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ASSESSMENT OF POLLUTANTS IN SOILS AND GROUNDWATER FROM THE COASTAL PLAIN OF PARAÍBA DO SUL RIVER DELTA, RJ, BRAZIL

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ABSTRACT:

In developing countries, the quality of the available freshwater is deteriorating mainly due to pollution. Underground water bodies are important resources, taking into account that they are usually more isolated and also protected from anthropogenic influence. Within this context, the present study aimed to assess trace metals, nitrate and organic contaminants in groundwater and soils from 10 bore wells located at the coastal plain of the Paraíba do Sul river delta. Groundwater of the study area revealed elevated concentrations of arsenic, iron, manganese and barium, surpassing the limits established by Brazilian legislation as well as the limits established by other regulatory agencies. As, Fe and Ba reached concentrations as high as 242.70, 31 919 and 4.041 µg.L^{-1} in groundwater. Despite the elevated values, results suggested a reducing environment and the contaminants appear to have a natural geogenic origin, which is corroborated by past studies in the same area. Soils of the aquifer presented low levels of trace metals, corroborating the hypothesis of geogenic contamination in groundwater. No significant differences among the bore wells were observed regarding trace metals in soils, and concentrations found in the present study were much lower than the ones found in impacted aquifers around the world. No PCB's were detected in groundwater or soils. Nitrate concentrations in groundwater were within the limits recommended by Brazilian legislation.

Keywords: Trace metals; PCB's; Groundwater, Soils, Paraíba do Sul, River Delta.

RESUMO:

Em países em desenvolvimento a qualidade da água doce está-se a deteriorar principalmente devido à poluição. Corpos de água subterrâneos são recursos importantes, se se condiderar que são mais isolados e protegidos da influência de atividades antropogênicas. Dentro deste contexto, o presente estudo teve por objetivo avaliar metais-traço, nitrato e contaminantes orgânicos em águas subterrâneas e solos em 10 poços localizados na planície costeira do delta do rio Paraíba do Sul. A água subterrânea da área de estudo revelou concentrações elevadas de arsênio, ferro, manganês e bário, ultrapassando os limites estabelecidos pela legislação brasileira assim como os limites estabelecidos por outras agências reguladoras. As, Fe e Ba atingiram concentrações máximas tão elevadas quanto 242.70; 31,919 e 4.041 µg.L^{-1} na água subterrânea. Apesar dos valores elevados os resultados sugerem um ambiente redutor e os contaminantes aparentam ter origem geogênica, o que é corroborado por estudos anteriores na mesma área. Os solos do aquífero apresentaram baixos valores de metais-traço, corroborando a hipótese de contaminação geogênica da água subterrânea. Não se observaram diferenças significativas para os teores de metais em solos entre os poços, e as concentrações encontradas no presente estudo foram muito menores que as encontradas em aquíferos impactados ao redor do mundo. Não foram detectados PCB's nas águas subterrâneas ou solos. As concentrações de nitrato nas águas subterrâneas mantiveram-se dentro dos limites recomendados pela legislação brasileira.

Palavras-chave: Metais-traço, PCBs; Aquíferos Subterrâneos, Solos; Paraíba do Sul, Delta Fluvial.

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1. INTRODUCTION

Of the total amount of water on Earth, freshwater accounts for only 3%. Among the freshwater resources, 30.1% is underground water, which makes it around 0.76% of the whole world's water volume. In the last decades, ground water reservoirs have been the target of substantial legislative, regulatory and scientific efforts (Samantara *et al.*, 2017; Vetrimurugan *et al.*, 2017; Burri *et al.*, 2019). Important data has been acquired about their geochemical characteristics to ensure their quality for human use since they represent an important water resource for mankind comprising different uses such as drinking, agriculture, industrial use, among others. Unfortunately, underground water may become a hazard if it becomes contaminated with toxic compounds (Amin *et al.*, 2011).

In areas dominated by agricultural activity, the contamination of water compartments, with nutrients, trace metals and organic compounds is a consequence of cultivation practices using large amounts of fertilizers and pesticides (Almasri and Kaluarachchi, 2007). Many studies reported the environmental increase of pollutant concentrations in groundwaters as a result of undue fertilization and pest control in farming sites (Larson *et al.*, 1997; Tang *et al.*, 2010; Wu *et al.*, 2015). Persistent pollutants, such as polychlorinated biphenyls (PCBs) and trace metals are commonly found in many parts of the world (Fu and Wu, 2006; Wu *et al.*, 2015), and represent a risk to human health, even at small levels (Brito *et al.*, 2005). PCB's use has been banned in many countries, however, these artificial chemicals still persist worldwide (Katsoyiannis, 2006). Neverthless, some of these chemicals are still used in tropical and subtropical countries and due to their extreme chemical stability PCB's levels will not be reduced substantially for many years (Rajendran *et al.*, 2005).

Trace metals are among the most concerning contaminants of drinking water, offering serious threats to human health, and being considered a major environmental concern. Toxicity of trace metals is associated with a continuous exposition to low levels of these elements, what can lead to concerning health issues (Momodu and Anyakora, 2010). The environmental balance of trace metals can be deregulated by anthropogenic activities (Smecka-Cymerman and Kempers, 2001). Urbanization of coastal areas, including industrial activities usually have the potential to contaminate its surroundings, a problem well reported all around the world (Fortunato *et al.*, 2012; Rasool *et al.*, 2016; Samantara *et al.*, 2017). The evaluation of contamination of underground water by trace metals has fundamental importance in order to prevent problems with potable water demand (Kumar *et al.*, 2017).

Contamination of underground waters by arsenic (As) is an environmental issue all around the world. Arsenic (As) is a metalloid, that dissolves in water, and its origins can be anthropogenic, through industrial discharges or mining operations, or natural through geological sources. Minerals such as Fe-Mn hydroxides can retain As in their structure, however, the reduction of these compounds by bacterial action can occur in anoxic environments, releasing the metalloid to the water. Arsenic bonded to sulfides in organic matter can also be released during the remineralization process (O'Day *et al.*, 2004). Arsenic is hardly detectable without analytical determination. This element cannot be tasted or smelled in potable water, however the ingestion of contaminated water with As can cause severe health issues such as cancer, skin problems, vascular diseases and damage to the nervous system, among many others (Chatterjee and Mukherjee, 1999; Roy, 2008; Chakraborti *et al.*, 2016). Arsenic is commonly detectable in shallow aquifers, around 30-70 m depth, rather than in deeper ones. Arsenic in underground water has been detected in 105 countries and it is estimated that over 200 million people have been exposed to As concentrations above the acceptable value established by World Health Organization (WHO) of $10 \mu g.L^{-1}$ (Chakraborti *et al.*, 2016). Several cases of contamination by arsenic through consumption underground water have been widely reported around the world (Chen *et al.* 1994; Hoppenhayn-Rich *et al.*, 1996; Borba, 2003; Yokota *et al.*, 2001; Erickson and Barnes, 2005, Rahman *et al.*, 2015).

The objective of the present study is to assess concentrations of trace metals, arsenic and PCB's in groundwater and soils from the aquifer locates at the coastal plain of Paraíba do Sul river delta, and evaluate the level of impact in the area. The study aims to establish a baseline for trace metals, arsenic, nitrate and organic contaminants on the study area.

2. MATERIALS AND METHODS

2.1 Study Area

The Paraíba do Sul drainage basin covers an area of approximately 57,000 km^2 including some of the most industrialized states in Brazil, such as Rio de Janeiro, São Paulo and Minas Gerais. In the state of Rio de Janeiro the basin covers around 20,600 km^2 (Azevedo *et al.*, 2018). This river basin is responsible for the water supply of the region of Paraíba Valley and also for approximately 75% of water consumption for the metropolitan area of the state of Rio de Janeiro (Paiva *et al.*, 2020). The river has a total extension of 1150 km and the area with watershed is highly urbanized. From the original vegetation of Atlantic Forest only 3% remains, whereas 70% of present vegetation is used as pasture for livestock and 27% for agriculture and reforestation (Ovalle *et al.*, 2013). The coastal plain of Paraíba do Sul is located in the lower river basin in the northern part of the state of Rio de Janeiro. The coastal plain itself has an area of 3000 km^2 with a very flat surface and 120 km length from north to south, an altitude of ~20 m and the lithology is composed of Tertiary and Quaternary terrains. The coastal plain is filled with lakes, ponds and swamps and has been extensively occupied by man, with construction of several artificial channels that reduced the volume of ground water and drained many pond and lakes (Ovalle *et al.*, 2013; Mirlean *et al.*, 2014). The city of Campos, located near the Paraíba do Sul river delta region, presents high water resource availability (Souza *et al.*, 2004). Caetano (2000) identified at this location, large underground water reserves, and one of them comprehends a reservoir of 11 billion m^3. According to Mirlean *et al.* (2014) the shallow groundwater in the delta region is found in a depth from one to several meters and is currently used by the local population. Environmental problems have already been identified as a result of the use and occupation of the area. The urbanization of the area with no sewage infrastructure, no treatment of industrial residues, the absence of domestic trash dumping sites and soil salinization problems were diagnosed (Marchioro *et al.*, 2011). This area is also home for Açu Harbor, operating since 2014 and one of the main poles in the sector of oil and gas operations in Brazil.

2.2 Sampling and analysis

Ten bore wells were randomly distributed in the study area (Figure 1). Sediments were sampled using a stainless steel tube corer and samples were stored in plastic bags properly identified and stored in ice until arrival the laboratory where they were frozen at -20ºC. The water samples for trace metals and arsenic determination were collected through pumping and immediately acidified with HNO_3. Water samples for determination of nitrate were collected and stored in 250 ml polyethylene bottles and kept in ice until arrival at the laboratory. Water samples were then filtered at the laboratory through cellulose acetate membranes of 0.45µm and frozen until the moment of analysis.

Filtered groundwater samples were analysed for determination of nitrate content through ionic chromatography. The determination of trace metals in groundwater were assessed using atomic absorption spectrophotometer (AAnalyst 800-Perkin Elmer®), after samples were filtered through 0.45 µm acetate membranes. In the laboratory sediment samples were freeze-dried and aliquots were separated for the determination of grain size analysis, nitrate, trace metals and arsenic. Grain size analyses were conducted using a Malvern 2600LC® laser analyzer after elimination the organic matter with hydrogen peroxide 10% (v/v). Determination of nitrate in soil samples was performed through ionic chromatography, after extraction of the nutrient from sediments with Milli-Q water and mechanical agitation for 24 hours, followed by centrifugation at 3500 rpm. PCB's were soxhlet extracted and then subjected to an alumina clean-up, silica fractionation and determination with GC–ECD and a capillary column (Smedes and Boer, 1997).

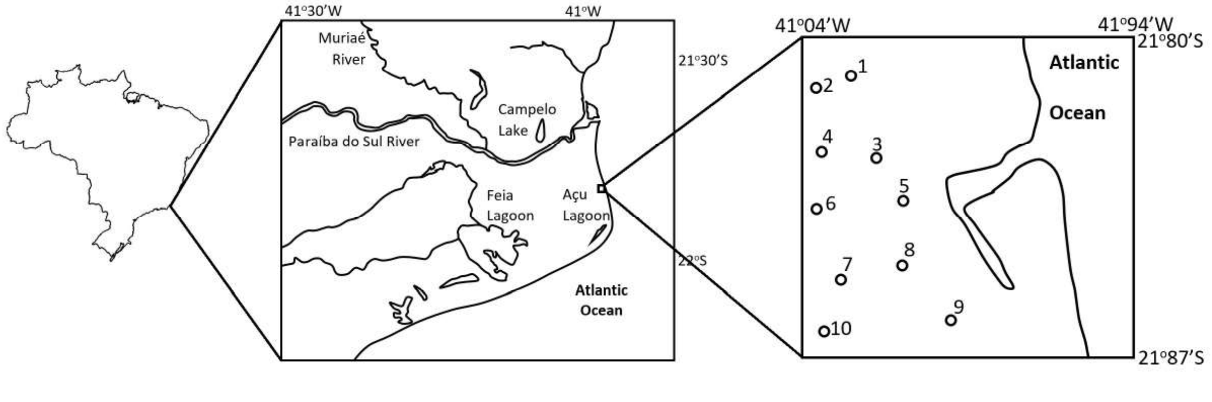

Figure 1. Sampling points for underground water and sediments at the coastal plain of Paraíba do Sul river delta.

The procedure for the determination of the trace metals (Al, Ba, Cd, Pb, Co, Cu, Cr, Fe, Mn, Ni, Ag, V, Zn) and As in the soils followed the method recommended by the EPA method 3050b (USEPA, 1996). Soil samples were grounded with mortar and pestle and 2 g of each sample was placed in digestion tubes with 5 ml of HNO_3 7 M and heated in a digestion block at 95ºC for 15 minutes and allowed to cool. Next to this, 2.5 ml of HNO_3 14 M was added to the digestion tubes and samples were heated again at 95oC for 30 minutes. The process of adding 2.5 ml of HNO_3 14 M was repeated, and after this, tubes caps were removed and samples were heated for another 2h at 95oC. After cooling, the tubes received 3 ml of H2O2 30% (v/v) and 1 ml of Milli-Q water and the mixture was heated with uncapped tubes at 95oC for 2h. After that, tubes were removed from the digestion block and capped and the mixture was left to rest for a period of 16 h. In the last step, the tubes received 2.5 ml of HCL 12 M and the samples were heated again at 95ºC for 30 minutes and allowed to cool. Samples were then filtrated through 0.45 μm acetate membranes and the filtrated was completed to 25 ml with Milli-Q water. Samples were determinate through flame atomic absorption spectrometry in a AAnalyst 800-Pekin Elmer®. Arsenic in ground water and sediments was determined through electrothermal atomic absorption spectrometry using a. Mercury analysis was performed according to USEPA method 7471B (USEPA, 2007).

The software Statistica 7.0® was used to perform Spearman analysis ($p<0.05$), to test significance of correlations among the variables, and Kruskal-Wallis test ($p<0.05$) in order to evaluate significant differences among the bore wells.

3. RESULTS AND DISCUSSION

3.1 Ground water

Among the established trace metals for determination in ground water only Ba, Fe, Mn and Zn were detected. Apart from trace metals, As levels were also found in ground waters from the study area (Figure 2). Table 1 shows current potable water quality guidelines around the world for trace metals and arsenic. In Brazil, the control of trace metals and arsenic in ground waters and sediments is established by CONAMA 420 (2009). The current results showed that the levels of trace elements were mostly far below the maximum allowed concentration, however, arsenic, barium, manganese and iron surpassed the levels established by CONAMA 420 (2009), as well as the levels proposed by other regulatory agencies around the world (Table 1).

Arsenic concentrations in ground waters were very concerning, varying from 1.11 to 242.7 $\mu g.L^{-1}$, surpassing CONAMA 420 (2009) guideline in all the bore wells, except 2 and 8 (Figure 2). Over the last decades, occurrence of high concentrations of arsenic in groundwater became a major environmental problem and started being recognized as a major public-health concern in several parts of the world (Shankar *et al.*, 2014). In Brazil, consternations arose about reports of human exposure to arsenic in drinking-water as an impact of gold-extraction in the region of Minas Gerais, located in southeastern Brazil (Mukherjee *et al.*, 2006). Costa *et al.* (2015) mapped the arsenic concentrations in water and stream sediments using data of 512 sampling points distributed over its 7,000km^2, located to the north from the present studied area. Although data have shown that arsenic occurs naturally in the Iron Quadrangle region, the authors concurred with the possibility that human action has increased these concentrations. In the same way, Borba *et al.* (2000), repeats the suggestion that in addition to the natural loadings of As from the rocks as a result of the weathering processes, the high concentrations of As currently registered in the soils of the Iron Quadrangle can also be faced as an influence of the residues discharged into the watershed during the 300 years of mining along the river margins. Still according to the same authors, since no arsenic minerals were identified in the environment, the arsenic concentrations registered in the river beds could be adsorbed on goethite, kaolinite and illite, minerals that are good “traps” of dissolved arsenic anions. On the other hand, Sakuma *et al.* (2010) suggested that human contamination already seems to be a problem in the area.

According to the same authors, the natural presence of arsenic in the southeastern region of Brazil, combined with the anthropogenic contamination resulted from mining activity may be the reason for the higher urinary arsenic levels among the local children. In 1998, urine exams were done for arsenic measuring in 126 school children. Results showed a mean level of 25.7μg/L. Further environmental evaluations in the surrounding areas found that the mean concentration of arsenic in surface water was 30.5μg/L; levels of arsenic in soil ranged from 200 to 860mg/kg, and sediments had a mean concentration of 350mg/Kg (Matschullat *et al.*, 2000). The study area of the present study, however is far from the problematic region of the Iron Quadrilateral and its upper geological section is mainly composed of quaternary alluvial sediments (Rocha *et al.*, 2013).

A study conducted by Mirlean *et al.* (2014) in the groundwater of the Paraíba do Sul river delta revealed that the aquifer is rich in arsenic fixed by authigenic sulfides. The referred authors have

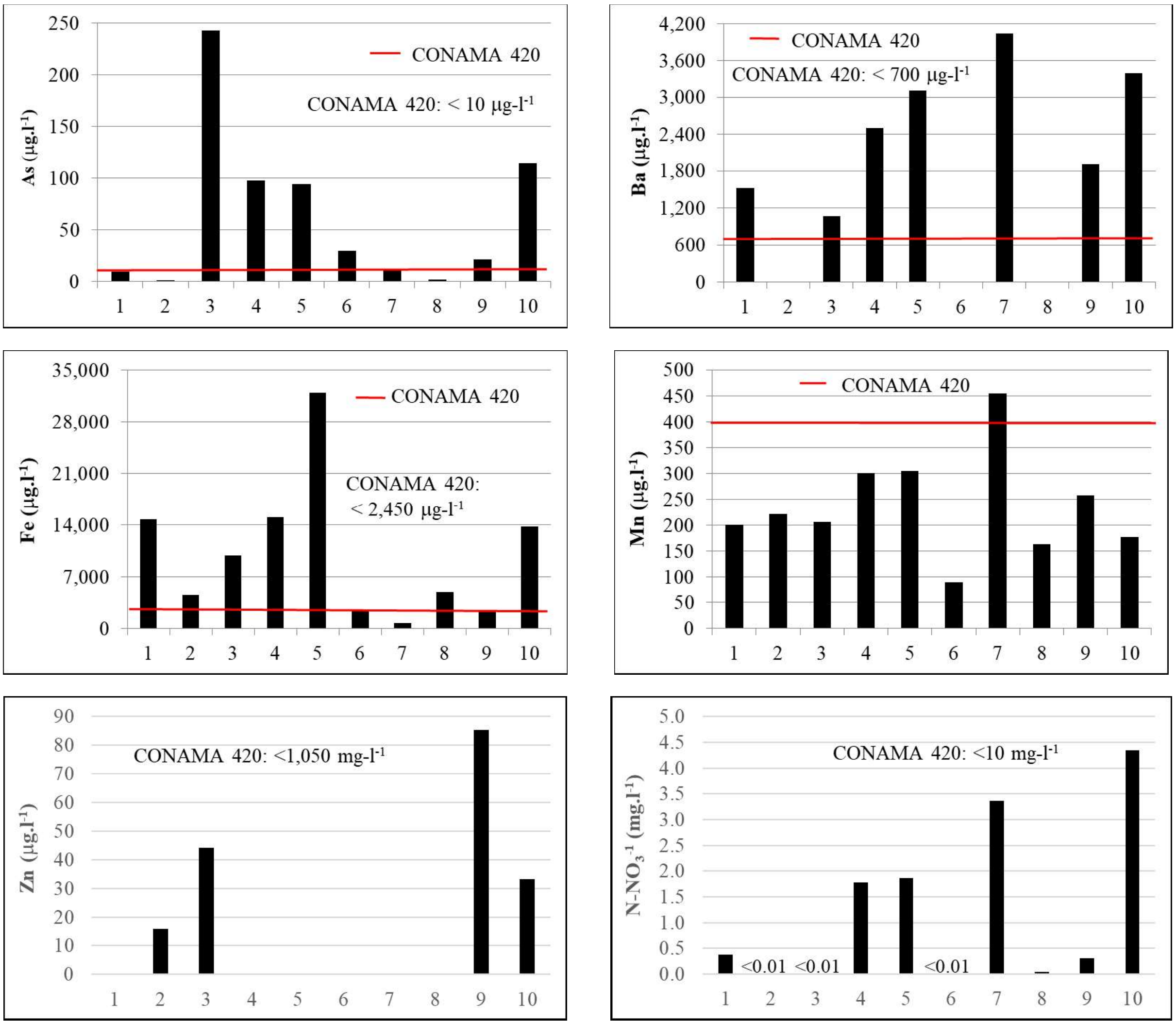

Figure 2. Results of arsenic (As), barium (Ba), iron (Fe) and manganese (Mn), zinc(Zn) and nitrate (N-NO3-) in ground water for the 10 bore wells in the coastal plain of Paraíba do Sul river delta.

described concentrations of As from 5 to 600 µg.L^{-1} in local tube wells and state that the arsenic in groundwater, corroborating the results of the present study, with values surpassing guidelines established by different health and environmental organizations all around the world (Table 1). Mirlean *et al.* (2014) conducted a very detailed study in the area of Paraíba do Sul river delta through a 20 m bore well core and also sampled the area of coastal inter-dune lakes/swamps 3.5km away from the coastline in the inner part of the beach ridge complex. The study of the bore well core included not only some trace metals, but also contents of organic carbon and palynomorphs. Combined results of the study made the refereed authors revealed that As in the ground water of the study area comes from the lower part of deltaic sediments, and that the sediment column has been formed during the coastal lagoon development through inter-dune swales to aquifer buried under eolian sands. The study of Martin *et al.* (1993) suggests that part of the geological profile of the study area may represent sediments of ancient freshwater shallow lakes/swamps or lagoons that existed during the first steps of the Paraíba do Sul delta formed within the 7060±260-5140±200BP period. The refereed authors demonstrated that this lake or swamp was later overlaid by sands, and that this process was long enough to form a 5-6 m layer enriched in organic matter. Aquifers associated with As are usually related to the input of organic matter, which can facilitate the release of this metalloid to ground waters (Herath *et al.*, 2016). According

Table 1. Current drinking water quality guidelines (µg L^{-1}) for trace metals from different regulatory agencies around the world and values found in the present study for ground waters.

Element	aWHO	bUSEPA	cECE	dFTP-CDW	ePCRWR	fADWG	gNOM-127	Present study
Sb	20	6	5	6	5	3	---	0
As	10	10	10	10	50	10	25	1.11-242.70
Cd	3	5	5	5	10	2	5	0
Ba	700	2000	1000	1000	1000	---	---	0-4,401
Cr	50	100	50	50	50	50	50	0
Cu	2000	1300	2000	1000	2000	2000	2000	0
Fe	---	300	200	300	---	300	300	749-31,919
Pb	10	15	10	10	50	10	10	0
Mn	100	50	50	50	500	500	150	89.70-454
Hg	6	2	1	1	1	1	1	0
Ni	70	---	20	---	20	20	---	0
Ag	---	100	---	---	---	100	---	0
Zn	---	500	---	5000	5000	3000	5000	0

a-World Health Organization (WHO 2011); b- United Stated Environmental Protection Agency (USEPA, 2011); c-European Commission Environment (ECE, 1998); d-Federal-Provincial-Territorial Committee on Drinking Water (CDW), Health Canada (FTP-CDW, 2010); e-Pakistan Council of Research in Water (PCRWR, 2008); f- Australian Drinking Water Guidelines (DDWG, 2011); g- Norma Oficial Mexicana NOM-127-SSA1-1994 (DOF, 1994).

to Mirlean *et al.* (2014), the As contents in the core was inherited by the metalloid earlier accumulated in organic sediments from an ancient inter-dune lake or lagoon. The release of As from microbial reduction of Fe (III) hydroxides and its subsequent migration to upper layers in the sediments to be fixed again in the oxic zone is well established (Campbell *et al.*, 2006), however, the diffusion downwards can also occur favoring the bonding of the metalloid with particulate sulfides, which is described to happen in the study of Mirlean *et al.* (2014) that proved the occurrence of sediments remarkably enriched in sulfide and organic carbon, especially at the bottom of the bore well core in the study area.

Concentrations of Ba in the bore wells surpassed the value established by CONAMA 420 (2009) up to 5 times, reaching the maximum concentration of 4,41.02 µg.L^{-1} in bore well 7 (Figure 2). Barium was not detected at bore wells 2, 6 and 8. Elevated concentrations of Ba in ground waters used as drinking water poses risks to human health since this element can cause hypokalemia, eletrocardiographic changes, increases blood pressure and affects the nervous system (Luu and Sthiannopkao, 2009; Bondu *et al.*, 2020). There are a number of sources that can account for Ba in groundwater. Aquifer solids play a similar role to estuarine particles, adsorbing Ba from groundwater which can be released in the event of exposure of the aquifer to salt water intrusion. Diagenetic controls of barium include the dissolution of Ba bonded to metal oxides phases or to authigenic barite ($BaSO_4$). Barite has low solubility and is very unstable in reducing environments due to the reduction of sulfate. High concentrations of sulfate would limit the concentration of Ba in ground waters due to saturation of barite (Giménez-Forcada and Vega-Alegre, 2015), and opposed to this, low concentrations of the anion (<5mg.l^{-1}) would increase Ba contents (Bondu *et al.*, 2020). The afore mentioned sources would be transients and maintained by the flow path of the low salinity desorption. The decomposition of organic material containing barium could release this element to ground water and this would suggest the existence of a large buried reservoir of organic matter enriched in Ba (Shaw *et al.*, 1998). The concentrations of Ba in the present study could be originated from sediment enriched with organic matter and controlled by sulfate reduction, since results found by Mirlean *et al.* (2014) confirm the existence of high concentrations of organic carbon and sulfides in the study area.

In the same way as the other metals, iron and manganese occur naturally in the global geology. In the underground reservoir, water accumulation shave contact with these solid materials dissolving and incorporating them, including Fe and Mn. Manganese has been known as a neurotoxin for at least 150 years, although it is still not clear whether eating or drinking foods and liquids with excessive levels of manganese can cause symptoms of manganism (ATSDR 2000). In the present study Mn varied between 89.7 and 454 µg.L^{-1}, surpassing CONAMA 420 (2009) guidelines only in the groundwater from bore well

Table 2. Concentrations of As, Ba, Fe, Mn, Zn (μg.L-1) and nitrate (mg.l-1) in different aquifers around the world.

Aquifer	Reference	As	Ba	Mn	Fe	Zn	NO_3-
*Espadan-Calderona Triassic Domain (Spain)	(Giménez-Forcada and Vega-Alegre, 2015)	2.31	90.5	4.25	92.2	--	46.4
Costal Aquifer Kalpakkam, Tamil Nadu (India)	(Samantara *et al.*, 2017)	--	--	n.d.-587.3	n.d.-89.9	1.8-220	n.d.-263.5
Calvery river basin, Tamil Nadu (India)	(Vetrimurugan *et al.*, 2017)	--	--	10-7000	50-550	--	--
Utar Pradesh (India)	(Kumar *et al.*, 2017)	0.07-237	--	0.9-301	40-12,700	4.8-1,500	--
*Pleistocene Aquifer Cambodia (Vietnam)	(Gillispie *et al.*, 2019)	146.9	--	1.8	2,900	--	143.2
Southern Quebec (Canada)	(Bondu *et al.*, 2020)	n.d.-280	n.d.-90,000	n.d.-7,500	n.d.-38,380	--	--
Aquifer System of Santa Catarina (Brazil)	(Carasek *et al.*, 2020)	--	--	n.d.-497	n.d.-2,685	n.d.-0.77	0.003-8.20

*mean values; n. d.- not detected

7 (Figure 2). Manganese concentrations in the groundwater, however, greatly overcame the limits established by other regulatory agencies around the world indicating threat to human health with regards to the use of groundwater by local population (Table 1). Iron varied between 749 to 31,919 μg.L-1, and surpassed the brazilian guideline in all bore wells, except for 7 (Figure 2). Iron concentrations also surpassed by far the guidelines established by other regulatory agencies (Table 1). The dissolution of water in groundwater is usually in the form of Fe (II), since Fe (III) forms insoluble hydroxides in water. The release of Fe then could be originated by microbial reduction of Fe oxyhydroxides, an import process in the geochemistry of iron in anaerobic soils and sediments (Roden and Zachara, 1996).

A high concentration of Hg had been detected in only one sampling station bore well 2 (12 μg.L-1). Zinc was also detected in the groundwater of some bore wells (Figure 2), but values were within the recommended limits by the brazilian legislation.

Overall, some of the results of groundwater from the present study are comparable to the ones found in aquifers impacted by anthropogenic activities (Table 3), as is the case of arsenic, which presented levels similar to the one found by (Samantara *et al.*, 2017; Gillispie *et al.*, 2019; Bondu *et al.*, 2020), however the previous studies in the study area suggest a natural source of the metalloid in the aquifer of the study area. The elevated levels of barium found in the present study, despite surpassing limits of current brazilian legislation, were much lower than the ones found by Bondu *et al.* (2020) in the aquifer of Quebec (Table 3).

The maximum acceptable concentration of nitrate in groundwater recommended by the brazilian legislation (CONAMA 420, 2009) is 10 mg.l-1, and all the samples for underground water presented concentrations under this value (Figure 2), between 0.04 and 4.34 mg.l-1. PBC's, were not detected in the groundwater of the ten bore wells in the present study.

3.2. Soils

Grain size influences the soil porosity, transport and deposition, and for this reason provides fundamental indications to the sediment depositional history and past environmental conditions (Pye and Blott, 2004). Results from showed predominance of gravel and sand at bottom sediments from the study sites, surpassing 80% of grain size for most samples. Fine sediments, composed of silt and clay varied between 7.8 and 31.9%, with highest values (>20%) at sites 1, 2 and 10 (Figure 2). Grain size analysis suggested the predominance of soils with a low retention capacity for trace metals and other pollutants, due to the low concentration of fine particles.

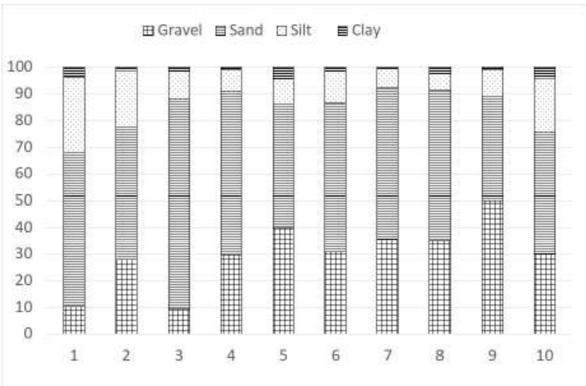

Figure 3. Grain size results for soils in bore well sites at the coastal plain of Paraíba do Sul river delta.

The trace metals environmental contamination can result from excessive fertilization, pesticide usage, irrigation, atmospheric deposition, and waste materials pollution (Aydinalp and Marinova, 2003). Unlike organic contaminants, trace metals do not experience microbial or chemical depuration (Kirpichtchikova, *et al.*, 2006), and their levels in soils are maintained for a long time after their input (Adriano, 2003). Studies assessing the use of sewage mud as fertilizer in sugarcane cultures suggested that the doses applied increased heavy metal concentration in the soil. The metals are also components of many pesticides, mainly Cu, Zn and Pb, which cause high soil contamination by these elements (Núñez *et al.*, 2006). The trace metal concentrations in soils obtained in the present study are presented in Table 3. Differences in metal content among the bore wells were not considered significant, except for copper (Table 4).

Table 3: Basic statistics for the trace metals concentrations detected in the bore wells from the study area. Mean, standard error, maximum and minimum values (mg.kg^{-1}).

Element	Mean±SE	Max	Min
Al	434.61±95.17	1615.94	84.49
As	1.25±0.47	7.03	n.d
Ba	261.81±51.85	774.73	61.81
Cu	0.99±0.24	3.13	n.d.
Cr	8.26±4.92	101.00	0.68
Fe	1554.98±429.99	5804.17	n.d
Mn	11.06±3.33	45.24	n.d
Hg	0.04±0.01	0.27	n.d
Mo	8.20±5.03	101.00	n.d
Zn	3.86±0.94	13.69	n.d

The registered concentrations in the present study can be considered low if compared with other studies of trace metals in aquifer soils. (Gillispie *et al.*, 2019) studied sediments from an aquifer located in a deltaic floodplain between Mekong and Bassac rivers in Cambodia (Vietnam) and found As, Mn and Fe with maximum concentrations of 24.9; 2,100 and 35,200 mg.kg^{-1}, respectively. (Kashouty and Sabbagh, 2011) found concentrations of metals much higher than the ones in the present study in sediments from an aquifer in Wadi El Natrum (Egypt), reaching values as high as 509; 1,849; 2,752; 243,000; 106 and 45,840 mg.kg^{-1}, for Ba, Cu, Cr, Fe, Mn and Zn, respectively. Mirlean *et al.* (2014) found a maximum concentration of As of 30.2 mg.kg^{-1} in a bore well core in the coastal plain or the Paraíba do Sul river delta, a value much higher than the maximum found in the present study, 7.03 mg. kg^{-1} (Table3). The maximum value of As found by Mirlean *et al.* (2014) was justified by the position of the sample in the core, around 15 m, coinciding with the end of the swampy period of profile development and beginning of the sediment overlap by eolian sands in the study area. These lower concentrations of metals compared to other study areas, could be explained by the sandy nature of the samples collected, with very low contents of fine sediments, which lowers the capacity of bonding metals. The Spearman analysis proved that there was no correlation between fine sediments and the metallic elements determined in this study (Table 5). The elements Fe, Mn, Zn, and Cr presented significant and direct correlation among them, suggesting a common origin (Table 5). The exception to low metal concentrations was Ba, that reached values over 700mg. kg^{-1}, surpassing values found in other aquifers by Kashouty and Sabbagh (2011) and Gillispie *et al.* (2019). Pérez *et al.* (1997), conducting a study covering 15 soil types distributed over 5 regions in Brazil registered concentrations of Ba varying between 0.09 and 201.4 mg.kg^{-1}, much lower than the concentrations obtained in the present study. Mercury values reached the highest concentration in bore well 8, 0.27 mg.kg^{-1}. No hg was detected in bore wells 1, 2 3 and 4. According to some authors, although not as expressive as the use of Hg pesticides, the usage of Hg in gold exploration activities in Rio Paraiba do Sul watershed between 1986 and 1987 has probably resulted in negative impacts like raising Hg sediments and biota levels (Primo, 2000). Souza el al. (2004) studied Hg levels in sediment cores distributed in some lagoons located in the same area of the present study. According to their study, in the Açú lagoon the levels ranged from 40.3 µg.g^{-1} to 50.7 µg.kg^{-1}. PCB's were not detected in the soils of the present study.

Table 4: Kruskal-Wallis test for trace metal content in soils among the bore wells from the study area ($p<0.05$).

Element	*p*
Al	0.9596
As	0.0659
Ba	0.8677
Cu	0.0487
Cr	0.8722
Fe	0.9571
Mn	0.9325
Hg	0.2581
Mo	0.1029
Zn	0.0640

Table 5: Spearman correlation ($p<0.05$) for the soil variables in the study area (significant correlations in bold).

	Al	As	Ba	Cu	Cr	Fe	Mn	Hg	Mo	Zn	Gravel	Sand	Silt	Clay
Al	1.00	0.28	**0.71**	-0.14	**0.77**	**0.94**	**0.86**	-0.37	-0.18	**0.54**	0.14	0.01	-0.12	0.18
As		1.00	0.05	**-0.62**	0.34	0.36	0.37	**0.52**	**-0.49**	**0.70**	**0.49**	-0.39	-0.22	-0.14
Ba			1.00	0.23	**0.53**	**0.73**	**0.71**	**-0.56**	0.15	0.22	-0.13	0.22	-0.10	0.01
Cu				1.00	-0.07	-0.16	-0.14	**-0.67**	0.39	**-0.77**	**-0.72**	**0.49**	0.38	-0.14
Cr					1.00	**0.64**	**0.59**	-0.43	0.18	0.35	-0.08	-0.05	0.08	0.24
Fe						1.00	**0.92**	-0.26	-0.31	**0.56**	0.22	0.04	-0.25	0.04
Mn							1.00	-0.25	-0.31	**0.55**	0.25	0.06	-0.30	-0.03
Hg								1.00	**-0.50**	0.34	**0.65**	**-0.55**	-0.27	-0.08
Mo									1.00	**-0.48**	**-0.54**	0.15	0.32	0.00
Zn										1.00	**0.71**	-0.40	-0.38	0.13
Gravel											1.00	**-0.65**	**-0.56**	-0.15
Sand												1.00	-0.14	-0.17
Silt													1.00	0.30
Clay														1.00

4. CONCLUSIONS

The study of the ground water in the aquifer from the coastal plain of Paraíba do Sul river delta, detected levels of arsenic, barium, iron, manganese, zinc and nitrate. Results showed high concentrations of iron, barium and arsenic in the goundwater, which in most bore wells extrapolated the limits of the brazilian legislation, as well as the limits from some other regulatory agencies around the world. Arsenic levels in groundwater were comparable to the levels of the metalloid found in other aquifers impacted by anthropogenic activities. Despite that, there are no activities in the surroundings of the study area that could justify these concentrations. Indeed, the origin of arsenic in groundwaters of the Paraíba do Sul river delta was already proven to be from lake/swamp origin resulting from sulfide complex deposition through oxidation, which can occur during the pumping to collect groundwater. Barium and iron concentrations suggest an anoxic environment in groundwater, since only the reduced form of Fe is soluble, and large concentrations of Ba are usually controlled by reduction of sulfate. The reducing environment could also contribute to the concentrations of arsenic in groundwater through the reduction of As rich minerals such as Fe-Mn hydroxides. Concentrations of metals in soils did not corroborate the findings in the groundwater with regards to pollution, reinforcing the hypothesis that levels of As, Fe and Ba can be of natural origin, and no significant differences were observed among the bore wells. Results suggested a common and natural origin for iron, manganese, zinc and chromium in soils. The low concentrations of silt and clay on soils did not seem to play an important role in retention of the metals in the study area. Apart from small concentrations of mercury in soils, results suggest that most of the elements determined in the present study have geogenic origin. The present study presented very useful information to be used by public policies in the management of ground water resources that serve the local population. Geogenic contamination of ground waters used for human consumption is a common issue around the world, and mitigation measures must be taken by public authorities in order to prevent population illness, like prohibiting the installation of supply and consumption wells, in addition to the provision of alternative water sources. Parallelly, health and nutrition of the local community programs may be stimulated in order to render people more resilient and to lower the incidence or seriousness of the health impact.

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