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Effects of a recent urbanization event on coastal groundwater in the southeastern coast of Brazil: a case study of the Macaé municipality

Efeito da urbanização recente em águas subterrâneas costeiras na Região Sudeste, Brasil: um estudo de caso do município de Macaé

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ABSTRACT

Coastal groundwater is extremely vulnerable to land-based human activities and seawater intrusion. In Brazil, a developing country, several coastal cities are undergoing recent urbanization with no planning, giving rise to problems such as groundwater overexploitation, sanitation, and chemical contamination. This study provides seasonal and spatial groundwater chemical and microbiological characterization of a recently urbanized coastal region, discussing contamination and salinization. The recent urbanization event affected both shallow and deep wells represented by the extensive presence of *Escherichia coli* on groundwater and nitrate, ammonium, arsenic, and lead (NO_3^-, NH_4^+, As and Pb) levels above groundwater safety guidelines. In contrast, iron and manganese (Fe and Mn) concentrations above the safety limit were associated with lithological enrichment, but might also restrict groundwater consumption. In addition to chemical and microbiological contamination, salinization of coastal aquifers did not pose a threat in this shoreline, but brackish groundwater was found in one well influenced by a coastal lagoon sandbar opening that allowed seawater to enter the aquifer.

Keywords: hydrochemistry; contamination; metal; *Escherichia coli*; salinization

RESUMO

As águas subterrâneas costeiras são extremamente vulneráveis a atividades localizadas no continente e à intrusão salina. Em países em desenvolvimento, a recente urbanização de muitas cidades costeiras ocorreu sem planejamento, levando a problemas como a sobre-explotação das águas subterrâneas, ausência de saneamento e contaminação química. Este estudo apresenta uma caracterização espacial e sazonal de aspectos químicos e microbiológicos das águas subterrâneas em uma região costeira urbanizada recentemente, discutindo a contaminação e a salinização desse recurso hídrico. A urbanização recente afeta tanto poços rasos quanto profundos pela presença extensiva de *Escherichia coli* e alguns valores de NO_3^-, NH_4^+, As and Pb superiores aos de referência da legislação. Em contraste, concentrações de ferro e manganês acima dos valores de referência foram relacionadas a um enriquecimento litológico, embora possam restringir o consumo da água subterrânea. Ao lado da contaminação química e microbiológica, a salinização dos aquíferos costeiros não representou uma ameaça para essa área, embora águas subterrâneas salobras tenham ocorrido em um poço, influenciado pela abertura de barra de uma lagoa costeira, que promoveu a intrusão salina no aquífero.

Palavras-chave: hidroquímica; contaminação; metais; *Escherichia coli*; salinização.

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Introduction

Groundwater is an important resource for human society (Graaf et al., 2019). However, groundwater quantity and quality have been increasingly vulnerable to pollution, overexploitation, and salinization (UNICEF and WHO, 2017). Coastal aquifers might be vulnerable to an intensification of land use and land cover changes, mainly associated with an increasing number of people settling in coastal cities. Coastal cities are expected to host around 800 million people by 2050, while being vulnerable to sea-level rise of 0.5 m (WEF, 2019). Consequently, urbanization, especially rapidly developing cities, has increased coastal aquifer exploitation and the emission of a myriad of untreated effluents (Machiwal et al., 2018). In addition, coastal groundwater salinization may occur by intensive groundwater withdrawal, land subsidence, and seawater intrusion, allowing hydraulic saline gradients into aquifers (Hoover et al., 2017; Gomes et al., 2019).

The Brazilian coast is 8,698 km long with an area of 388,000 km^2. Along the coastal plain, aquifers have important storage capacity, which might be influenced by surface and marine waters (Hu et al., 2017). However, the literature shows scarce data characterizing coastal groundwater pollution and salinization (Silva-Filho et al., 2009; Godoy et al., 2013; Mirlean et al., 2014; Bertrand et al., 2016; Paim et al., 2018; Gomes et al., 2019). Urbanization in several coastal cities has been intensified over the last 40 years, induced by the oil and gas industry, tourism, the naval industry, general services, and others. With no urban planning, such as a waste treatment system, the intensification of urbanization overloaded the carrying capacity of coastal ecosystems, resulting in groundwater vulnerability, for example, due to pollution, giving rise to problems related to sanitation, chemical contamination, and overexploitation (Silva-Filho et al., 2009; Lins-de-Barros, 2017). In addition, the permeability of coastal sandy soils and civil construction works along the shoreline have turned groundwater into a potential source of chemicals for coastal waters (Godoy et al., 2013).

Although some coastal cities in Brazil have moderate groundwater demand (Vilar, 2016), the recent population increase tends to intensify groundwater exploitation. Besides, more than half of the aquifers in Brazil are not regulated, adding unknown pressure on groundwater exploitation and water quality (Vilar, 2016). In this context, many studies have addressed the impact of megacities on groundwater (Bertrand et al., 2016; Gomes et al., 2019), but no studies have been described for small coastal cities, in which urbanization has been recently intensified, with unknown impacts on groundwater. Therefore, this study provides a seasonal and spatial groundwater chemical and microbiological characterization of coastal shallow and deep wells from sedimentary and fissured aquifers in a recently urbanized coastal region. It discusses contamination and salinization of aquifers, identifying patterns that might be occurring in many recently urbanized coastal regions in Brazil.

Material and Methods

The region studied is located on the coast of the Macaé municipality, state of Rio de Janeiro, Brazil. Over the last 40 years, urbanization increased to support the operational activities of the oil and gas industry in the Campos Basin (Figure 1). During this period, the population along the coastal plain increased from 40,000 to over 250,000 inhabitants. Unfortunately, urbanization occurred without any housing waste treatment, in addition to other pollution sources, such as those related to the oil industry. As a result, the anthropogenic sources are responsible for most of the nitrogen, phosphorous, and metal loads cycling in the region (Molisani et al., 2013).

The coastal wells are inserted in the fissured and sedimentary aquifers. Fissured aquifers are characterized by basement rocks represented by the Pre-Cambrian metamorphic sillimanite-biotite gneiss and orthogneiss with granitic crystals of potassium feldspar. Sedimentary aquifers are in the alluviate deposits composed of silty-clay, organic-rich sediment, and beach-ridge terraces constructed along the Pleistocene and Holocene (Barreto et al., 2000; CPRM, 2012). The climate of the region is subtropical, with hot summers and mild dry winters, with an annual rainfall of 1,000-1,500 mm, having the highest volume of 180 mm in December (summer) and the lowest in August, 40 mm on average (winter).

Groundwater samples were collected monthly during 2016 and 2017. Eleven wells were monitored, being six shallow wells (depth from 1.0 to 11 meters) and five deep ones (depth from 16 to 85 meters). Wells were sampled along the fissured (D1, D2, D3, S1, S3) and sedimentary (D4, D5, S2, S4, S5, S6) aquifers (Barreto et al., 2000), and encompassing the industrial (S3, D1, D5) and high-density urban (D2, D3, D4, S1, S2, S4, S5, S6) areas of the municipality (Figure 1). The distance between the wells and the coastal line varied from 0.36 to 8.50 km.

Before sampling, the initial static water levels were measured with an electric sounder, considering that the wells had not been pumped 24 hours before water collection. The water was sampled using a pump coupled to a polyethylene hose cleaned with 70% alcohol to avoid previous microbial contamination. The pump flows were adjusted at the lowest and continuous rate. The wells were purged to remove any stagnant water in the line before water collection was initiated. The water was stored in polyethylene bottles previously cleaned with acid and kept in a thermal box (Brasil, 2013).

Wells were analyzed *in situ* using a portable instrument for the following parameters: temperature (°C), electrical conductivity (EC), and pH. The EC and dynamic water depth were also hourly measured in one well at 0.25 km offshore to trace the influence of marine saltwater intrusion during a semidiurnal spring tidal cycle (0 to 1.3 m) in the dry season (September 2017). Major ions fluoride, bromide, sodium, potassium, calcium, magnesium, chloride, ammonium, nitrate, nitrite, phosphate, sulfate (F^-, Br^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{-2}) were analyzed by ionic chromatography (Metrohn 850 Professional IC). Dissolved organic carbon (DOC) was determined

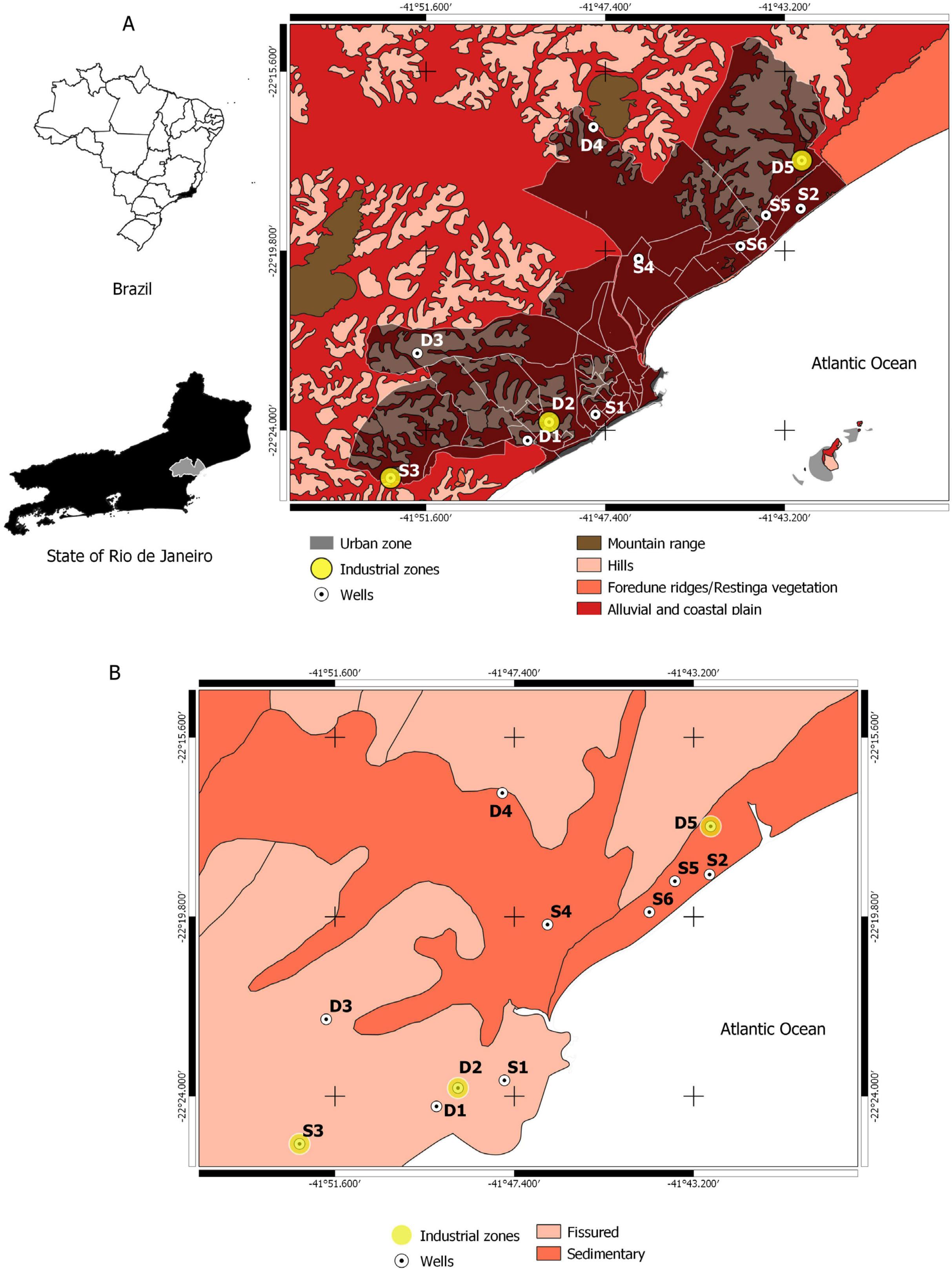

Figure 1 – Map of the studied area, including the (A) location of the monitored shallow (S) and deep (D) wells at the fissured and (B) sedimentary aquifers in the Macaé municipality.

by pyrolytic combustion (Shimadzu TOC analyzer). Metals were analyzed by inductively coupled plasma-mass spectrometry (Thermo Fisher Scientific, model X-Series 2). All samples were analyzed using replicates (coefficients of variations were less than 15%) and analytical blanks. Accuracy was checked using a certified reference solution (AccuTrace™ reference Standard) with recoveries ranging from 92% (Cr) to 106% (Ni). Detection limits were calculated as three times the standard deviation of repeated blank measurements.

For microbiological analysis, water samples were collected according to the standard guidelines, using 250 ml sterile bottles stored in an icebox and processed in the laboratory within four hours after collection (APHA, 2018). The presence or absence of *Escherichia coli* (*E. coli*) was checked using the Defined Substrate Technology (DST) with Colitag® medium and incubation for 24 hours at 37°C. The *E. coli* ATCC 29522 strain was used as a positive control and sterile water as a negative control. After incubation, the presence of *E. coli* was observed by exposing the positive samples to UV light, showing a blue fluorescence and comparing them to the control samples.

D'Agostino–Pearson omnibus normality test was previously used for the one-way analysis of variance (ANOVA) followed by Dunnett's (parametric) test or the Kruskal–Wallis test followed by Dunn's (nonparametric) test to obtain statistically significant differences ($P < 0.05$) of concentrations among wells and between the wet and dry season. A correlation matrix was used to determine data inter-correlations.

Results and Discussion

Groundwater microbiological contamination was the most important problem related to the recent urbanization in the coastal region. About 64% of 143 groundwater samples had *E. coli* (Figure 2). The shallow wells had 69% of the samples contaminated by *E. coli*, while deep wells had 57% of the samples with this pathogen, which is a sanitary indicator of groundwater fecal contamination. Shallow wells had more *E. coli* in the rainy season (72% of the samples) than in the dry season (67% of the samples). In contrast, deep wells had more contaminated samples (66%) in the dry season than in the rainy period (47%). According to the Brazilian Legislation and WHO Guidelines, for every 100 ml of water tested, no *E. coli* should be detected (Brasil, 2008, 2017; WHO, 2017). Thus, part of this coastal urban groundwater was contaminated, preventing direct water consumption. This result suggests poor well management during drilling or sealing and/or cross-contamination of aquifers by the untreated sewage, reported mainly in shallow wells, which are still common in developing countries (Vilar, 2016; Ferrer et al., 2020).

The systematic review and meta-analysis performed by Genter et al. (2021) showed that groundwater is vulnerable due to fecal contamination in low- and middle-income countries, where 36% of the monitored samples were contaminated by *E. coli*. Such results showed that self-supply shallow groundwater was more vulnerable to fecal contamination, mainly in low-income countries. In the coastal area studied, located in a middle-income country, 64 and 57% of the samples from shallow and deep wells, respectively, were contaminated by *E. coli*. Microbiological contamination was more extensive than that reported by the above-mentioned review, including a coastal area in low-income Ghana (Africa) where 33% of the groundwater samples were contaminated by *E. coli* (Lutterodt et al., 2021). Such comparisons indicated the deleterious effects of recent urbanization and untreated domestic sewage emission on groundwater in a region that has been receiving a lot of money in royalties from oil exploration, but its groundwater sanitary conditions are worse than that of low-income African countries.

Table 1 shows the physical and chemical groundwater parameters for shallow and deep wells in the studied area. Comparing the major ion composition with the Brazilian Groundwater Guidelines (BRASIL, 2008), it was observed that 10% of the samples had higher NO_3^- concentrations than the proposed limit for drinking water. According to Zhang et al. (2020), high groundwater nitrate concentrations in newly urbanized regions was two or more times higher than those in long-standing urbanized areas, and have a relationship to inadequate wastewater systems (Boumaiza et al., 2020). When comparing the NO_3^- values in wells from the fissured and sedimentary aquifers, higher values (8.9 mg L^{-1}) were observed in fissured aquifers than in sedimentary ones (1.2 mg L^{-1}). The predominance of NO_3^- on groundwater over NH_4^+ in the wells monitored was also attributed to the nitrification process, which also enhances NO_3^- contamination in recently urbanized coastal zones (Shi et al., 2018).

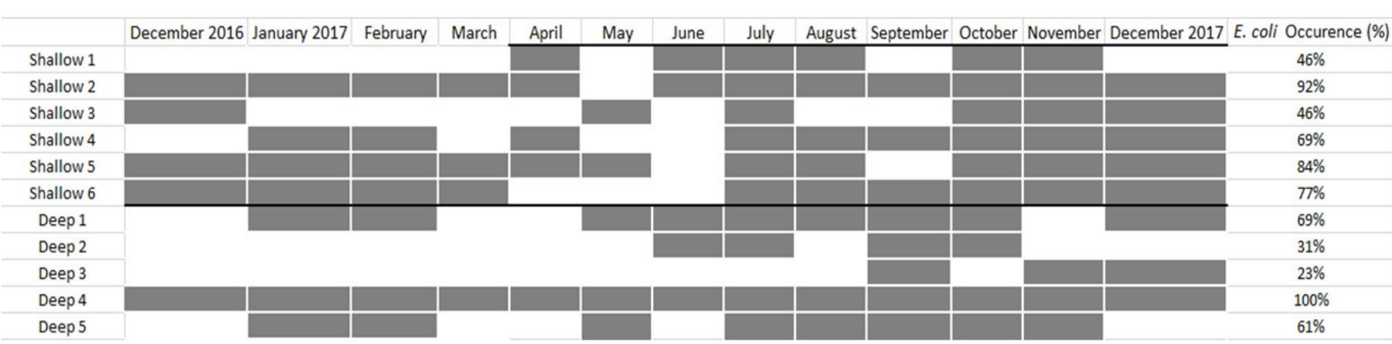

Figure 2 – Presence (grey) and absence (white) of Escherichia coli in shallow and deep wells monitored during the sampling period.

The relationship between nitrate and chloride (NO_3^- and Cl^-) is widely applied to trace nitrate pollution sources (Li et al., 2010). The correlation between NO_3^- and Cl^- from the shallow well that had higher nitrate values than the Brazilian Groundwater Guidelines showed a significant positive correlation ($r^2 = 0.62$, $P = 0.01$) (Figure 3), which suggested that nitrate could be originated from untreated sewage and residential buildings (Li et al., 2010; Güller et al., 2012; Boumaiza et al., 2020; Zhang et al., 2020). Similarly, the high variability of chloride on groundwater should be attributed to the widespread use of chlorine in the wells for water disinfection, as corroborated by extensive groundwater microbiological contamination. To obtain effective chlorine disinfection, the pH should be lower than 8 (WHO, 2017). However, the maximum pH values measured at some of the wells studied were higher than 8 (Table 1), which is more likely to be ineffective for chlorine disinfection, for example, for the *E. coli* measured on groundwater.

Table 1 – Minimum, maximum, and mean (coefficient of variation) values of the physical and chemical parameters for shallow and deep wells and comparison to the Brazilian Groundwater Guidelines (Brasil, 2008) and International Standards for Drinking-water (WHO, 2017)*.

Parameter	Shallow			Deep			Brasil (2008)	WHO (2017)
	Min.	Max.	Mean (CV)	Min.	Max.	Mean (CV)		
Water depth (m)	1.0	11	4.5 (48)	16	85	47 (63)	-	-
Temperature (°C)	22	31	26 (6.0)	21	29	26 (7.0)	-	-
Conductivity (mS cm^{-1})	0.14	1.02	0.39 (58)	0.059	1.06	0.39 (76)	-	1.7
pH	5.0	8.8	6.7 (14)	5.4	8.1	6.9 (10)	-	6.5-8.5
F^- (mg L^{-1})	0.01	0.67	0.12 (154)[a]	0.01	2.21	0.23 (167)[b]	1.0	1.5
Br^- (mg L^{-1})	0.03	0.30	0.12 (60)	0.03	5.2	0.87 (190)	-	-
Ca^{+2} (mg L^{-1})	0.25	41	14 (8.9)	0.68	57	18 (90)	-	150-300
Mg^{+2} (mg L^{-1})	0.1	9.8	3.8 (57)	0.26	23	5.4 (97)	-	150-300
Na^+ (mg L^{-1})	3.2	162	33 (91)	2.3	73	25 (66)	200	200
K^+ (mg L^{-1})	0.63	21	5.6 (73)[a]	0.40	11	3.6 (74)[b]	-	-
Cl^- (mg L^{-1})	2.9	166	37 (88)	1.0	225	41 (123)	250	250
SO_4^{-2} (mg L^{-1})	3.0	272	43 (119)[a]	1.0	67	15 (88)[b]	250	250
NO_3^- (mg L^{-1})	0.10	50	4.9 (231)	0.10	50	5.8 (196)	10	50
NO_2^- (mg L^{-1})	0.01	0.01	0.01	0.02	0.04	0.03	1.0	3.0
NH_4^+ (mg L^{-1})	0.01	2.6	0.45 (139)[a]	0.01	1.1	0.21 (129)[b]	1.5	1.5
PO_4^{-3} (mg L^{-1})	0.11	0.87	0.08 (203)	0.12	1.2	0.10 (185)	-	-
DOC (mg L^{-1})	0.41	15	6.7 (52)[a]	0.16	10	4.2 (67)[b]	-	-
Al (µg L^{-1})	0.92	162	65 (66)[a]	0.86	127	42 (87)[b]	200	200
Fe (µg L^{-1})	0.35	1,841	223 (174)[a]	0.16	225	55 (126)[b]	300	1,000
Mn (µg L^{-1})	8.0	1,583	140 (220)	0.1	818	78 (178)	100	400
Zn (µg L^{-1})	0.75	76	22 (92)	3.5	217	44 (58)	500	400
Cu (µg L^{-1})	0.17	19	5.5 (83)	0.51	12	4.1 (81)	2000	2000
Cr (µg L^{-1})	0.02	48	4.1 (10)[a]	0.03	2.5	0.54 (117)[b]	50	50
Ba (µg L^{-1})	8.4	293	72 (92)	8.4	211	79 (63)	700	700
Ni (µg L^{-1})	0.06	19	2.3 (183)	0.06	3.3	1.2 (77)	20	70
As (µg L^{-1})	0.11	4.7	1.8 (1.4)[a]	0.74	32	9.6 (13)[b]	10	10
Sr (µg L^{-1})	23	372	90 (87)	6.0	357	89 (106)	-	-
Pb (µg L^{-1})	0.10	12	2.5 (116)	0.24	4.3	1.9 (70)	10	10
Cd (µg L^{-1})	0.02	0.11	0.05 (63)	0.03	0.10	0.04 (28)	5.0	3.0
V (µg L^{-1})	0.001	15	2.7 (136)	0.07	7.5	2.3 (2.0)	50	-
Co (µg L^{-1})	0.01	6.5	1.4 (122)[a]	0.01	1.0	0.22 (133)[b]	-	-

*Upper case letters indicated that means are statistically different for a probability of 95%.

In another shallow well, in a recent large population settlement without sewage treatment in the municipality, all samples monitored during the sampling period had NH_4^+ values above the safety limits. In this shallow well, dissolved oxygen (%) had the lowest average (± SD) concentration measuring 63 ± 31%. Ammonium in wells from the sedimentary aquifer was higher (0.59 mg L^{-1}) than in the wells sampled in the fissured aquifers (0.1 mg L^{-1}). Ammonium is released into groundwater via landfill, septic tanks, and sewage disposal, or even produced *in situ* by anaerobic organic matter decomposition (Zhang et al., 2020). Because of a possible NO_3^- loss through denitrification and retention of NH_4^+ not oxidized to NO_3^-, NH_4^+ may be enriched in urban wells located at lowlands. The measured concentrations of NO_3^- and NH_4^+ in this study were lower than the values reported for highly urbanized coastal regions (> 20 mg L^{-1} and > 1 mg L^{-1}, respectively) (Shi et al., 2018; Zhang et al., 2020), indicating small to moderate enrichment of the nitrogen forms associated with the recent urbanization event.

On average, the shallow and deep wells were similar for most ions, except for F^- which was significantly higher in the deep wells. In contrast, K^+, SO_4^{-2}, NH_4^+, and DOC had significantly higher concentrations in the shallow wells. When comparing wells from fissured and sedimentary aquifers, only Br^- and F^- were significantly higher on groundwater from the fissured aquifers, while DOC was higher in the sedimentary aquifer. The results showed groundwater chemical heterogeneity, with a larger coefficient of variation for nitrate, phosphate, fluoride, and sulfate in the shallow wells; and for nitrate, bromate, phosphate, fluoride, and chloride in the deep wells (Table 1). Heterogeneity may reflect the influence of anthropogenic emission (Santucci et al., 2017), although the lithological diversity has been considered at chemical concentrations in such coastal region (Silva-Filho et al., 2009).

Higher DOC and nitrogen concentrations in the shallow wells in the sedimentary aquifer should confirm the connection of groundwater to the runoff (Barbosa and Silva Jr., 2005), including the urban runoff carrying organic matter from anthropogenic sources, including untreated sewage. A potentiometric survey indicated that aquifers in the study area have a strict connection to surface waters, being recharged by adjacent upstream areas and discharged seaward (Barbosa and Silva Jr., 2005). Thus, groundwater contamination may be linked to infiltration of contaminated surface water (Engström et al., 2015; Siqueira, 2017; Soares et al., 2020). In the study area, Molisani et al. (2013) estimated that the anthropogenic loads represented 90% of the total nitrogen input in the coastal plain where the wells are located. Livestock, mainly cattle, and untreated domestic sewage were both the major nitrogen sources, contributing to 620 ton $year^{-1}$ and 550 ton $year^{-1}$, respectively, for surface waters and soils of the coastal plain.

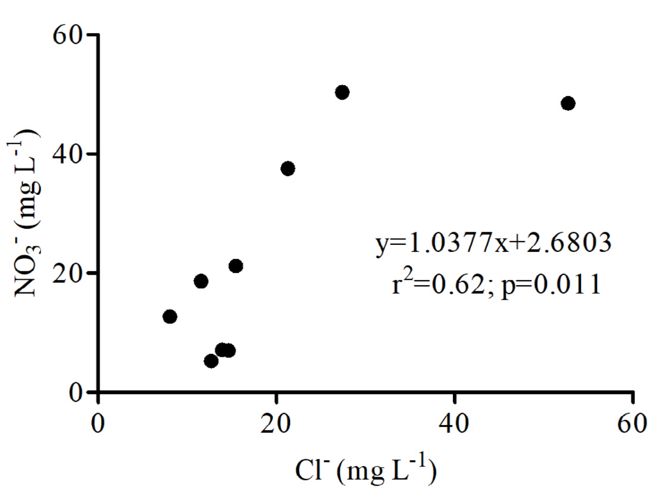

Figure 3 – Relationship between NO_3^- and Cl^- in a nitrate-contaminated well.

In addition to the human influence on the chemical features of the coastal groundwater, natural processes also determine such conditions. The pH and electrical conductivity were similar among the wells during the monitoring period. Such values were reported for coastal aquifers from the granitic-gneiss lithology and diverse regional geochemical facies, as also related to marine-derived atmospheric deposition and anthropogenic contamination (Silva-Filho et al., 2009; Gomes et al., 2019). For major ions, coastal groundwater from the shallow and deep wells had a predominance of Cl^-, SO_4^{-2}, Na^+, Ca^{2+} (Table 1) that should be attributed not only to the local granitic lithology and weathering, but also to the marine droplet atmospheric deposition, seawater intrusion and soil organic matter decomposition (Silva-Filho et al., 2009; CPRM, 2012). As a result, the groundwater samples were grouped into four dominant facies:

- Group 1: sodium chloride facies;
- Group 2: sodium bicarbonate facies;
- Group 3: calcium bicarbonate facies;
- Group 4: sulfate magnesium facies.

This classification was also reported for another survey in the study area which described the predominance of sulfate and chlorine on the groundwater, explained by the coastal proximity and potential salinization of the aquifers (Bento, 2006). The range of Na^+, Ca^{2+}, Mg^{2+}, and Cl^- concentrations for the shallow wells were similar to other adjacent coastal aquifers in the state of Rio de Janeiro, in which the groundwater was influenced by sea salts (Silva-Filho et al., 2009). However, assuming that Cl^- in the seawater is about 536 mEq L^{-1}, the contribution of marine chloride on the groundwater of the shallow wells of this study is 0.8%, which is lower than the 1.5% reported by Silva-Filho et al. (2009).

Ionic ratios have been applied to trace the hydrochemistry dynamic of groundwaters, based on the following ratios, rMg^{+2}/rCa^{+2}, rK^+/rNa^+, rNa^+/rCl^- (Chidambaram et al., 2018). Such ratios were calculated for the wells in the sedimentary and fissured aquifers along with the coastal municipality. The results indicated that wells inserted in the sedimentary and fissured aquifers, respectively, had the following ratios: rMg^{+2}/rCa^{+2} (0.30 and 0.60), rK^+/rNa^+ (0.11 and 0.07), rNa^+/rCl^- (1.35 and 1.08). The interpretation of the calculated ionic ratios indicated that groundwater in the studied coastal region has a continental source and a relationship with water circulation in the granitic crystalline rocks. This analysis corroborates the assumption that aquifers in the study area have a strict connection to surface waters, being recharged by adjacent upstream areas (Barbosa and Silva Jr., 2005), where the lithology is composed of gneiss and orthogneiss with granitic crystals (CPRM, 2012).

Comparing the metal concentrations with the Brazilian Groundwater Guidelines (BRASIL, 2008), higher values for Fe, Mn, As, and Pb were observed in the monitored wells. Similarly, Pb was observed at higher concentrations than that provided for in the Brazilian Groundwater Guidelines (BRASIL, 2008) for one sample in a well in the industrial zone. The As values were higher than the safety limit in three sampling events of a well located in the industrial region of the municipality, where metal framework manufacturers are located. High concentrations of this metalloid were described in a deltaic shallow aquifer near the study area and were related to the long-term atmospheric fall out over the sediments (Mirlean et al., 2014), similarly to other coastal areas influenced by anthropogenic As sources (Mirlean et al., 2003). Thus, considering the atmospheric As a pathway for some areas of the Brazilian coast, the high values in one well located in the industrial area suggested the anthropogenic source of this metalloid in the municipality.

On the contrary, Fe and Mn concentrations in some shallow and deep wells were higher than the concentrations proposed by the guidelines, but were related to natural processes. Fe and Mn are common elements found in the regional granitic-gneiss lithology. Their values range from 1 to 7% of Fe_2O_3 and from 0.02 to 0.17% of MnO (CPRM, 2012). Consequently, the weathering of Fe and Mn-rich minerals is responsible for mobilizing such metals and their high concentrations on groundwater are controlled by the redox potential and dissolution of such minerals found in aquifers (Güller et al., 2012). A maximum Fe concentration of 2.3 mg L^{-1} was reported for intensive anthropogenic coastal areas, being this level considered a moderate-to-heavy pollution risk level (Wen et a., 2019) and similar to those measured in some shallow wells in this study (1.8 mg L^{-1}). In contrast, elevated Mn levels (> 0.4 mg L^{-1}) were measured in coastal aquifers from rapidly urbanized regions and related to untreated sewage and industrial wastewater, as well as decomposition of organic matter, reduction of Fe (hydr)oxides, and Mn-rich runoff (Hou et al., 2020). Maximum values of 1.5 mg L^{-1} measured in the study area highlight the enrichment of such metal, mainly in the sedimentary aquifer (mean of 0.16 mg L^{-1}), compared to the fissured aquifer (mean of 0.07 mg L^{-1}). In addition, the recent human occupation of the coastal lowlands of our study requires, in many cases, an extensive embankment foundation, which consists of a series of compacted layer soils removed from local hills to raise ground height, thus enhancing the weathering of Fe and Mn minerals. No matter their origin, Fe and Mn excess on groundwater may cause taste deterioration, staining of laundry, and potential effects to the human health (WHO, 2017). Fe, Mn, and As enrichments in aquifers were also found in recently urbanized coastal regions and such metals may be indicators of the recent human occupation on the coastal zone (Huang et al., 2018; Wen et al., 2019; Hou et al., 2020; Islam et al., 2020).

During the sampling period, concentrations were more detectable for Al, Fe, Mn, Zn, Cu, Ba, Sr than for Cr, Ni, As, Pb, V, Co, Cd. On average, higher values of Al, Fe, Cr, and Co were found in the shallow compared to the deep wells. In contrast, deep wells had higher values for As only (Table 1). The wells located in the sedimentary aquifer had significantly higher Fe, Cu, and Al values than those in the fissured aquifer (255 and 48 µg L^{-1} for Fe; 6.2 and 3.6 µg L^{-1} for Cu, 73 and 32 µg L^{-1} for Al, respectively for the sedimentary and fissured aquifers). Most of the chemical data had a high deviation, which did not provide a statistical differentiation between the dry and rainy seasons (Table 2). The large variability of metal and major ions concentrations

Table 2 – Seasonal variation of physical and chemical parameters (mean ± standard deviation) measured in the shallow and deep wells*.

Parameter	Shallow		Deep	
	Dry	Rainy	Dry	Rainy
Water depth (m)	4.9 ± 2.2	3.8 ± 1.9	47 ± 29	47 ± 31
Temperature (°C)	25 ± 1.5	26 ± 1.7	25 ± 2.1	26 ± 1.4
Conductivity (mS cm^{-1})	0.36 ± 0.2	0.43 ± 0.27	0.40 ± 0.3	0.40 ± 0.3
pH	6.6 ± 0.8	6.8 ± 1.3	6.9 ± 0.7	7.0 ± 0.7
F^- (mg L^{-1})	0.08 ± 0.13	0.05 ± 0.05	0.23 ± 0.41[a]	0.13 ± 0.06[a]
Br^- (mg L^{-1})	0.12 ± 0.10	0.13 ± 0.10	0.97 ± 1.9	0.66 ± 1.2
Ca^{+2} (mg L^{-1})	15 ± 10	13 ± 7.0	19 ± 17	18 ± 16
Mg^{+2} (mg L^{-1})	4.7 ± 2.3	5.4 ± 5.8	3.5 ± 2.1	5.5 ± 4.4
Na^+ (mg L^{-1})	36 ± 35	30 ± 23	26 ± 18	22 ± 14
K^+ (mg L^{-1})	6.1 ± 5.0	4.7 ± 3.0	4.3 ± 3.2	2.5 ± 1.2
Cl^- (mg L^{-1})	35 ± 31	41 ± 37	44 ± 56	36 ± 41
SO_4^{-2} (mg L^{-1})	53 ± 62	28 ± 22	19 ± 16	10 ± 6.0
NO_3^- (mg L^{-1})	4.1 ± 11	6.0 ± 12	5.5 ± 11	6.3 ± 12
NH_4^+ (mg L^{-1})	0.42 ± 0.63	0.46 ± 0.61	0.16 ± 0.24[a]	0.39 ± 0.33[a]
PO_4^{3-} (mg L^{-1})	0.04 ± 0.05	0.16 ± 0.26	0.08 ± 0.12	0.14 ± 0.28
DOC (mg L^{-1})	6.7 ± 3.6	6.8 ± 3.4	4.2 ± 3.0	4.1 ± 2.3
Al (µg L^{-1})	76 ± 32	68 ± 51	52 ± 40	33 ± 32
Fe (µg L^{-1})	304 ± 505	136 ± 171	86 ± 86	38 ± 57
Mn (µg L^{-1})	213 ± 420	66 ± 72	112 ± 197	49 ± 47
Zn (µg L^{-1})	25 ± 21	15 ± 17	48 ± 59	39 ± 59
Cu (µg L^{-1})	7.0 ± 4.5[a]	3.1 ± 3.3[a]	6.1 ± 3.2[b]	1.8 ± 1.4[b]
Cr (µg L^{-1})	7.0 ± 14	1.6 ± 1.8	0.73 ± 0.70	0.24 ± 0.30
Ba (µg L^{-1})	77 ± 72	65 ± 58	90 ± 56	63 ± 35
Ni (µg L^{-1})	3.3 ± 5.2	0.78 ± 0.80	1.5 ± 1.0	0.75 ± 0.60
As (µg L^{-1})	2.2 ± 1.4[a]	0.34 ± 0.1[a]	7.6 ± 12	Nd
Sr (µg L^{-1})	118 ± 90[a]	54 ± 38[a]	121 ± 106	46 ± 51
Pb (µg L^{-1})	2.5 ± 3.2	2.7 ± 2.5	2.4 ± 1.2	0.71 ± 0.5
V (µg L^{-1})	2.9 ± 3.8	2.7 ± 4.2	2.2 ± 2.3	1.6 ± 1.6
Co (µg L^{-1})	1.6 ± 1.8	1.3 ± 1.5	0.2 ± 0.3	-

*Upper case letters indicated that means are statistically different for a probability of 95% (n = number of samples).

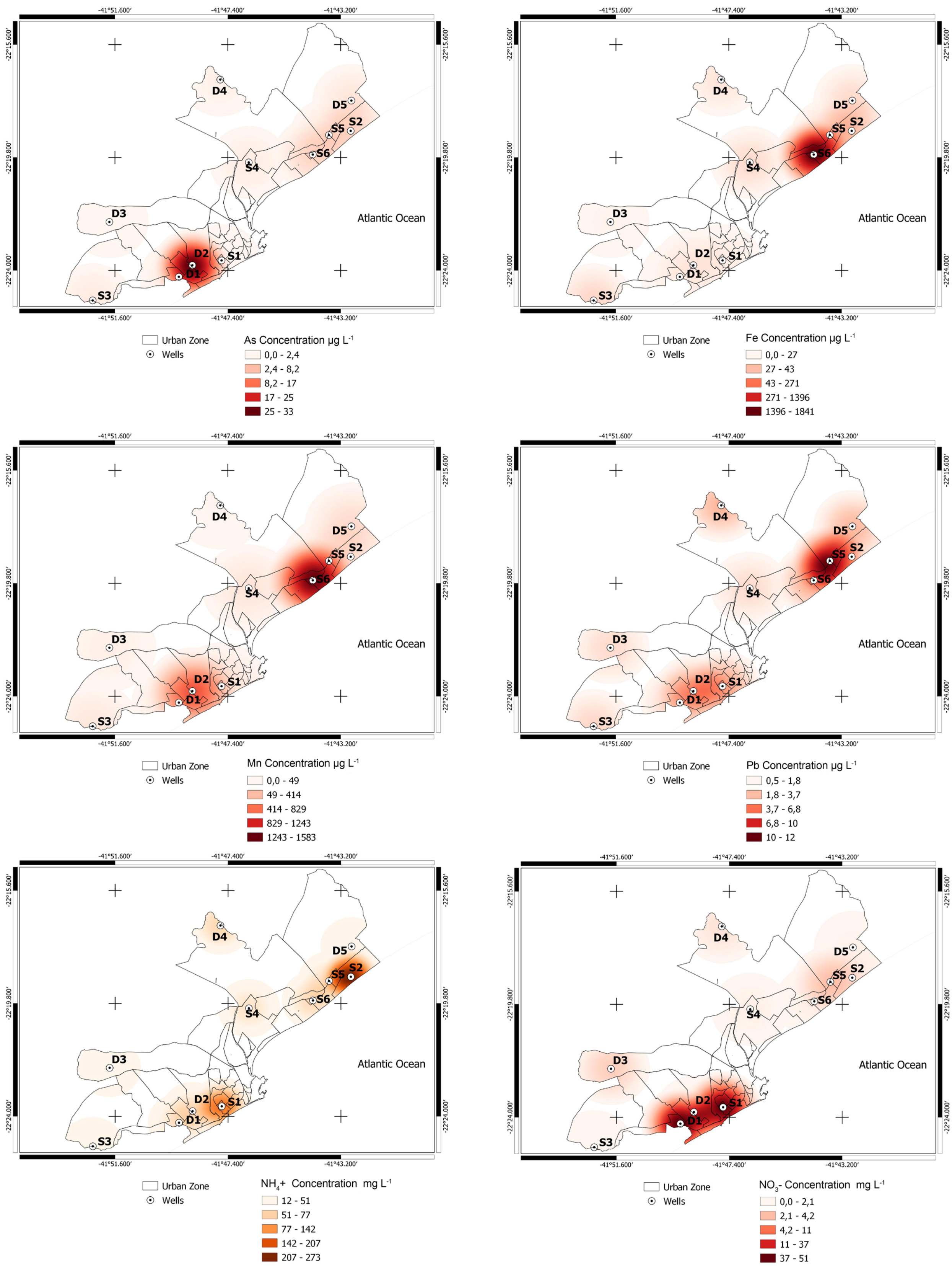

Figure 4 – Spatial variation of maximum concentrations of the critical parameters measured on the groundwater of the recently urbanized coastal municipality.

on groundwater has been attributed to the human influence, mainly to the leaking of effluents, although the aquifer also influenced such variability (Santucci et al., 2017). In contrast, the shallow wells had higher Cu, As, and Sr values during the dry season, while the deep wells had higher F^- and Cu concentrations in the dry season, and higher NH_4^+ levels during the rainy season. Increased chemical concentration in the rainy season may be a result of the desorption from organic matter or aquifer minerals, as observed for NH_4^+, while dilution may also occur mainly in the shallow coastal sand aquifers (McDonough et al., 2020). Thus, higher groundwater Cu, As, Sr, F^- enrichments in the dry season may indicate a reduced dilution capacity due to the lower water volume of aquifers, mainly reported for shallow wells, intensifying the effects of the recent urban occupation on the coastal zone.

Our findings showed that urban groundwater from several shallow and deep wells were not suitable for proper human consumption. However, the extension of groundwater contamination was lower than those measured in recently-urbanized larger coastal cities with over one million inhabitants (Zhang et al., 2015; Bertrand et al., 2016; Huang et al., 2018; Shi et al., 2018; Wen et al., 2019; Islam et al., 2020; Zhang et al., 2020), in contrast to small and medium-sized cities such as the Macaé municipality and others (Samantara et al., 2017). However, similar qualitative groundwater contamination by NO_3^+, NH_4^+, As, Pb, Fe, and Mn was reported for such large cities, as for this recently urbanized coastal municipality, mainly in the industrial zone and low-income urban settlements without sanitation (Figure 4).

Besides the chemical and microbiological contamination of recently urbanized coastal areas, salinization may risk groundwater consumption (Hoover et al., 2017; Gomes et al., 2019). During the monitoring period, the electrical conductivity ranged from 130-1,010 µS cm^{-1} for the shallow and 590-1,060 µS cm^{-1} for the deep wells, with significant differences between the dry and wet seasons (Tables 1 and 2). The average values for the shallow and deep wells were plotted against the distance to the seashore, which showed that the wells close to the seafront had the highest conductivity values (Figure 5). However, the conductivity range showed relatively low or even no groundwater salinization for the study area (Cary et al., 2015; Gomes et al., 2019). In contrast, the hourly monitored well during the semi-diurnal spring tidal cycle showed higher electrical conductivity, typical of brackish water. The initial measurement at the low tide presented a conductivity of 14,000 µS cm^{-1}, with the peak tide indicating maximum values of 26,000 µS cm^{-1}. During the tidal cycle, the dynamic depth of the well varied by 20 cm (Figure 5). The presence of brackish groundwater in this well is apparently associated with the proximity to a coastal lagoon that had its sand barrier artificially opened in the previous rainy season for urban flood control. Thus, the sand barrier opening induced seawater inflow into the lagoon, salinizing the adjacent aquifer. Groundwater salinity and mixing processes with adjacent surface water are complex, with shallow wells being more susceptible (Das and Mukherjee, 2019).

Conclusion

This study concluded that the intensification of urbanization over the last 40 years, with no domestic waste treatment, has compromised the sanitary and chemical aspects of coastal groundwater, as shown by extensive *E. coli* contamination of both shallow and deep wells of this coastal municipality. The recent urbanization also compromised the coastal groundwater with NO_3^+, NH_4^+, As, and Pb, but to a lower extent compared to microbiological contamination, represented by one-time concentrations higher than that provided for by the Brazilian Groundwater Guidelines in wells in the industrial zone and urban settlements. The large spatial and temporal heterogeneity of the chemical concentrations may reflect not only the lithological diversity of the coastal region, but also confirm the influence of anthropogenic emissions on groundwater. Furthermore, Fe and Mn concentrations above the Brazilian Groundwater Safety Limits indicated the influence of a natural lithologic

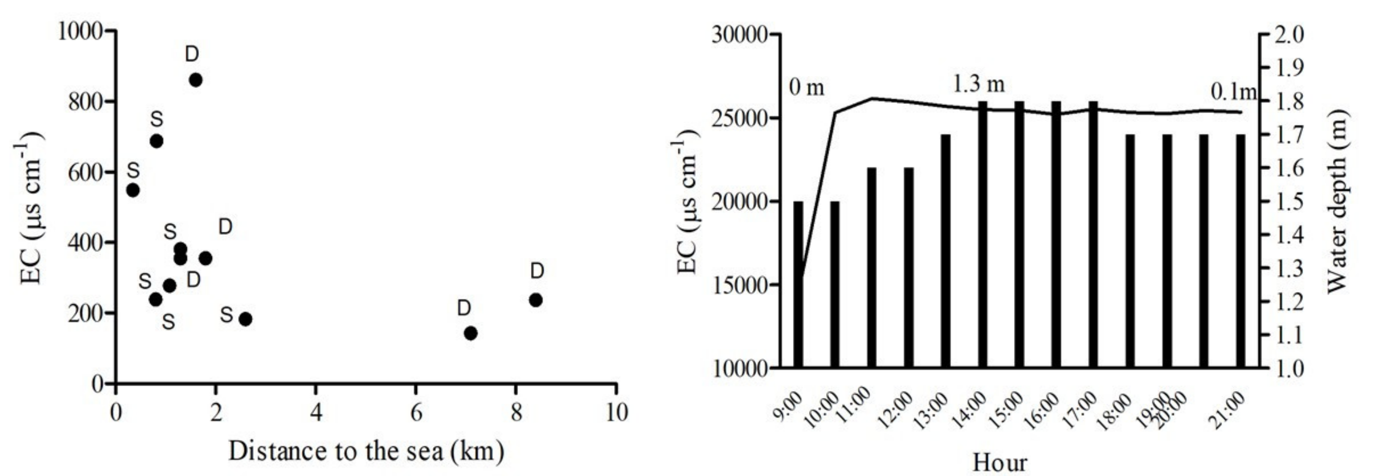

Figure 5 – Mean electrical conductivity (EC) in the shallow (S) and deep (D) wells relative to seafront distance (left) and hourly electrical conductivity and water depth of one well monitored during a semi-diurnal tidal cycle (numbers on top indicate the tidal range) (right).

enrichment that may synergically affect groundwater consumption. Corroborating the literature, this study proposes that *E. coli*, NO_3^+, NH_4^+, As, and Pb are indicators of the influence of recent urbanization on the coastal groundwater, in synergism with the geochemical processes, as exemplified by the high Fe and Mn content on groundwater.

In general, shallow wells located at the urban settlement were more intensively impacted than deep wells, usually drilled in industrial zones. Well drilling and water withdrawal in industrial areas are legally regulated by protocols and standards. On the contrary, domestic wells, mainly in low-income urban settlements, are usually drilled without any regulation and inspection, and thus shallow wells (1 to 11 m) sitting at a short distance from septic tanks are affected by cross-contamination, represented by the widespread presence of *E. coli*. Furthermore, both industrial and domestic wells in the studied municipality have extensive water withdrawal, which influences the contamination scenario and the well conditions, for example, reducing the water dilution capacity and intensifying water recharge from the urban area.

Besides the chemical and biological aspects of urban groundwater, salinity did not pose a threat to the monitored coastal wells. In contrast, brackish groundwater was measured in a well from an aquifer that was salinized by seawater intrusion during a sandbar opening of a coastal lagoon for urban flood control.

Contribution of authors:

SILVA, J.H.C.: Conceptualization, Formal Analysis, Investigation, Resources, Writing — Original Draft, Writing — Review and Editing.; MOLISANI, M.M.: Conceptualization, Formal Analysis, Investigation, Resources, Writing — Original Draft, Writing — Review and Editing.; SILVA-FILHO, E.V.: Methodology, Validation, Formal Analysis, Resources, Writing — Review and Editing.; LEITE, A.M.O.: Methodology, Validation, Formal Analysis, Resources, Writing — Review and Editing.

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