



Element contents in the lower São Francisco river assessed by inductively coupled plasma optical emission spectrometry (ICP OES) analysis.

Análise elementar das águas do Baixo Rio São Francisco avaliados por espectrometria de emissão óptica de plasma indutivamente acoplada (ICP OES).

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RESUMO: A bacia do rio São Francisco, também conhecida como Velho Chico, tem uma extensão de mais de 640 mil km² e percorre 2.700 km de Minas Gerais até chegar à foz no Oceano Atlântico, na divisa dos estados de Alagoas e Sergipe. Os corpos d'água são classificados em classes de acordo com os usos a que se destinam e de acordo com os requisitos estabelecidos. No presente trabalho, o objetivo foi traçar o perfil dos teores de B, Ca, Fe, K, Mn, V, Zn e Mg, presentes no rio São Francisco, por meio de espectrometria de emissão óptica com plasma indutivamente acoplado (ICP OES). Assim, propomos avaliar a qualidade da água do rio São Francisco com base em seus conteúdos de micro e macroelementos. De acordo com os resultados obtidos, a potabilidade da água do rio é avaliada com base nos padrões do Ministério da Saúde do Brasil. Pelos dados obtidos, as concentrações desses elementos estão abaixo dos limites máximos de tolerância e, portanto, essas águas atendem aos padrões de potabilidade nas condições testadas.

Palavras-chave: São Francisco, Qualidade da água, Potabilidade.

ABSTRACT: The São Francisco river basin, also known as Velho Chico, exhibits an extension of over 640,000 km² and runs 2,700 km from Minas Gerais to reach its mouth in the Atlantic Ocean, on the Alagoas and Sergipe states coast border. Water bodies or springs are classified according to the uses they are destined, concerning the established requirements. In the present work, the objective was to trace the profile of B, Ca, Fe, K, Mn, V, Zn e Mg contents present in the São Francisco river using inductively coupled plasma optical emission spectrometry (ICP OES). Hence, we propose to assess the water quality of the São Francisco River based on its micro and macro elements contents. According to the obtained results, the river water potability is assessed based on the Brazilian Ministry of Health standards. The concentration of these elements was below the maximum tolerance limits, and, therefore, these waters meet the potability standards under the conditions tested.

Keywords: São Francisco, Water quality, Potability.

INTRODUCTION

The São Francisco river spring is located at 1600 m of altitude, in the Serra da Canastra, in Minas Gerais state. The São Francisco river basin, also known as Velho Chico, exhibits an area of over 640,000 km², and runs 2,700 km from Minas Gerais to reach its mouth in the Atlantic Ocean, on the Alagoas and Sergipe states coast borders (SOARES; SILVA; NAVAS, 2020; SILVA; GALVÍNCIO; ALMEIDA, 2010). This river is bathes, along its route, six states: Minas Gerais, Bahia, Pernambuco, Alagoas, Sergipe, and Goiás, in addition to the Federal District. The lower São Francisco arises in the city of Paulo Afonso (BA) towards its mouth (BEZERRA et al., 2019; ARAÚJO; PEREIRA DE SÁ, 2008).

The São Francisco River has great ecological, economic, and social relevance for the regions in its course. Its waters are used in electricity generation, irrigation, navigation, water supply, fishing, and aquaculture. The hydroelectric plant systems being the most relevant cause of anthropic impact in its medium-low course, where the retention of materials and flow regulation by the dams contribute as a predominant parameter of river characteristics, the formation of the coastal plume, and the supply of materials in the ocean (ANDREWS; GROSS; HUTTON, 2017; PEREIRA et al., 2021; VASCO; NETTO; SILVA, 2019; MEDEIROS et al., 2011).

The discharge of pollutants through sewage systems, effluents, and diffuse contaminants also impacts the quality of aquatic bodies. Pollution and contamination of water resources can be caused by accelerated demographic growth, the lack of planning in urban development, especially in metropolitan regions, and the large population density (DANTAS et al., 2020; ANDRADE et al., 2019).

The present work aimed to trace Ag, B, Ca, Cu, Fe, K, Mn, and Mg contents present in the lower São Francisco river assessed by inductively coupled plasma optical emission spectrometry (ICP OES).

MATERIAL AND METHODS

Water sample collection

The water sample collecting points were determined by geoprocessing and are indicated by two initials letters regarding the city's name that holds the portion of the river where sample collection took place. Besides, the initials are followed by letters: A for the riverbank adjacent to the state of Sergipe; B for the middle of the river; and C that indicates the riverbank belonging to Alagoas.

Element determination by ICP OES

Element concentration in the water samples was determined by ICP OES (CARRILHO et al., 2002), and the operational parameters of the spectrometer are presented in Table 1. The choice of the analytes spectral lines was based on both their sensitivity and spectral interference. Blank solutions (15 replicates) were analyzed to determine the limits of detection (LOD) and quantification (LOQ) of each element (SHRIVASTAVA; GUPTA, 2011).

Table 1: ICP OES Operational parameters.

Power	1.10 kW
Plasma Gas Flow	15.0 L min ⁻¹
Gas flow auxiliary	1.5 L min ⁻¹
Flow nebulizer	0.65 L min ⁻¹
Sampling rate of	1 mL min ⁻¹
Wavelength	(nm)
V	311.837
B	249.772
Ca	422.673
S	181.972
Zn	213.857
K	766.491
Mg	280.270
Fe	238.204

The water sample collections were carried out during an expedition to cities alongside the São Francisco river, from November 18 to 26 in 2019. The samples were collected on the river banks, referring to Alagoas (left margin) and Sergipe (right margin) and in the middle of the river, according to georeferenced points in Table 2.

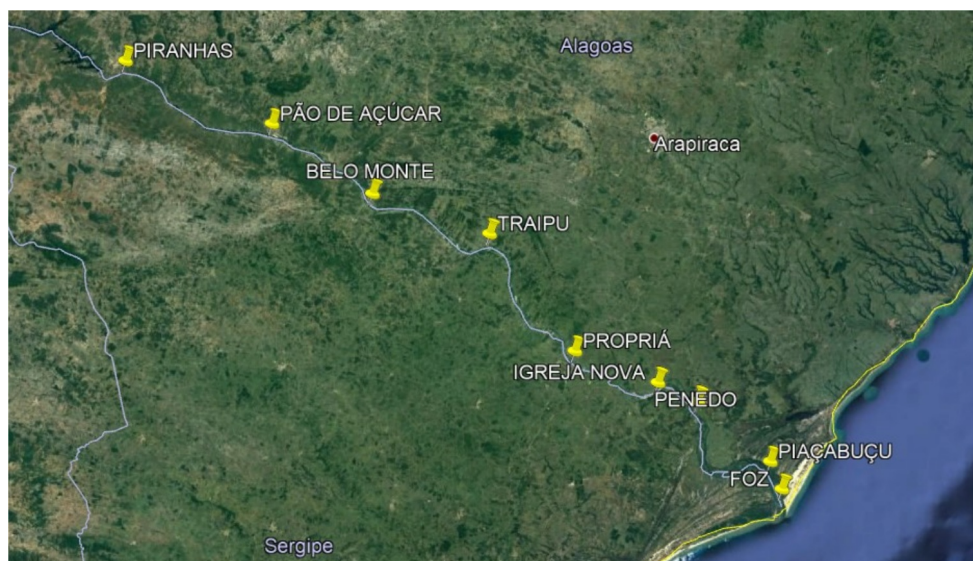
Table 2: Collection points according to georeferenced location, Sergipe (A) middle of the river (B) and Alagoas (C).

POINT	A		B		C	
	LATITUDE	LONGITUDE	LATITUDE	LONGITUDE	LATITUDE	LONGITUDE
Foz	10°28'35.00"S	36°23'54.96"W	10°28'53.36"S	36°24'28.44"W	10°29'9.02"S	36°24'39.24"W
Piçabuçu	10°24'43.45"S	36°25'50.52"W	10°25'34.15"S	36°25'54.84"W	10°25'25.47"S	36°26'33.47"W
Penedo	10°17'58.60"S	36°34'56.64"W	10°18'21.86"S	36°34'48.36"W	10°19'37.76"S	36°34'17.40"W
Igreja Nova	10°15'58.72"S	36°40'21.00"W	10°16'7.84"S	36°39'42.48"W	10°16'18.20"S	36°39'38.52"W
Propriá	10°11'32.07"S	36°50'12.48"W	10°12'23.39"S	36°49'52.68"W	10°12'44.18"S	36°49'40.80"W
Traipu	9°58'17.14"S	37° 0'21.96"W	9°58'21.39"S	37° 0'19.80"W	9°58'29.57"S	37° 0'24.12"W
Belo Monte	9°53'23.63"S	37°14'40.20"W	9°53'33.95"S	37°14'40.20"W	9°53'34.51"S	37°14'50.12"W
Pão de Açúcar	9°45'3.29"S	37°26'50.28"W	9°45'9.01"S	37°26'58.20"W	9°45'13.92"S	37°27'1.44"W
Piranhas	9°37'27.65"S	37°45'4.68"W	9°37'28.92"S	37°44'59.28"W	9°37'34.69"S	37°44'57.84"W

The linear distance from the first point in Piranhas to the last point in Foz measures 175 km. The collection points are plotted in the map of Figure 1.

(BRASIL, 2017). The legislation states that for elements of Fe, Mn, and Zn and the maximum concentrations 0.03, 0.1, and 5.0 mg/L, respectively.

Figure 1: Map of the collection points of the water samples located in the lower São Francisco River.



Some of the elements investigated, which the Ministry of Health does not regulate, were examined according to the water quality standards by the guidelines of CONAMA Resolution nº 430 (BRASIL, 2011). This legislation aims to regulate and inspect the exploitation of qualified water bodies to maintain their quality following social needs and the benefit of the

users. The legislation states the maximum level for B, Fe, Mn, and Zn as 5.0, 15.0, 1.0, 1.0 and 5.0 mg/L, respectively.

RESULTS AND DISCUSSION

In this work, we assessed the water quality of the lower São Francisco river to verify its potability according to the Ministry of Health established policies (Decree No. 5, of September 28, 2017; Chapter II, item III: "Potability standard: standard values of water quality parameters for human consumption")

Macro and microelements analysis

In Table 4, the concentration of the elements varies between the banks and the middle of the river and among the collection points is presented and varies significantly.

Table 3: Concentration (mg/L) of elements determined by ICP OES, in the water samples collected at different points of the lower São Francisco river. A: Sergipe; B: Meddle river; C: Alagoas.

COUNTY	POINT	MICROELEMENTOS (mg/L)					MACROELEMENTS (mg/L)			
		B	Fe	Mn	Zn	V	Mg	Ca	K	
FOZ	A	37.80	0.27	0.040	0.015	3.23	473.20	377.20	432.60	
	B	37.16	0.17	0.003	0.043	3.17	471.90	371.50	447.10	
	C	37.59	0.13	0.002	<0.0009	3.17	473.90	375.30	418.00	
PIAÇABUÇU	A	> 0.0066	0.22	0.007	0.052	< 0.0016	2.30	8.20	3.00	
	B	0.43	0.28	0.007	> 0.0009 < 0.0030	0.260	125.70	45.72	56.80	
	C	> 0.0066	0.19	0.007	< 0.0009	< 0.0016	2.40	7.82	2.90	
PENEDO	A	> 0.0066	0.12	0.005	< 0.0009	< 0.0016	2.20	7.82	2.60	
	B	> 0.0066	0.2	0.007	0.067	< 0.0016	2.20	8.06	2.60	
	C	> 0.0066	0.11	0.006	< 0.0009	< 0.0016	2.10	7.75	2.10	
IGREJA NOVA	A	> 0.0066	0.68	0.010	0.054	< 0.0016	2.30	8.47	3.10	
	B	> 0.0066	0.45	0.007	0.035	< 0.0016	3.10	9.00	2.70	
	C	> 0.0066	0.24	0.016	0.035	< 0.0016	2.20	7.57	2.40	
PROPRIÁ	A	> 0.0066	0.18	0.005	> 0.0009 < 0.0030	< 0.0016	2.20	8.01	2.20	
	B	> 0.0066	0.22	0.006	0.072	< 0.0016	3.60	8.60	2.70	
	C	> 0.0066	0.23	0.006	< 0.0009	< 0.0016	2.20	8.11	2.20	
TRAIPU	A	0.02	0.13	0.004	> 0.0009 < 0.0030	< 0.0016	21.50	8.15	2.30	
	B	> 0.0066	0.10	0.004	< 0.0009	< 0.0016	2.10	8.10	2.00	
	C	> 0.0066	0.16	0.004	0.006	< 0.0016	2.20	8.36	2.20	
BELO MONTE	A	> 0.0066	0.22	0.006	0.069	< 0.0016	2.10	8.14	2.50	
	B	> 0.0066	0.28	0.006	0.048	< 0.0016	2.20	8.23	2.80	
	C	< 0.0066	0.14	0.004	0.003	< 0.0016	2.10	7.95	2.10	
PÃO DE AÇÚCAR	A	< 0.0066	0.12	0.004	0.006	< 0.0016	2.20	8.06	2.10	
	B	> 0.0066	0.14	0.004	0.010	< 0.0016	2.20	8.04	2.30	
	C	< 0.0066	0.10	0.005	< 0.0009	< 0.0016	2.00	7.79	2.20	
PIRANHAS	A	> 0.0066	0.02	0.001	> 0.0009 < 0.0030	< 0.0016	2.00	7.94	2.00	
	B	> 0.0066	0.03	> 0.0002	> 0.0009 < 0.0030	< 0.0016	2.10	7.88	2.00	
	C	> 0.0066	0.09	0.001	0.035	< 0.0016	2.10	8.11	2.80	

<, below the limits of detection (LOD) of the method; > and <, above the limits of detection and below the limits of quantification (LOQ) of the method. * V: Concentration in µg/L.

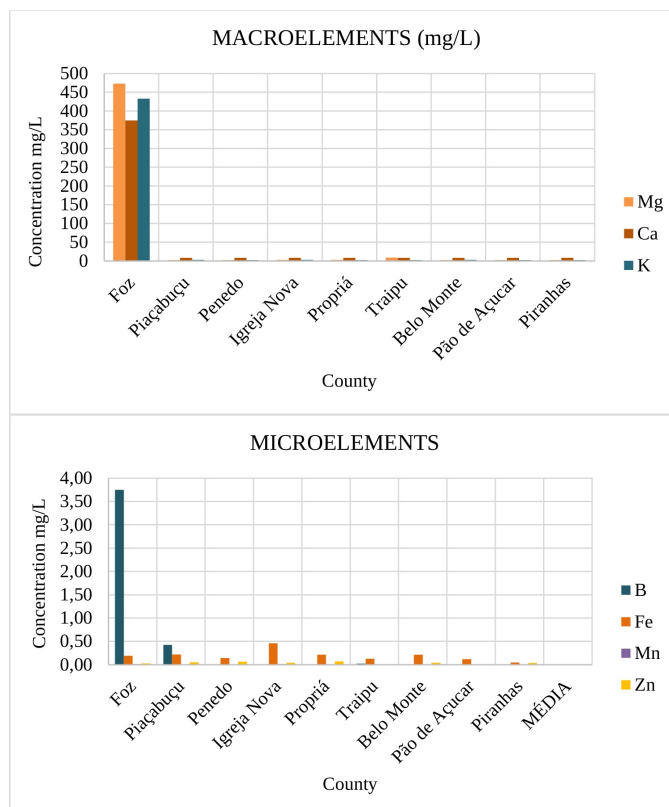
Table 4: Statistical functions (mg/L) of the elements identified in the waters collected on the banks of the lower São Francisco River according to the Sergipe, Alagoas, and Middle River margins.

POINT	STATISTICAL FUNCTIONS	B	Fe	Mn	Zn	*V	Mg	Ca	K
ALAGOAS	Average	3.76	0.15	0.07	0.02	3.17	54.58	48.75	48.55
	Maximum	3.76	0.24	0.02	0.04	3.17	473.90	375.30	418.00
	Minimum	3.76	0.09	< 0.00	< 0.00	3.17	2.03	7.57	2.12
SERGIPE	Average	1.90	0.22	0.01	0.04	3.23	54.52	49.11	50.28
	Maximum	3.78	0.68	0.04	0.07	3.23	473.20	377.20	432.6
	Minimum	0.02	0.02	< 0.00	0.07	3.23	2.03	7.82	2.01
MIDDLE	Average	2.07	0.28	0.01	0.05	1.71	68.34	52.79	57.89
	Maximum	3.72	0.45	0.01	0.07	3.17	471.90	371.50	447.1
	Minimum	0.43	0.03	< 0.00	0.01	0.26	2.07	7.88	2.00
ALL RIVER	Average	2.58	0.23	0.01	0.03	2.70	178.06	144.21	162.28
	Maximum	3.78	0.68	0.04	0.07	3.23	473.9	377.20	447.1
	Minimum	0.02	0.02	< 0.00	< 0.00	0.26	2.03	7.57	2.00

The results in Tables 3 and 4 show concentrations below the limits of harmfulness determined by the Ministry of Health and CONAMA, except for sea salts ions from the ocean, found in the regions of Piaçabuçu and Foz. The low concentrations of the elements found below the detection limits of the analysis method may be associated with the absence of anthropogenic activities in areas along the river.

As shown in Tables 3 and 4 and Figure 2, the concentration of the elements along the river's course, between the right and left banks, remains constant. The observed variations are discreet, indicating that the origin of the recurring elements may be endogenous. However, there is a significant increase in the B, Ca, K, Mg, and V contents between Piaçabuçu and Foz. The presence of these elements at high levels indicates that the tide is advancing to a sampling area bringing sea salts beyond the mouth of the river, at more than 11 km from the coast.

Figure 2: Profile of the elements along the lower São Francisco River. Average between the water collection points Sergipe, Alagoas, and Middle of the river.



Vanadium (*V) is a transition and ubiquitous element present in the soil, air, and water. As its presence in aquatic bodies, it can occur from natural sources (volcanic erosion and derogatory) or anthropic (industrial, that is, metallurgical works and combustion of crude or residual oil and coal (CHIARELLI et al., 2021). Surface water contains less than 3 µg/L in areas with significant geochemical sources, in seawater, in the open ocean range, 1 to 3 µg/L (COSTIGAN; CARY; DOBSON, 2001). Boron (B) occurs naturally in seawater, mainly in the form of boric acid (H₃BO₃), contributing to its alkalinity. In sea waters, the typical concentration of B is 4 to 5 mg/kg and varies mainly in response to the degree of dilution or concentration (KASEMANN et al., 2009; LEE et al., 2019).

From the data set provided in the graphs of Figure 2, the Baixo São Francisco water samples from Penedo to Foz, in Sergipe and Alagoas borders and middle of the river were within the potability limits of the Ministry of Health. These samples could be classified as freshwater for the adopted parameters. However, due to the significant increase in the B, Ca, K, Mg, and V contents between Piaçabuçu and Foz, these waters are inadequate for human consumption. Romão, Pavani-Filho, and Alves (2020), Cavalcante, Miranda Medeiros (2017) and Fonseca et al., (2020) studied the dynamic profile of the river and identified salinity entering the estuary region beyond 11 km.

CONCLUSIONS

According to the results found for all water samples collected, it can be implied a constant element content profile along the river, between the margins of Sergipe and Alagoas, and the middle portion of the river. The concentrations of all the elements investigated were below the maximum tolerance limit determined by the Ministry of Health. Therefore, the waters of the evaluated

regions meet the drinking requirements in the conditions tested until the Penedo region. However, considering the striking presence of the B, K, Mg, Ca, and V cations from the Piaçabuçu region to the mouth, the process of salinization of the waters of the lower São Francisco is taking place. The high salinity represents a risk to the ecosystem and causes a shortage in the region, compromising the quality of life of the riverside communities.

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