazil boundaries with the State of Sergipe (red colour), b Sergipe state and the Japarutuba River Basin. c Carmópolis Oil Field location in relation to Japarutuba River Basin

The pre-Rift supersequence is characterised in the study area by wind-reworked sandstones of Serraria Formation and the lacustrine red shales of Bananeiras Formation (Campos Neto et al. 2007). The Rift supersequence is represented by sandstones and shales of the Feliz Deserto Formation, shales of Barra de Itiúba Formation, fluvio-deltaic sediments of Coqueiro Seco Formation and carbonates of Morro do Chaves Member. Sandstones and shales of the Maceió Formation appear on top of the supersequence. The Post Rift supersequence is represented by the first marine incursions that lead to the deposition of the evaporitic sequences which comprise the Muribeca Formation. The Drift supersequence is characterised by the start of deposition of sandstones, carbonates and shales of Riachuelo Formation. The shales of the Cotinguiba Formation were deposited as part of a transgressive event during the Neocenomanian to Coniancian (Feijó 1994).

The Barreiras Group covers the rocks of the Sergipe Basin and the Sergipano Belt (Siqueira and Silveira 2017). The Barreiras Group sediments are predominantly continental in origin (Lima 2010). However, studies show that there is also the influence of transitional and marine environments (Bezerra et al. 2006; Arai 2006). Although extensive discussion exists regarding the Barreira's sediments' provenance, the group is predominantly described as terrestrial sedimentation with predominance of sands

ranging from conglomerates, gravels, and clays (Santos et al. 1998).

Geology of Carmópolis field

The Carmópolis field, which is about 170.857 km² in length, is the fourth largest oil field in Brazil and the largest onshore field (Campos et al. 2005; ANP 2016; Petrobrás 2017). Its main source rocks are the black shales of Ibura Member and Muribeca Formation as well as the Albian–Cenomanian shales of the Angico (K1ra), Marium (K1rm) and Taquari (K1rt) members from the Riachuelo Formation (Santos et al. 1998; Haeser 2015). The system is also formed by grey shale and calcilutite deposits of the Cotinguiba (K2cts) and Calumbi Formations (K2ca) (Fig. 2).

The rocks that generate these formations have been deposited in a restricted marine environment and can reach up to 12% organic carbon content. In the Carmópolis field, these rocks are composed of Precambrian muscovite–shale and garnet–biotite shales. Conglomerates of the Muribeca Formation and the fractured crystalline basement act as the main reservoirs of the oil system. A system of geological aptian faults-block shales act as a trap and seal, respectively (Milani and Araújo 2003).

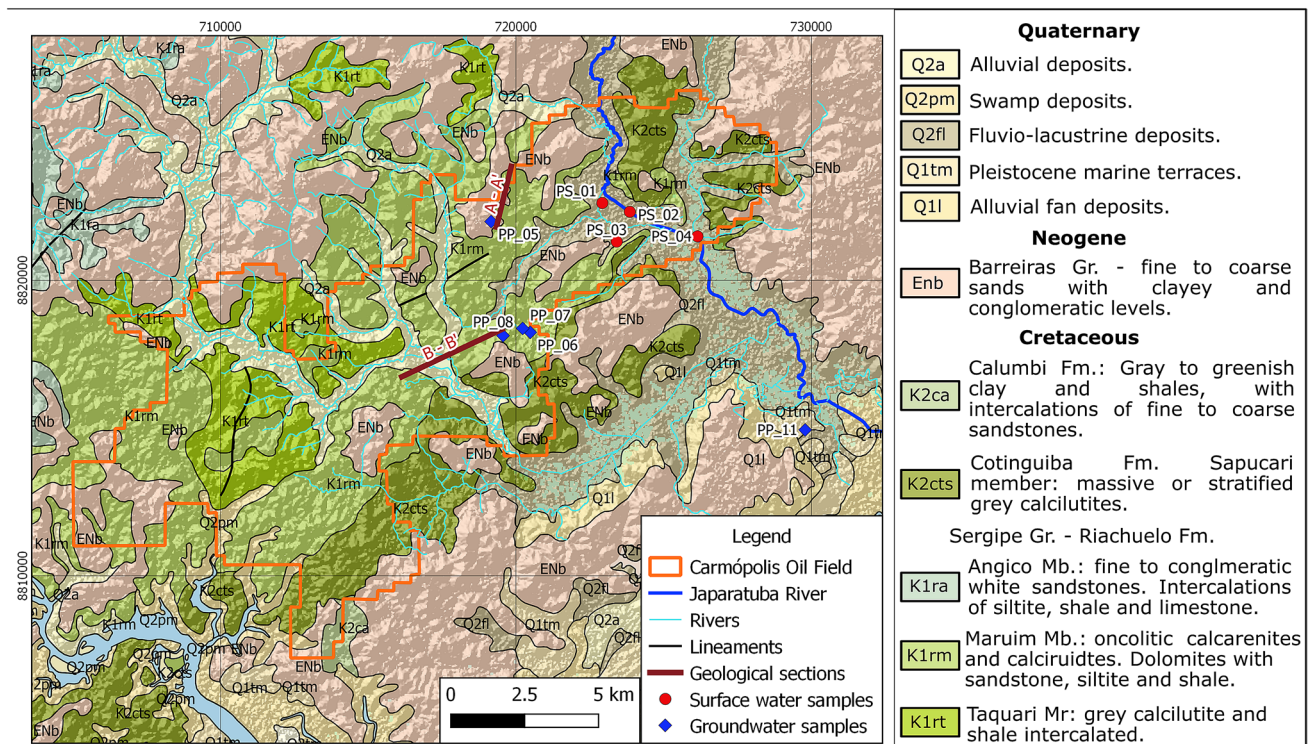


Fig. 2 Geological map of Carmópolis Oil Field. Source: Santos et al. (1998)

Hydrogeology of the study area

According to CPRM (2003), the study area contains two distinct hydrogeological units that host groundwater flow systems: i.e. the Taquari/Maruim and Tacaratu (Barreiras Group) systems (Fig. 3). The stratigraphy of the hydrogeographic units was reconstructed based on the lithological

information from corresponding water wells registered on the groundwater information system *Sistema de Informações de Águas Subterrâneas* (SIAGAS) (CPRM 2011) and are represented on two geological sections (Fig. 4). The location of the geological sections is shown on Fig. 2.

da Araújo et al. (2009) define the Taquari/Maruim hydrogeological unit as the aquifer system formed by Taquari and

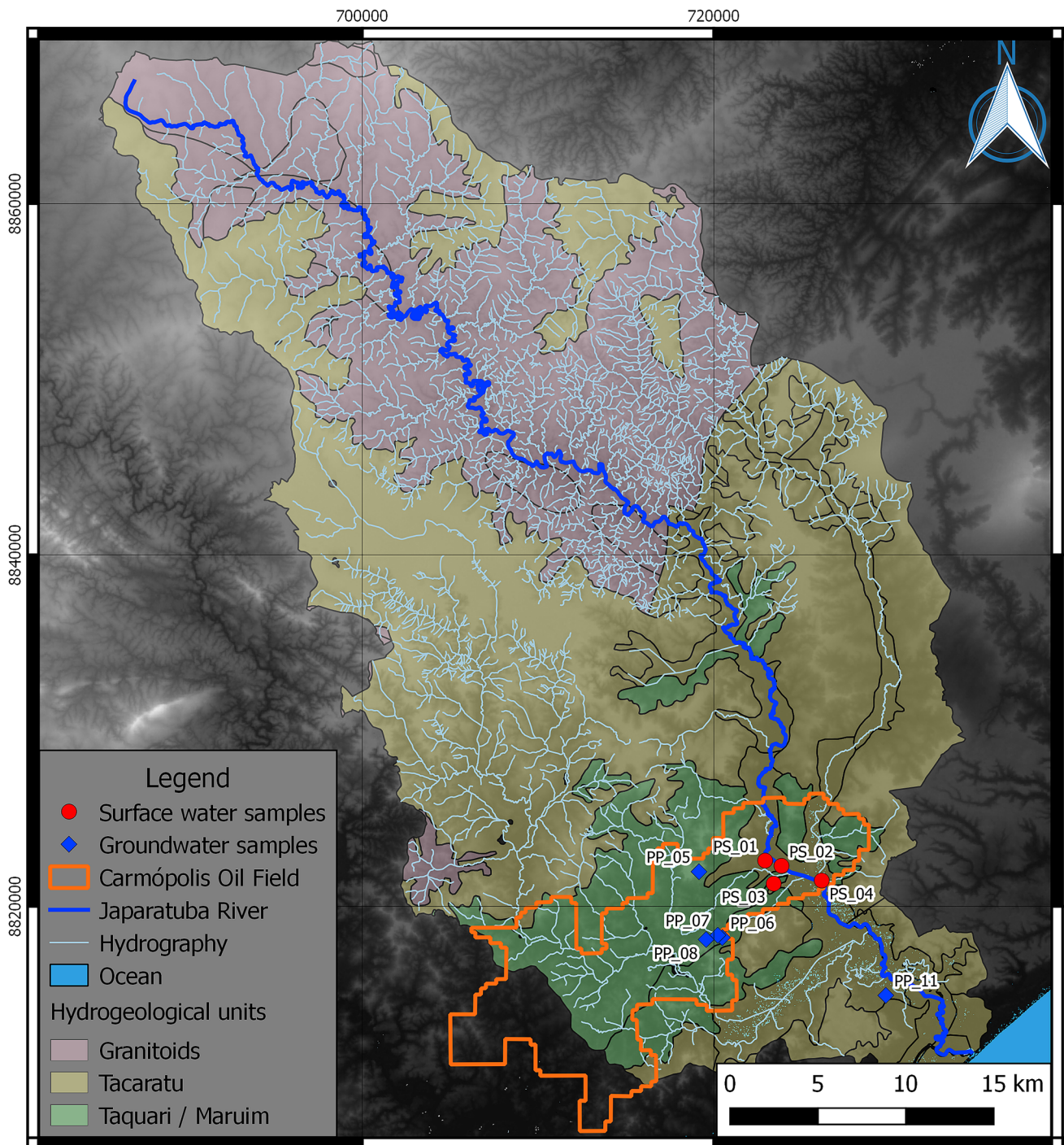


Fig. 3 Hydrogeology map of Japarutuba River Basin. Source: CPRM (2003). SRTM image courtesy of the U.S. Geological Survey

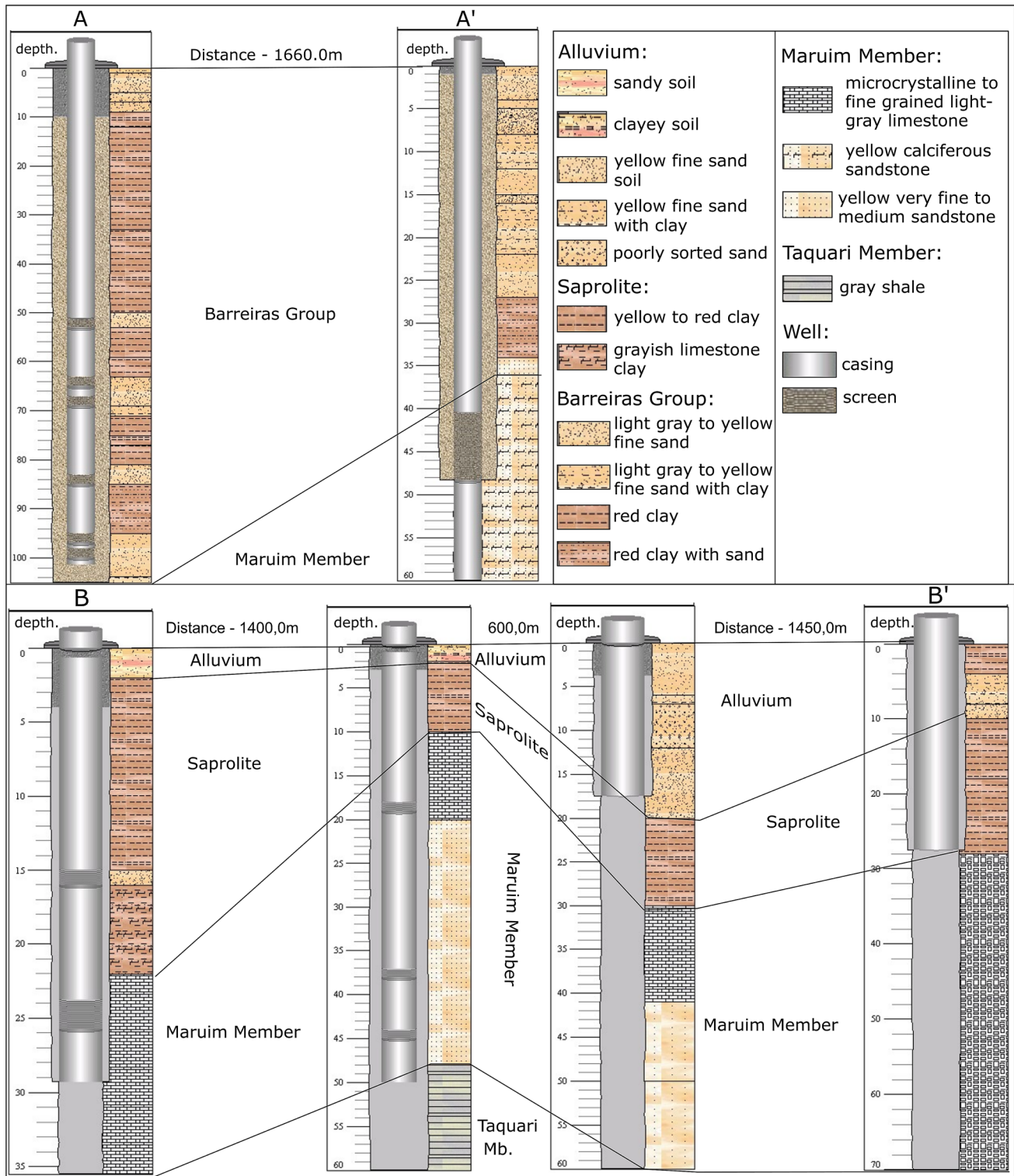


Fig. 4 Geological sections A–A' (top) and B–B' (bottom) based on well stratigraphic correlations from lithological information referenced in SIAGAS

Maruim members from Riachuelo Formation. The Maruim Member is mainly formed by calcarenites, oolite–oncolite calcirudites and dolomites with intercalations of sandstones,

siltstones, and shales. The member, which is 100–350 m thick, is laterally alternated with the Taquari Member. The latter is formed by grey calcilitites with interspersed

shales. The aquifer system is classified as heterogeneous and anisotropic with an average flow rate of $15.2 \text{ m}^3 \text{ h}^{-1}$ being obtained from existing wells. The Taquari/Maruim hydrogeological unit contains about 35% of the exploitable groundwater reserves of the area (SEMARH 2015; Ribeiro et al. 2017). In the study area, the Maruim Member is represented by microcrystalline to fine limestones and very fine to medium sandstones (Fig. 4). Yellow calcareous sandstones also occur, although less frequently. Considering the construction of the wells found in the study area, we could affirm that these horizons are being used as water capture zones, as the presence of filters is observed on well profiles and there is no casing when the water is captured directly from the rock, as indicated by the sandstones and limestones from Maruim Formation.

The Tacaratu Aquifer, which has a moderate to low permeability, is formed by unconsolidated sediments including silts, poorly sorted sands and clays. Several authors classify this aquifer as the Barreiras Aquifer since it is part of the Barreiras Group (da Araújo et al. 2009; SEMARH 2015). The aquifer has a maximum thickness of 170 m and occurs discontinuously covering the crystalline basement while acting as a capstone layer of the Taquari/Maruim Aquifer unit. According to SEMARH (2015), the (Tacaratu) Barreiras Aquifer has a high hydrographic potential and contains more than 60% of the exploitable groundwater reserves of the basin.

In the study area, groundwater is mainly exploited from the sandstone facies of the Barreiras Group, as shown on section A–A' in Fig. 4. In the proximal portion of the Japarutuba River, the Tacaratu Aquifer encompasses the Cenozoic deposits and the average flow rate from existing wells is $15.3 \text{ m}^3 \text{ h}^{-1}$.

Materials and methods

Water sampling was carried out in December 2018, during a period of moderate rainfall in the region. The sampling points were chosen in accordance with physical and historical characteristics of the study area. Regions where episodes of oil leakage had been registered and reported to the competent authorities were chosen as points of interest, as well as those representing important hydrological features, such as tributary river connections. Thus, we collected superficial and groundwater samples at ten different sites along the Japarutuba River and its distributary channels, within the area where reported oil leakage had occurred. Groundwater samples were collected from public supply wells and private wells. Coordinate information was collected with Garmin GPS map 60CSx on the SIRGAS 2000 Datum with UTM coordinates in Zone 24S.

For the collection of surface and groundwater for TPH and physicochemical analyses, we adopted the procedures described on the guidelines established by the Standard Methods for Examination of Water and Wastewater (APHA 2017). When considering a turbulent water environment, surface-water samples were collected at a depth of 20 mm below the water surface. In all cases, 1 L of water was collected in a polyethylene or glass container (for TPH analysis) positioned at 45 degrees from the water surface. The groundwater samples were collected after the well had been pumped for 10 min. The samples were cooled in iceboxes, aiming to stabilize the temperature between 0 and 4 °C. In samples destined to TPH analysis, 2 mL of hydrochloric acid (HCl) was added for stabilization at $\text{pH} < 2$. The universal pH measurement strip KASVI was used for pH measurement on site.

For the evaluation of petrogenic contaminants, we performed the analysis of the total petroleum hydrocarbons (TPH) to explore the relationship between the type and origin of the contaminants found in the study site. TPH analyses were executed at the Laboratory of Petroleum and Energy from Biomass (PEB) of the Federal University of Sergipe (UFS), following the standard protocols from the United States Environmental Protection Agency (US EPA 1996 and 1999). Physicochemical analyses were carried out at Sergipe Sanitation Company Laboratory (DESO) in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA 2017). In total, 27 parameters were analysed: potential of hydrogen (pH), colour, turbidity, electrical conductivity (EC), hardness, acidity, alkalinity, iron (Fe), nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3), chloride (Cl^-), phosphorus (P), fluoride (F^-), sulphate (SO_4^{2-}), bromate (BrO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+) bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), aluminium (Al^{3+}), manganese (Mn^{2+}), total dissolved solids (TDS), chlorite (ClO_2^-) and glyphosate. The analyses were performed in duplicate and the mean value for each parameter was considered.

For the TPH analysis, we submitted the samples to an extraction process according to the guidelines established in US EPA Method 1664 (US Environmental Protection Agency 1999). The TPH concentration was determined by performing triplicate measurements for each sample. The analysis was executed on a GC–FID system (LECO/Agilent, 7890A) equipped with a DB-5 fused silica capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). A volume of $1 \mu\text{L}$ of the extract was injected in 1:10 split ratio in an injector at 290 °C, and the carrier gas (H_2) was adjusted to a constant flow of 1.0 mL min^{-1} . Hydrogen was utilised as carrier gas because it provides the best separation performance in the capillary column. When compared to other carrier gases, hydrogen outperforms nitrogen, helium and argon in the van Deemter plot as it produces a shorter theoretical plate,

reducing the time and temperature required for the separation process. This leads to an increase in column longevity and efficiency (Heseltine 2010; Fidelis 2011). The initial temperature of the oven was 50 °C, followed by a ramp of 8.0 °C min⁻¹ to 290 °C and held for 15 min. The detector temperature was 300 °C for the entire analysis, which had a total duration of 81 min. Data acquisition and processing were performed with ChromaTOF[®] software 4.34.

We executed a calibration curve and method validation to obtain threshold figures of merit. The standard solutions were prepared using petrodiesel diluted in *n*-hexane (95%) at a concentration range of 100–1000 µg kg⁻¹. We performed the extraction and fraction procedure for the curve in triplicate, allowing the detection and quantification of hydrocarbons between *n*-C₈ and *n*-C₃₀. The recovery obtained for the method was 87.1%. The linearity (R^2) was 0.99, the detection limit was 90.72 µg kg⁻¹ and the quantification limit was 274.9 µg kg⁻¹.

The assessment of the values obtained in the analysis were based on CONAMA (National Environment Commission) resolutions and the *Ministério da Saúde* (Ministry of Health) directives. Among them, two served as reference to classify water systems and correlate physicochemical values: (1) the CONAMA Resolution 357/2005, which provides the classification and regulation for water bodies and establishes guidelines for the discharge of effluents (Brasil 2005); and (2) CONAMA Resolution 420/2009, which accounts for the criteria and values for contaminants in soil and groundwater (Brasil—*Conselho Nacional do Meio Ambiente* 2009).

To establish the comparative parameters for water quality and potability, we utilised the *Portaria de Consolidação N° 5, 2017*. The maximum permitted values (MPV) of organic, inorganic, and organoleptic substances for water intended for human consumption are set out in Annex XX, assigned in Chapter V, Art. 27 to 39 (Brasil 2017).

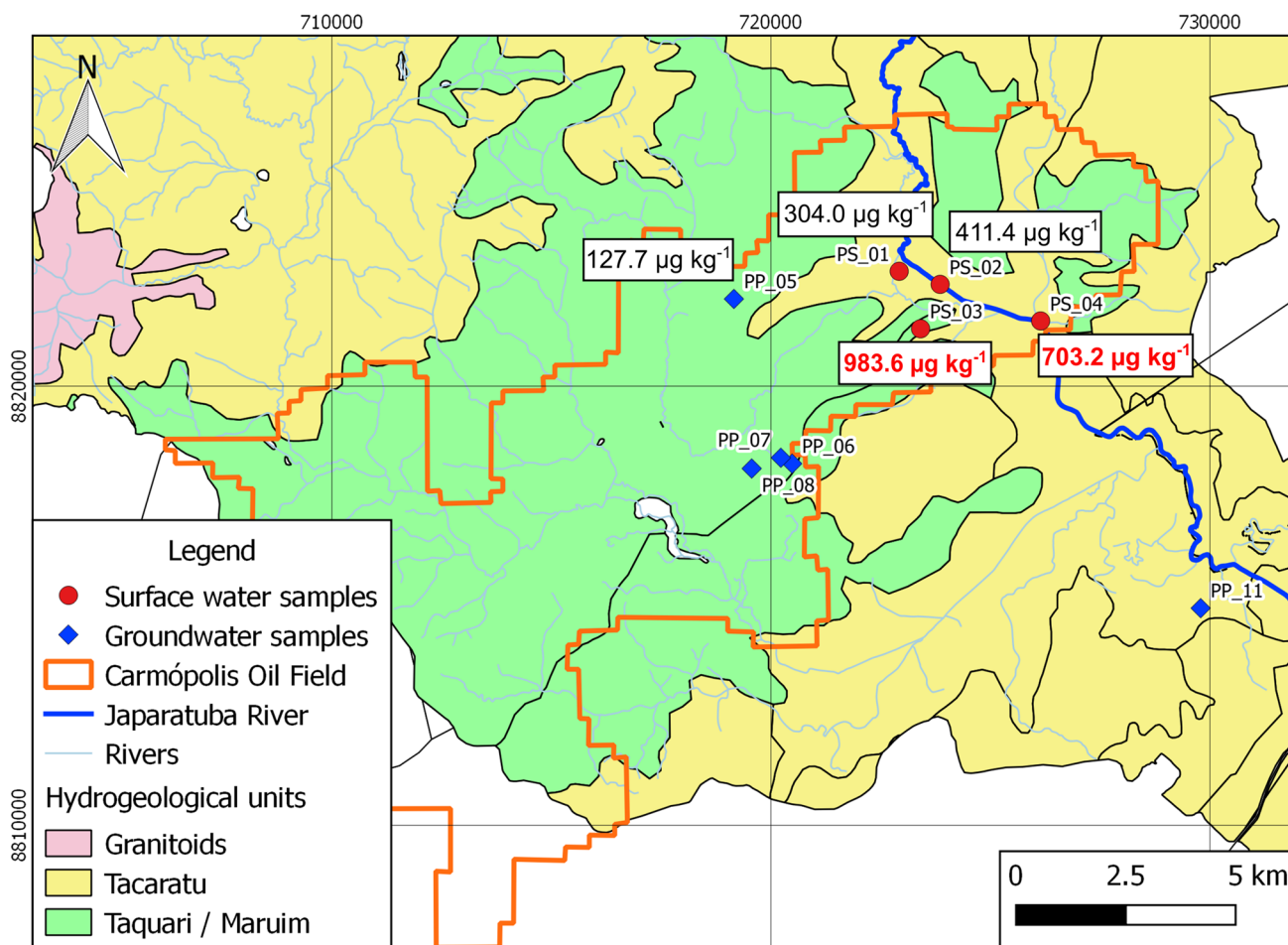


Fig. 5 TPH concentrations obtained for water samples. Values above the maximum permitted value (MPV) are in red

Results

TPH results

All five samples analysed by GC–FID detected significant concentrations of TPH (Fig. 5). Two samples, PS-03 and PS-04, had concentrations above the maximum permitted values (MPV) established by CETESB ($> 600 \mu\text{g kg}^{-1}$) (Fig. 5, values in red). PS-01 and PS-02 presented concentrations below the intervention limit. One groundwater sample, PP-05, presented values ($127.7 \mu\text{g kg}^{-1}$) below the limit of quantification for the calibration curve ($274.9 \mu\text{g kg}^{-1}$). Although the concentration of TPH was measured in this sample, no n-alkane peaks could be identified on the chromatogram profile.

The chromatograms obtained for the five samples (PS-01, PS-02, PS-03, PS-04 and PP-05) are shown in Fig. 6. The peaks of n-alkanes represented as a homologous series are identified in each chromatogram.

Physicochemical results

We categorized the physicochemical results into surface water (PS) and groundwater (PP). The following tables show the results for surface water samples (Table 1) and groundwater (Table 2) together with maximum permitted values (MPV) by consolidation ordinance No. 5 from the Ministry of Health in Brazil.

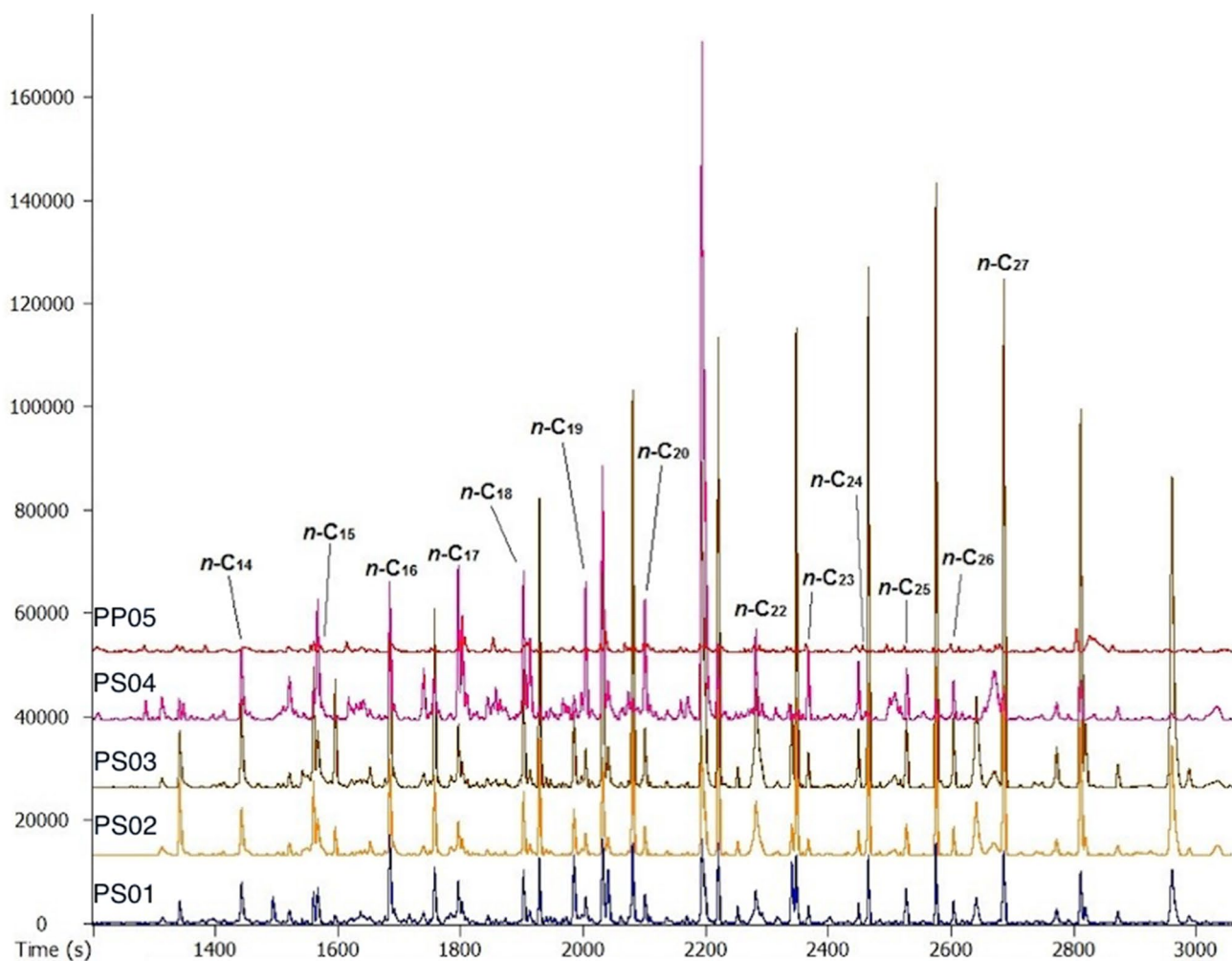


Fig. 6 Chromatograms of the samples with the peaks of n-alkanes assigned

Table 1 Values obtained from the physicochemical analysis of surface water samples

Surface water					
Parameter	MPV	PS-01	PS-02	PS-03	PS-04
Colour (µH)	15	96	55	111	37
Turbidity (NTU)	40	17.4	10.3	26.8	10.6
pH	6–9	3.0	7.7	8.0	7.5
Conductivity (µS cm ⁻¹)	–	45,320.0	659.8	931.3	563.8
Total hardness (mg L ⁻¹)	500	16,345.77	231.58	317.52	265.63
Fe (mg L ⁻¹)	0.3	3.3	0.7	1.2	0.3
Alkalinity	–	7.09	13.57	8.94	8.46
NH ₃ (mg L ⁻¹)	1.5	<0.10	<0.10	<0.10	<0.10
NO ₃ ⁻ (mg L ⁻¹)	10	4.5	1.6	0.3	1.5
NO ₂ ⁻ (mg L ⁻¹)	1	<0.10	<0.10	0.04	<0.10
P (mg L ⁻¹)	0.1	0.0	0.0	0.1	0.0
Cl ⁻ (mg L ⁻¹)	250	20,026.33	117.81	181.91	77.79
F ⁻ (mg L ⁻¹)	1.4	3.15	0.13	0.08	0.04
SO ₄ ²⁻ (mg L ⁻¹)	250	222.86	11.63	19.51	6.78
BrO ₃ ⁻ (mg L ⁻¹)	0.01	<0.01	<0.01	<0.01	<0.01
Ca ²⁺ (mg L ⁻¹)	–	2221.30	47.12	71.56	67.14
Mg ²⁺ (mg L ⁻¹)	–	2590.20	27.31	33.27	23.47
K ⁺ (mg L ⁻¹)	–	691.05	6.55	6.51	4.50
Na ⁺ (mg L ⁻¹)	200	6306.95	68.47	95.99	48.54
HCO ₃ ⁻ (mg L ⁻¹)	–	0.00	0.00	46.77	87.26
CO ₃ ²⁻ (mg L ⁻¹)	–	0.00	231.58	270.75	178.37
Al ³⁺ (mg L ⁻¹)	0.2	0.32	0.01	0.01	0.01
Mn ²⁺ (mg L ⁻¹)	0.1	<0.02	<0.02	<0.02	<0.02
T.D.S ^a	500	23,113.20	336.50	162.46	287.54
Chlorite	1	<0.10	<0.10	<0.10	<0.10
Glyphosate	500	<100	<100	<100	<100

Values above the MPV are marked in bold

^aTDS total dissolved solids

Discussion

TPH analysis

Regarding the chromatographic profiles obtained for the surface water samples, the locations PS-01, PS-02 and PS-03 presented a similar pattern with respect to the nature of the oil. It could be interpreted that the source of contamination in these three points comes from oils of the same nature, since the ratio between n-alkanes and other hydrocarbons is equivalent.

Another hypothesis to be considered is that oils with similar nature have been exposed to equivalent conditions of biodegradation and, therefore, the relationship between n-alkanes and other hydrocarbons presented a similar pattern in the chromatogram fingerprints (Peters

and Moldowan 1993). It is noteworthy that these samples were from the Japaratuba River (PS-02), its distributary stream (PS-03), and its floodplain (PS-01). Therefore, they undergo a similar seasonal regime.

The samples PS-03 and PS-04 presented concentrations of 983.6 µg kg⁻¹ and 703.2 µg kg⁻¹, respectively, which is above the MPV (<600 µg kg⁻¹). This may be related to the proximity to the oil pumps and pipes where chances of surface leaks are high.

When considering the time elapsed between the leaking episodes and the collection (16 months later), the low incidence of light hydrocarbons at these points can be justified by the processes of biodegradation, evaporation and dissolution. As the areas where the samples were collected are fluvial environments, microbiological activity plays an essential role in this sense, since bacteria use this type of organic matter for metabolic activities (Varjani 2017).

It is important to note that, for the chromatograms obtained from samples PS-01, PS-02, PS-03, where the retention time of the compounds is > 2500 s, a larger area for the peaks at the end of the chromatographic profile is observed. According to Wang et al. (2002), this chromatographic behaviour is indicative that there are probably more hydrocarbons to be detected and/or quantified. Thus, the quantified concentrations for these samples may be higher than those presented in this work.

The sample PS-04 stands out from the other samples analysed. The chromatogram obtained for this sample shows a considerably higher paraffinic hydrocarbon (n-alkane) distribution than that observed for the others, where the ratio between the peaks of n-alkanes and other hydrocarbons was lower.

Thus, the analysis of the chromatographic profile supports the interpretation that PS-04 comes from an oil of a different nature to the other points analysed. Another interpretation is that the oil comes from a recent leak, since the paraffins in the range of n-C₁₄ to n-C₃₀ show no signs of biodegradation.

According to Nunes et al. (2017), the presence of n-alkanes and the absence of isoprenoids indicate that the oil has not yet undergone biodegradation processes, as was assumed for samples PS-01, PS-02, and PS-03. As PS-04 was collected at the intersection of the Japaratuba–Mirim River and the Japaratuba River, which is downstream from the collection site of the other samples, there is a high chance of contamination from multiple oil sources.

Despite the presence of TPH in the PP-05 sample (TPH 122.7 µg kg⁻¹), the concentration was below the limit of quantification established by the calibration curve used (274.91 µg kg⁻¹). It is important to note that the sample originated from a public artesian well, popularly known as the Matinha's well, from which water is utilised for human consumption and domestic use with no prior chemical or biological treatment.

Table 2 Values obtained from the physicochemical analysis of groundwater samples

Groundwater						
Parameter	MPV	PP-05	PP-06	PP-07	PP-08	PP-11
Colour (μH)	15	2	12	21	57	23
Turbidity (NTU)	5	0.5	2.4	8.4	32.2	3.2
pH	6–9	5.2	6.1	6.2	5.6	4.9
Conductivity ($\mu\text{S cm}^{-1}$)	–	210.7	360.4	667.4	120.2	313.1
Total hardness (mg L^{-1})	500	39.27	124.58	192.54	22.15	24.39
Fe (mg L^{-1})	0.3	0.04	0.02	0.40	0.50	1.60
Alkalinity	–	4.28	0.40	8.69	0.30	4.76
NH_3 (mg L^{-1})	1.5	<0.10	<0.10	<0.10	<0.10	<0.10
NO_3^- (mg L^{-1})	10	12.12	12.17	2.18	6.13	0.02
NO_2^- (mg L^{-1})	1	<0.10	<0.10	<0.10	<0.10	<0.10
P (mg L^{-1})	–	0	0	0	0	0
Cl^- (mg L^{-1})	250	43.97	33.70	116.92	25.59	86.19
F^- (mg L^{-1})	1.40	0.03	0.10	0.11	0.02	0.01
SO_4^{2-} (mg L^{-1})	250	19.34	39.10	73.88	5.50	8.73
BrO_3^- (mg L^{-1})	–	<0.01	<0.01	<0.01	<0.01	<0.01
Ca^{2+} (mg L^{-1})	–	6.12	22.41	33.65	2.99	2.19
Mg^{2+} (mg L^{-1})	–	5.75	16.45	26.02	3.52	4.54
K^+ (mg L^{-1})	–	5.00	1.15	2.84	0.55	2.04
Na^+ (mg L^{-1})	200	29.48	35.67	106.31	20.38	60.52
HCO_3^- (mg L^{-1})	–	30.09	39.18	97.57	14.17	13.42
CO_3^{2-} (mg L^{-1})	–	9.18	85.39	94.97	7.98	10.97
Al^{3+} (mg L^{-1})	–	0.01	0.01	0.01	0.01	0.13
Mn^{2+} (mg L^{-1})	0.1	0.01	0.01	0.01	0.01	0.01
TSD ^a	1000	107.46	183.80	340.37	98.40	0.00
Chlorite	–	<0.01	<0.01	<0.01	<0.01	<0.01
Glyphosate	500	<100	<100	<100	<100	<100

Values above the MPV are marked in bold

^a TDS total dissolved solids

The presence of TPH in 100% of the analysed samples highlights the health and socioeconomic risks posed to the population owing to the lack of water management in the region and the need for continuous monitoring and treatment of these resources, not only by local authorities but also oil companies acting in the area.

Physicochemical analysis

In relation to the physicochemical results, we verified the presence of iron above the MPV established in approximately 66% of the samples. It should be emphasised that PS-01 presented a value ten times greater than the MPV for iron (0.3 mg L^{-1}). PP-11, which is from a well utilised for human consumption, presented values approximately five times above the MPV (1.6 mg L^{-1}). Samples PS-02 and PS-03 presented values approximately two times greater than the MPV. The sample PS-04, which was collected at

the intersection of the Japarutuba and Japarutuba–Mirim rivers, presented an acceptable value.

The high iron content present in the samples can be related to a range of factors, e.g. the geological composition of the hydrogeological unit and the physicochemical signature of the water, especially the pH, Eh, HCO_3^- and CO_2 dissolved values (Picanço et al. 2002).

When considering the geology of the region, where a large outcrop area of the Barreiras Group is observed, the high concentrations of iron detected may be explained by the fact that these geological units have lateritic soil horizons and are composed of sediments of continental provenance with mineral compounds that can release iron when in solution which, in advanced weathering stages, can influence the groundwater chemical signature (Picanço et al. 2002). Studies carried out in the same region by Correa et al. (2008) and Stefano et al. (2019) also suggested that the iron presence in groundwater can be related to Barreira's Group sediments.

In relation to the presence of ammonia and nitrites, there are no surface water samples with concentrations above the MPV, which we consider a positive sign in terms of anthropogenic contamination. However, concentrations were high and above the MPV in 40% of the groundwater samples. Considering that the samples were collected from wells located in urban areas, the contamination may come from anthropogenic activities such as effluent discharge. It is noteworthy that the water from these wells is utilised for human consumption with no prior biological or chemical treatment, especially PP-05 (Matinha's Well), which, as mentioned before, is the main source of water for a considerable part of the residents.

The concentrations of chloride, fluoride, sodium, carbonates and bicarbonates in the sample PS-01 (surface water sample) are greatly above the established MPVs. The hardness was also classified as "very hard" as it was approximately 32 times higher than the established MPV (see Table 1). The values obtained for PS-01 may be related to the seasonal water regime, the lacustrine characteristic and small size of the water body, the high content of organic matter which contributed to restricted water circulation and flow energy changes during low-precipitation months. It is worth mentioning that the area is surrounded by oil and gas pipes, which represents intense anthropogenic activity that can contribute to the abnormal physicochemical signature of the sample and explain the TPH concentration previously mentioned.

Previous studies have also related the high concentration of chlorides with the presence of contamination derived from human waste (Mendes and Oliveira 2004). Fortunately, most of the samples obtained showed low concentrations of these compounds.

Regarding turbidity, the samples PP-07 and PP-08 presented values above the allowed MPV. It is important to note that PP-08 showed values six times higher than MPV, which indicates a high concentration of solid materials suspended in water. A possible cause for high turbidity in this sample may be related to poor well conditions. The proximity of this point to a cemetery can also be a factor of influence. However, further analyses based on potentiometric and groundwater flow maps are required.

As previously mentioned, the current Brazilian legislation does not determine a maximum permitted value (MPV) for electrical conductivity (EC). However, according to literature, drinking water considered of good quality has values lower than $750 \mu\text{S cm}^{-1}$ (Mendes and Oliveira 2004). It was observed that samples PS-01 and PS-03 presented extremely high EC values ($45,320.0 \mu\text{S cm}^{-1}$ and $931.3 \mu\text{S cm}^{-1}$, respectively). EC properties are related to the concentration of salts dissolved in water, i.e. the quantity of mono and multivalent ions in liquid matter (Rhoades 1996; Sampaio et al. 2007). It is observed that, when compared to other samples,

PS-01 and PS-03 present high concentrations of cations and anions such as: Fe^{2+} , Cl^- , SO_4^{2-} , Ca^{2+} , and Mg^{2+} which influence not only the EC, but also the hardness of the water, especially when considering Ca^{2+} and Mg^{2+} concentrations. These factors, when added to the other parameters, decrease the quality of these waters for human consumption.

As for colour, the samples PP-07, PP-08, and PP-11 presented values above those recommended for drinking water. As an organoleptic parameter, colour is restrictedly a sensorial influence. However, changes in this parameter may be due to the presence of iron ions, manganese, and the decomposition of organic matter, as well as the lithology present in the region.

Glyphosate pesticide is one of the most widely used in the control of weeds (Queiroz et al. 2011). As several plantations are present in the region, typically sugarcane, it could be expected that high concentrations of this compound would be found. However, the concentrations of glyphosate were below the detection limit ($< 100 \mu\text{g L}^{-1}$) and are much lower than the allowed MPV. This probably occurs because the compound in question is easily absorbed by soils, making its drainage to water difficult.

Further considering the action of pesticides, phosphorus is a very present element in pesticide compounds in general. The low levels of phosphorus observed in both surface water and groundwater do not indicate that agricultural activities represent a major contribution to environmental impacts in the Japarutuba River Basin.

Conclusions

The analyses of physicochemical and TPH parameters in surface water and groundwater were extremely important for the characterisation of possible contamination scenarios in the southern Japarutuba River Basin.

The flame ionisation gas chromatography method was efficient to identify the concentrations of TPH. Of the five samples collected, two presented values above the maximum permitted value determined by Brazilian federal regulations. The chromatograms obtained indicate biodegradation signs in petroleum hydrocarbons originating from crude oil which indicates that contamination is not recent. Additionally, a possible new contamination point was identified, PS-04, which presented a concentration of $703.2 \mu\text{g kg}^{-1}$. The presence of hydrocarbon contaminants highlights the lack of effective water management in the Japarutuba and Japarutuba–Mirim rivers as well as the need for detailed environmental assessments on sites that are proximal to oil fields.

Physicochemical analyses indicated high levels of iron and nitrate in the cities of Carmópolis, General Maynard and Santo Amaro das Brotas, which are areas where the population rely on well systems to collect water. Whilst

groundwater samples did not show abnormal physicochemical signatures besides the nitrate and iron concentrations, the surface water samples that were contaminated represent a potential risk for aquifer contamination.

The results restate the need for remediation of certain areas, as well as the re-evaluation of water use for human consumption in specific locations. Specifically, point PS-01 requires significant remediation and control actions as the point can serve as a source of secondary contamination during periods of high river flow.

Given the complexity of the Japarutaba River Basin, continuous monitoring, expansion of the sampling grid and the addition of new physicochemical and soil sampling parameters are recommended. Future work should also include bacteriological analyses that can refine the results found in this study. Nevertheless, we recommend that both the responsible companies and the competent authorities should undertake remediation and mitigation measures to avoid further deterioration of water quality in the region. Failure to do so could represent severe health risks to the local population.

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