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Investigação sobre a concentração de ferro em águas de abastecimento público no município de Breves (PA)

Research on the iron concentration in public supply waters in the municipality of Breves (PA)

Investigación sobre la concentración de hierro en el agua de abastecimiento público del Municipio de Breves (PA)

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Resumo
O ferro está entre os padrões de potabilidade da água estabelecidos pela Portaria do Ministério da Saúde nº 2.914/2011, limitado a 0.30 $mg.L^{-1}$, estabelecido devido a problemas estéticos relacionados à presença de ferro na água e seu sabor. Os estados de oxidação do ferro são Fe^{+2} e Fe^{+3}, e o íon ferroso (Fe^{+2}) é mais solúvel que o férrico (Fe^{+3}), embora substâncias não tóxicas resultem em vários problemas. Abastecimento público de água, principalmente para pessoas carentes que não têm recursos para tratar adequadamente suas casas. O objetivo do presente trabalho foi investigar a concentração total de ferro no abastecimento de água municipal localizado no bairro Riacho Doce na Cidade de Breves (PA). As amostras foram preparadas e analisadas nas mesmas condições que as soluções de calibração duplicadas padrão. As análises da água foram realizadas pelo método de absorção atômica com chama, assim todas as amostras passaram por um procedimento de pré-tratamento para remoção de matéria orgânica, porém os resultados de todas as amostras estão fora dos padrões de qualidade estabelecidos pelos órgãos. Alguns são mais de 20 vezes o máximo, tornando a água imprópria tanto para consumo quanto para uso doméstico.
Palavras-chave: Ferro total; Abastecimento de água; Riacho doce.

Abstract
Iron is among water potability standards established by Ministry of Health Ordinance No. 2914/2011, limited to 0.30 $mg.L^{-1}$, established due to aesthetic problems related to the presence of iron in the water and its taste. Iron oxidation states are Fe^{+2} and Fe^{+3}, and ferrous ion (Fe^{+2}) is more soluble than ferric (Fe^{+3}), although not toxic substances result in several problems. Public water supply, especially for needy people who do not have the resources to properly treat their homes. The objective of the present work was to investigate the total iron concentration in municipal water supply located in the Riacho Doce neighborhood in the city of Breves (PA). Samples were prepared and analyzed

under the same conditions as standard duplicate calibration solutions. Water analyzes were performed by the flame atomic absorption method; thus all samples underwent a pre-treatment procedure for the removal of organic matter, however the results of all samples are outside the quality standards established by the organs. Some are more than 20 times the maximum making water unsuitable for both consumption and home use.
Keywords: Total iron; Water supply; Riacho doce.

Resumen
El hierro se encuentra entre los estándares de potabilidad del agua establecidos por la Ordenanza Nº. 2914/2011, limitada a 0.30 mg.L^{-1}, establecida por problemas estéticos relacionados con la presencia de hierro en el agua y su sabor. Dáselo los estados de oxidación del hierro son Fe^{+2} y Fe^{+3}, y el ion ferroso (Fe^{+2}) es más soluble que el férrico (Fe^{+3}), aunque las sustancias no tóxicas dan lugar a varios problemas. Abastecimiento público de agua, especialmente para personas necesitadas que no cuentan con los recursos para tratar adecuadamente sus viviendas. El objetivo del presente trabajo fue investigar la concentración de hierro total en el suministro de agua municipal ubicado en el barrio Riacho Doce en la ciudad de Breves (PA). Las muestras se prepararon y analizaron en las mismas condiciones que las soluciones de calibración por duplicado estándar. Agua realizada por el método de absorción atómica a la llama, por lo que todas las muestras fueron realizadas por el procedimiento de pretratamiento para la remoción de materia orgánica, sin embargo los resultados de todas están fuera de los estándares de calidad establecidos por los órganos. Algunos son más de 20 veces el máximo, lo que hace que el agua no sea apta tanto para el consumo como para el uso doméstico.
Palabras clave: Hierro total; Abastecimiento de agua; Riacho doce.

1. Introduction

Water is an extremely important resource for the existence and maintenance of life, in the configuration we know. The first traces of life developed in the water, and it would be difficult to idealize the survival of any form of life in the absence of this precious resource (Grassi, 2001). It is naturally found present in high proportions in the constitution of all living beings and in man it reaches approximately 75% of its body mass (Lemos, 2011).

Water has been an extremely important asset for man in ancient Egypt, after the agricultural revolution that took place some 5,000 years before Christ, the discovery that food production depended on the supply of water, made cities to develop close to rivers that meet their domestic and agricultural demands. Subsequently, running water also started to be used in the movement of machines that cut wood, in grain mills and finally in industrial processes (Grassi, 2001).

Certainly, water is the most abundant chemical species on the Earth's surface. The planet Earth is the only one in the solar system in which this substance can be found naturally, in the three physical states: solid (ice), liquid (liquid water) and gaseous (vapor), and changes in the physical state of the water in the hydrological cycle they are essential and influence the biogeochemical processes in terrestrial and aquatic ecosystems (Tundisi, 2003a).

Compared to other hydrides, water has much higher melting and boiling temperatures, as can be seen in Table 1. These characteristics are of fundamental importance for the existence of life on Earth, since the liquid form is the predominant physical state (Bunce, 1993).

Table 1 - Physical properties of some simple hydrides.

Substance	CH_4	NH_3	HO_2	HF	HS_2
Fusion point, ° C	-182	-78	0	-83	-86
Boiling point, ° C	-164	-33	+100	+19	-61

Source: Grassi (2001).

Another important characteristic of water, but unusual, is that the liquid form has a higher density than the solid form. Normally, water solidification occurs in winter, in countless rivers and lakes located in the northern hemisphere of our planet.

Through this property the ice is concentrated on the surface, and in summer, with the increase in temperature, the melting happens naturally. If the opposite were true, during periods of low temperatures, the waters, when frozen, would settle at the bottom of rivers and lakes. Under these conditions, they probably would not merge again in the summer (Grassi, 2001).

According to Tundisi (2006), the main specialty of water regarding its availability and distribution on the planet, is from the hydrological cycle. This cycle is continuous, in which liquid water evaporates from the surface of the Earth, the oceans and other reserves and, by the movement of the winds, is incorporated into the atmosphere in the gaseous state, being transported to the continents and returning to the liquid state in the form of rain or snow, through solar energy.

Annually, the sun's energy causes an approximate volume of 500 thousand km^3 of water to evaporate, mainly from the oceans (Fernandes, et al., 2008). The speed of the hydrological cycle varied from one geological era to another, as well as the volume of fresh and marine waters (Tundisi, 2006).

Although the hydrological cycle is unique for the entire planet, its specifications are not homogeneous, the volume of each of its components varies in different regions of the planet and by hydrographic basin (Pielou, 1998). As a result, there is an uneven distribution of water on Earth. There are 26 countries with water scarcity and at least 4 countries (Kuwait, United Arab Emirates, Bahamas, Gaza Strip - Palestinian territory) with extreme water scarcity (Tundisi, 2003b).

In the Municipality of Breves (PA) the water supply is made by the Companhia de Saneamento do Pará (COSANPA), however, the supply does not cover all neighborhoods in the city, because due to population growth, especially in the peripheral regions, there was a need to increase supply services. However, the company did not expand the networks to these peripheral areas, being restricted to only the central neighborhoods of the city where it already contained plumbing networks for supply. The reasons for the lack of interest in increasing services is that COSANPA de Breves generates losses for the company, as there is no collection for the services provided and neither the help of the municipality to finance, at least, the materials used in the treatment. As a result, employees need to request in advance so as not to lack the necessary products.

In the Riacho Doce neighborhood, in the peripheral region, water is supplied through a small supply station under the city hall. In this one, according to the employees, no type of chemical treatment takes place, which generates a lot of complaints from local residents about the color and taste of the water available, implying a high iron content. With this, the research was carried out seeking to check the amount of iron in the water supplied by the municipality, comparing these values with the limits for potability recommended by Ordinance 2914/2011 of the Ministry of Health and Resolution 357/2005 of the National Council for the Environment (CONAMA).

Distribution of Water on Earth

Fresh water is needed to survive, however, approximately 97.5% of the water on our planet is salty, that is, unfit for human consumption. Only 2.5%, which contemplate the total of existing water is fresh, however, 2/3 are stored in the glaciers and polar caps in solid state. Only about 0.77% of the total water is available for our consumption, being found in liquid form in rivers, lakes, groundwater, including water present in the soil, in the atmosphere (humidity) and in biota. Drinking water, therefore, is an extremely reduced resource (Grassi, 2001). Brazil, approximately 16% of the planet's fresh water is available, unevenly distributed in its regions (Tundisi, 2003b).

Table 2 - Water distribution on our planet.

Reservoirs	Volum, km^3	Percent, %
Oceans	1,320,305,000	97.24
Glaciers and polar caps	29,155,000	2.14
Groundwater	8,330,000	0.61
Lagos	124,950	0.009
Seas	104,125	0.008
Soil moisture	66,640	0.005
Atmosphere	12,911	0.001
Rivers	1,250	0.0001
Total	1,358,099,876	100

Source: USGS (1999).

On planet Earth, water is present in different rooms, as can be seen in Table 2. The amount of water present in each of these compartments, as well as their residence time, varies greatly. The oceans form the largest of these rooms, where water has a residence time of approximately 3,000 years. They are also the source of most of the water vapor that appears in the hydrological cycle, being large accumulators of heat from the sun. Oceans play a fundamental role in Earth's climate (Grassi, 2001).

The second largest water reservoir on the planet and the first when it comes to fresh water are the glaciers and polar ice caps. The Antarctic continent contains approximately 85% of all ice in the world. The rest can be found in the Arctic Ocean and in Greenland (Grassi, 2001).

Freshwater bodies in direct contact with the atmosphere are collectively titrated from surface waters that cover lakes and reservoirs. The concentration of salts in the water causes the surface waters to be divided into two broad categories. Fresh waters are different from salt waters due to their low salt content, and are normally found in rivers and lakes (Grassi, 2001).

The replacement of fresh water found on the planet is mainly the responsibility of the hydrological cycle, through the evaporation of ocean waters and precipitation (manahan, 1997). However, the occurrence of rain on the planet occurs in a very different way. The dense forests sprout in regions with high levels of rain, so there is enough water for the entire natural biota, as well as for humans. Other regions are deserts due to the practically absence of rain. Because of this, we can imagine very variable volumes of water circulating over different regions of the globe (Grassi, 2001).

There are countless cases of stressed ecosystems around the planet due to water scarcity. In addition, in drier regions, especially those with high population density, the number of conflicts and disputes between countries that have the same source of water increases due to human needs, agricultural, urban and industrial activities (Ortolano, 1997).

Global changes on the planet cause changes in the hydrological cycle, which should have impacts on evaporation, water balance and biodiversity of aquatic systems (Tundisi, 2006). Furthermore, expectations for the future are not promising, two thirds of the world population will be living in water stressed regions by 2025. In many developing countries, the low availability of water resources will affect growth and the economy, pollution will remain affecting continental and coastal waters and inappropriate land use will affect river basins, coastal waters and estuaries (Watson, et al., 1998).

According to Tundisi (2003a), based on the results of analysis by specialists from the World Resources Institute - World Resources Institute (WRI), the volumes of water available and the consequences of multiple uses point to a crisis unprecedented in human history. Grassi (2001) points out that experts believe that within a maximum of 2 or 3 years, there will be a crisis in the world related to the availability of water of similar quality to that of oil, in 1973.

Even Brazil should not escape the water crisis that is being predicted. It is worth mentioning that more than 80% of the total volume of surface water available in Brazil is located in the Amazon region. The remaining 20% are distributed throughout the country, in an uneven manner, and are intended to supply approximately 95% of the Brazilian population (Rebouças, et al., 1999).

The availability of quality water is already a serious problem, with regions and countries on the verge of collapse (Margat, 1998). The situation is also worrying in China, the United States, Hungary, India, Mexico and Thailand (Costa, 2007). The availability of less than 1000 m^3/inhab/year already represents a condition of "water stress" and less than 500 m^3/ inhab./Year results in "water scarcity" (Falkenmark, 1986).

The constant increase in the volume of water used, the increase in pollution and water contamination has caused the degradation of springs and water supply, making one of the main consequences of this deterioration to be on human health, reflecting on the increase in infant and child mortality. hospital admissions, in addition to the high economic costs to recover water sources for supply (Tundisi, 2003b).

Of all substances absorbed by plants, water is needed in greater quantity because it is the main constituent of plant cells, reaching up to 95% of the total weight (Sutcliffe, 1980). Water is fundamental in the production of plants, as it participates in all the physical, chemical and biological phenomena vital to its development (Fernandes et al., 2008).

Brazil stands out on the world stage for the enormous amount of fresh water in its rivers. However, even having large hydrographic basins, it still suffers from a lack of water, due to the poor distribution made by the dominant population mass, which grows rapidly and exaggeratedly concentrated in areas of insufficient water availability (Costa, 2007).

Underground Waters

Groundwater represents a margin of 98.8% of the available liquid drinking water, however, only half is used, since the other part is located at depths greater than 800m, making collection difficult (Setti, 1995). As it is found in the subsoil, the waters in aquifers, have more protection against contamination than the surface waters. Despite this, groundwater can present quality problems, limiting its use. Among these, what occurs most frequently is the presence of dissolved iron in high levels (Picanço, 2002).

Aquifers are porous rock formations, where groundwater is stored, these waters are influenced by the chemical composition and minerals contained in the rocks (Grassi, 2001). The supply of underground reserves occurs through the slow infiltration of surface water through the soil, these waters are accommodated at different depths, being sustained by pressure, on several occasions. Through groundwater, wells used in rural areas are supplied, in addition to being used as a source of supply for small and medium-sized cities (Fernandes, et al., 2008).

Named artesian wells, especially those of great depth, whose height exceeds the natural water level of the water table, form important sources, given the almost complete absence of microorganisms in their waters (Fernandes, et al., 2008). However, groundwater has a higher cost than surface water, it is considered a strategic reserve that must be protected and cannot be treated differently from surface water. Water flows from underground deposits remain abundant with rainwater. However, when the use overcomes the natural recharge of these springs, a problem of scarcity will begin to appear (Rodriguez, 1991).

The appropriate exploration of groundwater has left several regions of the planet above the minimum water value per capita of 1000 m^3/inhab./Year, an example is the northeastern city of Recife, in Brazil (Nebel & Wright, 2000).

Water Quality

The question of the quality of the water available is as or more important than the quantity of water available. Our planet is flooded by a volume of almost 1.4 billion km^3 of water, covering 71% of the Earth's surface. Despite all this abundance, many localities still suffer from a lack of water with adequate drinking characteristics for human consumption (Grassi, 2001). It is necessary to understand that the quality of the water refers to chemical, physical and biological characteristics, and that, according to these attributes, different purposes are stipulated. Thus, the national normative policy, through CONAMA Resolution 357, sought to establish parameters that determine the acceptable limits of foreign bodies, considering the different purposes.

Water consumption for the most varied purposes has been increasing continuously and its availability with appropriate quality is becoming increasingly scarce. Water resources are renewable, but finite. In this way, its preservation becomes even more important and management needs to be reviewed by countries. The lack of water is an environmental problem, where the consequences tend to be increasingly serious. Currently, more than a billion people suffer from a lack of clean water, which has become insufficient to meet their basic daily needs (Fernandes, et al., 2008).

The condition of the water has deteriorated significantly around the planet, especially in the last 50 years. Problems caused by water pollution intensified, especially in the post-war period. To facilitate understanding, the Company of Technology and Environmental Sanitation of the State of São Paulo (CETESB) defined pollution as “any substance that can make the environment inappropriate, harmful or offensive to health, inconvenient to public well-being, harmful to materials, fauna, flora or harmful to security, the use and enjoyment of the property and the normal activities of the community”. Thus, any substance that falls under any of these established definitions is called a pollutant (Grassi, 2001).

Several factors influence water quality. Among them are biological factors, which comprise organisms such as bacteria in the fecal coliform group. There are also physical-chemical factors, which include: acidity, alkalinity, color, total hardness, pH, temperature, turbidity and chemicals such as iron, lead, fluorine, chlorine, among others (Ciminelli, 2014).

The Ministry of Health, the body that controls and inspects the condition of water for human consumption, by Decree 2914/2011 and CONAMA by Resolution 357/2005, established minimum quality standards for the consumption and use of water. If the factors are outside the required quality standards, they can cause health risks, such as diseases related to microorganisms associated with water transmission resulting from inadequate water treatment (Texeira, 2002).

Between 1985 and 2000 the supply of drinking water available to each inhabitant on the planet decreased by approximately 40% (Nebel & Wright, 2000). While the amount of drinking water for human consumption decreases dramatically, consumption has been increasing due to population growth. Between 1940 and 1990, total water consumption jumped from 1 thousand to 4.13 thousand km^3 / year. Expectations only get worse when we look at the predictions for the current century (Ghassemi, et al., 1995).

With the increase in population and the State's insufficiency to promote the preservation of fresh water, the quality of this finite resource tends to worsen, especially due to the pollution of natural reservoirs. Annually, approximately twelve million people die from problems caused by water quality. In Brazil, the Unified Health System (SUS) highlights that 80% of hospital admissions are related to diseases caused by the improper quality of water for human consumption (Merten & Minella, 2002).

The largest consumer of water on Earth is agriculture, mainly through irrigation, which removes almost 70% of the planet's drinking water. The water used for irrigation does not return to the same source from which it was taken, having a so-called consumptive use. Industrial activities, in turn, which consume approximately 23% of drinking water, exercise non-consumptive use, these waters, despite being often contaminated by waste, return to the primary source, where it remains available for reuse. Finally, the human being is responsible for the consumption of 8% of good quality water, through direct use (Grassi, 2001).

Iron

Iron is one of the most well-known metals today, it is a chemical element found in the solid state at room temperature, due to its high melting point of 1535 °C and boiling point of 2750 °C. Classified as Fe symbol transition metal with atomic number 26 and atomic mass equal to 55.845 $g.mol^{-1}$. It belongs to group 8 of the periodic table with four known natural isotopes: ^{54}Fe, ^{56}Fe, ^{57}Fe e ^{58}Fe (Vaitsman, et al., 2001).

Iron is one of the most abundant metals in the earth's crust, and with changes in the climate, lack of soil maintenance, extensive pasture with erosive probability and weathering of rocks, which are part of the drainage basin, accelerate the arrival of this substance at the population's water collection sites (Franco, 2008).

It is an important metal in both animal and plant life, essential in the composition of biomolecules such as hemoglobin (red blood cell pigment), which is responsible for transporting oxygen from the lungs to the tissues in our body. Iron deficiency can cause anemia and its excess can cause generalized fibrosis of the internal organs (Vaitsman, et al., 2001).

The compositions of the element iron are easily found in aquatic environments, where it has a more complex geochemical composition compared to other environments and strongly defined by the ease of its valences, even in small quantities. The most important oxides of iron are: FeO, Fe_2O_3 e Fe_3O_4, all being oxidized or reduced with moderate ease in other forms (Franco, et al., 2010).

Although iron is a beneficial element for several organisms, if ingested in high concentrations, they can accumulate in human tissues, causing neurological disorders, such as Parkinson's disease and Alzheimer's dementia (Fernandez, et al., 2007). Iron when it accumulates in organs also causes diseases, for example: in the heart it causes heart failure, in the liver it causes cirrhosis and liver tumors and in the pancreas it generates hormonal disorders causing diabetes mellitus (Devlin, 1998).

Another consequence of the excess of iron in the body is the exaggerated formation of free radicals that attack cellular molecules, in this way the amount of potentially cancerous molecules increases (Mahan, 2000). As a form of prevention, so that it does not have consequences with the exaggerated storage of iron in the body, the maximum daily consumption of 0.8 mg/kg^{-1} of weight is advised (Who, 2006). Therefore, if the individual's main source of iron is water, a concentration of 2 mg/L^{-1} would not pose a health risk if it does not exceed 10% of the daily total. However, in this concentration, taste and appearance would be negatively affected (Matos, 2008).

The WHO (World Health Organization) does not establish a specific value for iron dissolved in water, as it does not pose a health risk. However, considering the obligation to provide the population with a water supply within the quality standards, CONAMA Resolution 357, of 17 March 2005 and Ordinance 2,914/2011 of the Ministry of Health establish the maximum allowed amount of iron in the water used for human consumption of 0.3 mg/L^{-1}, and that values above affect the water quality. Thus, in waters with excess of this metal, it is necessary to apply appropriate techniques in the treatment systems (Brasil, 2011; CONAMA, 2005).

Iron Excess in Water

Iron is found in all aqueous environments on the planet, however, when it is in excess of 0.5 mg/L^{-1}, this environment has a changed color and flavor and begins to exhale odor, decreasing the acceptance of the population (Custódio & Llamas, 1983). When above this value, people restrict the use of water, as it causes stains on clothes and floors, in addition to other inconveniences. As a result, the population uses other methods that are not very viable for water supply, such as low excavated wells, where they may have high amounts of nitrate (NO_3^-) and ammonium (NH_4^+), which are substances toxic, in addition to causing poor filtration due to the precipitation of iron in the wells, which causes a drop in its efficiency. Therefore, quality water should be made available with low iron content in its components, thus increasing acceptance by the general population. (Driscoll, 1987).

Iron generates soluble compounds when it is in the ferrous ion (Fe^{+2}) state, especially in the form of ferrous hydroxide or iron hydroxide II, whose formula is $Fe(OH)_2$. In an oxidation environment, Fe^{+2} gives rise to the ferric ion Fe^{+3}, giving rise to $Fe(OH)_3$ which is insoluble, causing precipitation, staining the water vigorously. In this way, the waters of wells with high concentrations of iron, before entering the environment with oxygen, are colorless, but turn yellow when contact with air occurs, which gives it an unpleasant aspect. The precipitation of the iron contained in the waters is the main cause of the loss of efficiency of the deep wells, as it stains clothes, dishes and tiles and still attributes bad taste to water (Libânio, 2010).

Removal of Excess Iron

There are several processes for removing excess iron in water, the most used procedure for water treatment, is based on oxidation $Fe^{+2} \rightarrow Fe^{+3}$, followed by precipitation Fe^{+3}. The simplest method of oxidation is accomplished through aeration. In this procedure, aerators are used, the most common ones being board ones. Normally, aeration is not sufficient for effective oxidation, needing to apply a strong chemical oxidant, usually a chlorinated compound, such as sodium hypochlorite (Piveli, 2012).

Several processes are used to remove excess iron from the water, including aeration accompanied by filtration and aeration combined with solidification, followed by decantation and filtration. The selection of the procedure will depend on the configuration of how the iron impurities are organized. In relation to clean waters such as underground waters that do not require chemical treatment, where in the absence of oxygen it contains dissolved ferrous bicarbonate, the most suitable process is the first (Richter & Neto, 1991).

Water contamination, especially by heavy metals, promotes the need for the development of technologies to assist in the treatment of water for human consumption, since these metals are resistant to their removal by common methods, such as precipitation (Nascimento et al., 2014).

The objective was evaluate the concentrations of total iron found in the waters for human consumption purposes, in the municipal public supply of the Riacho Doce neighborhood in the city of Breves (Pará), comparing the values obtained with the limits recommended by Decree 2914/2011 of the Ministry of Health and by Resolution 357/2005 of CONAMA. The objective specific were study, analyze and compare the concentrations of total iron present in the public water supply at each stage of treatment, determine the likely factors that influence the concentrations of iron present in the water, assess whether the water quality is in accordance with the quality standards recommended by Ordinance 2914/2011 of the Ministry of Health and CONAMA Resolution 357/2005 for human consumption and check if there is a change in the total iron concentrations in groundwater for different seasons, taking into account the Amazon climate.

2. Methodology

The methodology used for research was in stages being qualitative and quantitative. The qualitative stage was carried out through photographic images of the municipal treatment plant in the Riacho doce neighborhood in the City of Breves in the State of Pará. Soon after, water samples were collected and sent to the Natural Sciences Laboratory of the Federal University of Pará. The water samples were sent to Universidade Federal do Ceará, Laboratório de Núcleo de Águas (LANAGUA) of the Department of Analytical Chemistry, so the samples were all acidified with 5 drops of nitric acid P.A for determination of iron concentration, being a quantitative analysis.

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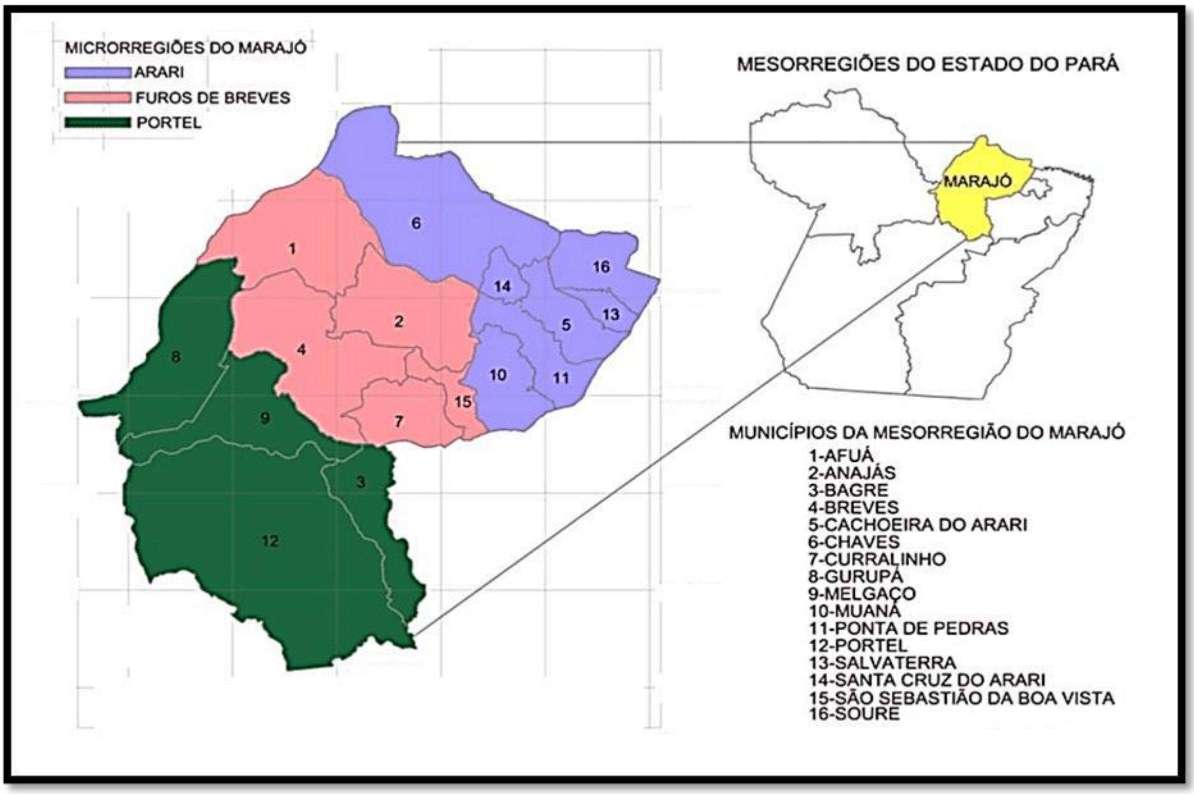
2.1 Chemical reagents

Nitric acid (HNO_3 P.A) from Vetec LTDA; Polyethylene bottles with a capacity of 30 mL; PET bottles (mineral water) with a capacity of 330 mL; Benetech digital infrared thermometer, model GM320, with a range between 50°C-330°C; Super Max disposable gloves, size M and GL; $Fe(NO_3)_3$, Iron Nitrate Salt with 99.9% purity from Vetec LTDA; Standard Iron Solutions of 0.5-10 mg.L^{-1} and Flame Atomic Absorption Equipment (Varian Fast Sequential 240 FS).Survey of the study area.

2.2 Survey of the study area

The Municipality of Breves is located in the southwest portion of Marajó Island, in the Microregion of Furos de Breves, at a distance of 221 km from the state capital, Belém, in a straight line. It is limited to the North with the municipalities of Afuá and Anajás; to the South, with the Municipalities of Melgaço and Bagre; to the East with Anajás, Curralinho and São Sebastião da Boa Vista; and to the west with the municipalities of Melgaço and Gurupá.

Figure 1 - Microregions of Marajó.



Source: Crispim et al. (2016).

In the 2010 demographic census, the municipality contained a population of 92,860 inhabitants, but the latest surveys estimated that in 2018 the number increased to 101,891 people. Breves is characterized by being the most populous municipality in Mesoregion of Marajó, representing 19.07% of the entire Mesoregional population. Population and demographic data for the Furos de Breves Microregion can be seen in Table 3.

Table 3 - Population of the Furos de Breves Micro-region.

Furos de Breves	Censo 2010	Estimate 2018
Afuá	35.042	38.863
Anajás	24.759	28.859
Breves	92.860	101.891
Curralinho	28.549	33.893
São Sebastião da Boa Vista	22.904	26.301
Total	204.114	229.807

Source: IBGE (2018).

The percentage of urbanization of the population of Breves in the 2000 Census points to a balance between the number of people in the urban area (46.560 people) and the rural area (46.300 people), that is, an urbanization rate of 50.14% (Atlas, 2010). With the particularities of the Furos de Breves Microregion, this statistical data becomes relevant, since the rural area is mostly populated by riverside dwellers; boats are the means of transport used and homes are far from each other; in most locations, basic sanitation, electricity and health services are deficient, and the only source of water is the river itself. In the following figure, you can see the territory of the municipality of Breves from the Territorial Division that occurred on July 1, 1960.

Figure 2 - A: Territory of the Municipality of Breves; **B**: Highlight of the city of Breves on the banks of the Parauaú River; **C**: Neighborhood Riacho Doce (collection place).

Source: Authors (2019).

2.3 Definition of sampling points

For sample collection, six points were initially defined, four of which were located within the filling station of the Municipality of Breves (PA) and the other two were on the consumer plane. These points were chosen according to the trajectory of the water and its possible changes in quality. The points are: 1. Well (first water outlet, after passing through the cascade aerator); 2. Filter; 3. Cistern (when the water was at rest); 4. Station Box (first exit); 5. Consumer 1a (near the station); and 6. Consumer 1b (after chemical treatment, for commercial use).

After the fifth collection there was a need to replace point 6 (six), where the water received a treatment with aluminum sulfate $Al_2(SO_4)_3$ carried out by the consumer for commercial use, initially because the results were not changing beyond than was previously expected when the chemical treatment is effective with values below the reading of the equipment, with no relevance in the results for research. As there is an obligation to compare the concentration of iron in relation to the distance of the pipe traveled by water, a new point was added, named consumer 2 (far from the Station), which would offer the opportunity to analyze the results obtained in relation to consumer 1 (close to the Station), checking for possible factors that may be contributing to excess iron.

In this way, consumer 1b was replaced by a consumer 2 residing at the ends of the neighborhood, at the last points of water supply. 7. Consumer 2 (far from the station).

2.4 Characterization of the collection points of the Station

This Water Treatment Station (ETA) has only a 175m deep tubular well covered by a protective ring that runs from the surface to the water pump that is 85m underground. The piping is made of iron, as it is more resistant, making it difficult to crack and break, in addition to being internally lined with a concrete layer to isolate water from contact with the iron in the tube, as can be seen in Figure 3C. Only the internal piping of the well is made of iron, the others both from the station and the piping networks that take water to the residents are made of PVC (polyvinyl chloride).

After leaving the well, water falls directly into the tray-type aerator, as it is the first available water outlet, the collections of the iron samples for point 1 occurred at this location, before falling into the aerator.

Figure 3 - Well (A), B: Inside the well ring (B) and Water tube (C).

Source: Authors (2019).

Aerators are used to oxygenate water, thus removing volatile and oxidizing compounds, as well as unwanted gases. Tray-type aerators for efficiency consist of a set of at least four overlapping perforated trays, allowing a maximum of 100 m³ of water per square meter of area in horizontal projection / day, thus they are the most recommended for ETA's as they facilitate the oxidation of ferrous compounds ($Fe^{+2} \rightarrow Fe^{+3}$) leading to precipitation of Fe^{+3} due to insolubility (NBR 12.216, 1992).

The first tray to come into contact with the water is used to distribute the water evenly, through perforations along its surface. The other trays contain trellises, where a layer of granular material is organized, preferably ½ ”to 6” (inches). This layer accelerates the oxidation reactions providing a larger contact surface (Lima, 2006).

Figure 4 - Tray type aerator.

Source: Authors (2019).

With the arrival of water in the tray-type aerator, oxygenation should occur. However, in the case of the station in question there is only a single platform of perforated trays, as can be seen in Figure 4, serving only for uniform distribution of water, which generates little efficiency for this structure.

After this process, the water falls directly into the concrete funnel just below the aerator platform, descending through the pipeline and entering the filter structure from below (submerging).

For a filter to work properly in an ETA it is necessary that it has an internal coating, where the water when submerged passes through the filtering material, this coating depends on the size of the particles to be removed. For example, in COSANPA (Breves) sand is used, which filters particles from 5 to 25 microns (μ). However, in the ETA where the collections were carried out, there is no internal coating except the sediments left by the water itself.

Another important detail can be seen in Figure 5C, where employees improvised an opening for the passage of water, making it impossible to pass through the first chute, establishing an undue "shortcut" because there is no justification for opening it, in addition to leaving the filter still less functional for water purification procedures.

Figure 5 - (A) Aerator and filter (arrows showing the water path); B: Sediment from the filter wall; C: Compartment 1 (circle showing “shortcut”) and 2 of the filter; D: Filter compartment 2.

Source: Authors (2019).

In this way, we can assume that no filtration takes place and the water that comes from the well passes directly to the cistern without any effective type of removal of contaminants. Leaving only the larger sediments that come in the water deposited on the walls and soil of the filter, forming a thick layer of sediments mixed with sludge.

The water collections at this location were carried out in the filter outlet tube to the cistern, which can be better observed in Figure 6C.

The station contains two cisterns, the largest with a capacity of 100 thousand liters and the smallest with 40 thousand liters connected by an inner tube below the ground line. At this stage, there is also no treatment, just the rest of the water generating a slight sedimentation. The larger cistern (Figure 6A) remains closed during the entire operation process, with its total load being filled by the underground pipe.

Figure 6 - A: Cistern; B: Interior of the supplied cistern; C: Plumbing coming from the filter to supply the cistern.

Source: Authors (2019).

The collections were carried out in the cistern of greater capacity when the water was at rest, which was opened only for the capture of the samples, soon after reaching this state, the pumping into the reservoir of the station happened, the plumbing connecting the cistern and the water pump sucks only the supernatant part leaving the bottom body seated in the internal part, however, this sedimented material does not clean frequently, being left deposited inside the cistern for months.

The station's reservoir holds 100.000 liters of water, is located 15m from the surface and there is no pumping of the box for consumers, only the pressure of free fall. The collections were performed in the first outlet valve inside the WTP. This structure also does not receive any type of weekly or monthly cleaning for the disinfection of its internal environment, leaving the favorable environment for the proliferation of pathogens that will take shelter inside.

Figure 7 - A: Water reservoir; B: Pumps for pushing water into the reservoir; C: Water outlet valve for the consumer.

Source: Authors (2019).

The outlet valve (Figure 7C) is opened twice a day, in the morning the supply is made from 6 am to 11 am, with total drainage from the reservoir and in the afternoon from 4 pm to 7 pm because it is the closing time for employees. The outlet piping from this reservoir is located directly at the bottom, draining any sediment formed inside the box directly to residents.

2.5 Sample collection and preservation procedure

Water samples were collected at each point in 330 ml PET bottles, previously washed with distilled water. All samples had their temperatures measured by a digital infrared thermometer. Then, they received an addition of 10 drops of HNO_3 P.A, in order to acidify them to pH 2, that is, to maintain the conservation of the samples and to avoid the precipitation of iron in the form of hydroxides. Thus, the samples were identified and stored in a freezer to be taken to the Núcleo de Águas Laboratory (LANAGUA) of the Federal University of Ceará (UFC), to carry out the analysis of total iron in the samples, using a Flame Atomic Absorption Equipment (Air-acetylene).

2.6 Quantification of Iron

Heavy metals can be quantified in water using atomic absorption spectrophotometry. The choice of the method to be used depends on the degree of precision required, the number of samples to be processed and, obviously, the availability of material and human resources.

The determination of iron in water by the flame atomic absorption method when the sample contains a lot of organic matter needs pre-treatment to remove this matter. Mixtures of acids, such as nitric and sulfuric, nitric and hydrochloric or nitric and perchloric, are used for this process.

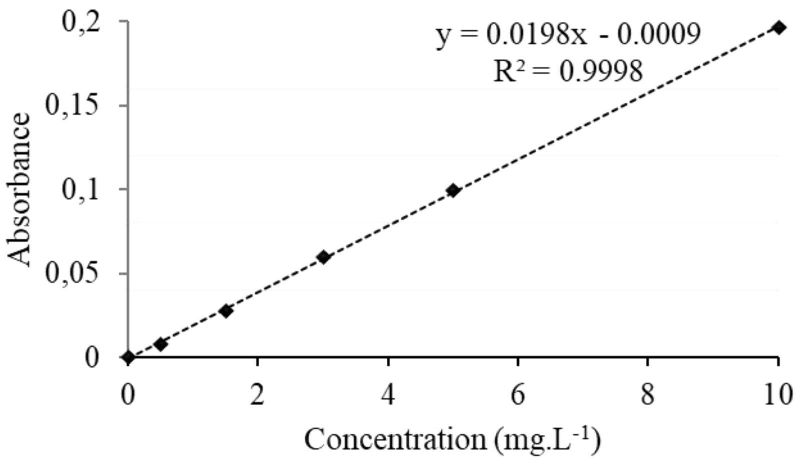
Atomic absorption is a highly versatile technique for the chemical determination of several metallic and some non-metallic elements. For the direct determination of the concentration of an element by atomic absorption, four fundamental components of the equipment must be considered: Light source with defined and intense lines, which emits resonant radiation, characteristic of the element to be determined; atomizer system, to atomize the sample in the flame; monochromator, which isolates the resonance line from other lines emitting the source and detector system, which converts light radiation into electrical current that, once conveniently amplified, can be read on the indicator instrument.

The function of the atomizer is to convert the sample into atomic vapor. Usually a flame heats and excites the atoms for absorption. The atomizer and the flame are positioned between the light source and the monochromator. Atomic vapor absorbs part of the resonant radiation emitted by the source, usually a hollow cathode lamp, whose absorption of the radiation intensity by the sample is proportional to the concentration of the analyte, that is, according to the Beer - Lambert law.

2.7 Calibration curve

The iron calibration curve was prepared with the following standard concentrations: 0.5 $mg.L^{-1}$, 1.5 $mg.L^{-1}$, 3.0 $mg.L^{-1}$, 5.0 $mg.L^{-1}$e 10.0 $mg.L^{-1}$, which were prepared from the stock solution of 1000 $mg.L^{-1}$ of iron in nitric acid medium (1% w/v HNO_3). Then, for each standard concentration, the reading of the absorbance measurement was performed in the FAST SEQUENTIAL 240 FS atomic absorption spectrophotometer with flame, available at LANAGUA of the Federal University of Ceará, Campus do Pici.

Figure 8 - Iron analysis calibration curve.



Source: Authors (2019).

The linear regression coefficient R^2 shows that the graph presents a linear behavior, with the points close to the line. The closer to $R^2 = 1$ means that the Lambert-Beer law is being obeyed for diluted solutions.

2.7.1 Instrumental parameters of the analysis

For determination of total iron in public water samples, instrumental parameters of the flame atomic absorption technique were described in Table 4. At the same time, it can be observed that the calibration curve (Figure 8) for the analyte (Fe) has a good linear correlation coefficient, the value of R^2 was 0.9998, whose equation of the line (Y = 0.0198x - 0.0009).

Table 4 - Instrumental parameters of atomic absorption with flame.

Analito	Fe
Linerarity range (mg.L^{-1})	0.5 – 3.0
λ_{onda} (nm)	248.3
Intensity (mA)	5
Slit width (nm)	0.2
Burner height (cm)	13.5
Flame type (Ar/Acetilene, L.min^{-1})	13.5/2
R^2 value of the calibration curve	0.9998
Detection limit (mg.L^{-1}), LOD	0.01
Quantification limit (mg.L^{-1}), LOQ	0.005

Source: Authors (2019).

3 Results and Discussion

Fourteen collections were carried out in different climatic periods, covering the last three months of the rainy season (seven collections) and the others in the dry season (seven collections), considering that the rainy season with high rainfall in the Amazon region is comprised among the the months of November and March and the dry period between the months of May and September, however, in this season there is still rain, but to a lesser extent. The months of April and October between the seasons are months of transition between periods (Fisch et al., 1998).

Table 5 - Dates of collections performed.

Collect	Date	Nº of samples
1	1/25/2018	5
2	2/01/2018	5
3	2/08/2018	5
4	2/15/2018	5
5	2/22/2018	6
6	3/01/2018	6
7	3/08/2018	6
8	6/21/2018	6
9	6/28/2018	6
10	7/12/2018	6
11	7/26/2018	6
12	8/23/2018	6
13	8/30/2018	6
14	9/20/2018	6

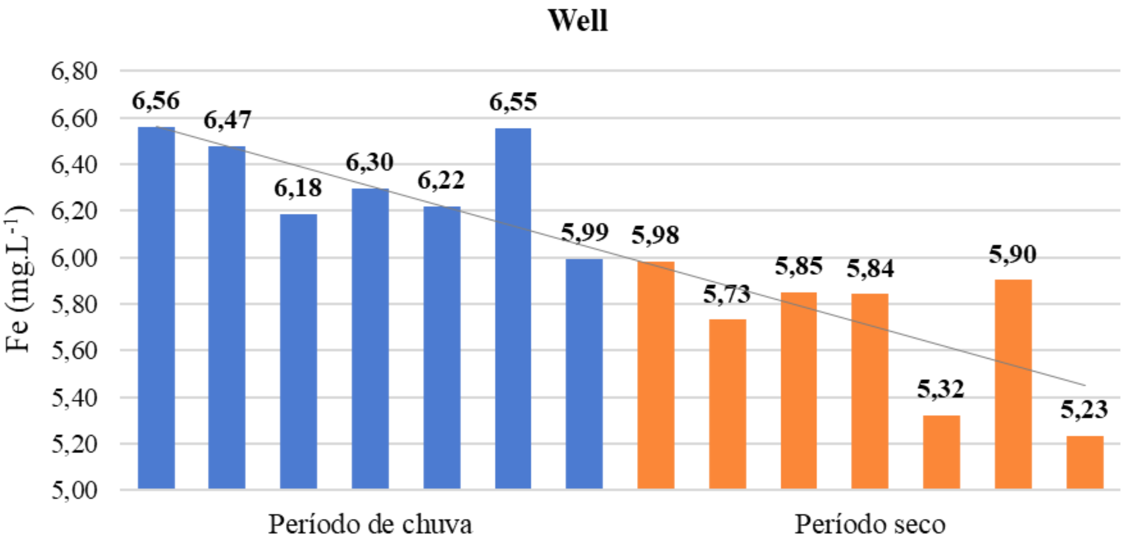
Source: Authors (2019).

3.1 Individual results

Point 1

The iron concentration monitoring analysis for selected collection sites is discussed below. The initial location was the water capitation well, in which the values found are described in the graph illustrated in Figure 9.

Figure 9 -Total iron concentration of samples collected in the capitation well.



Source: Authors (2019).

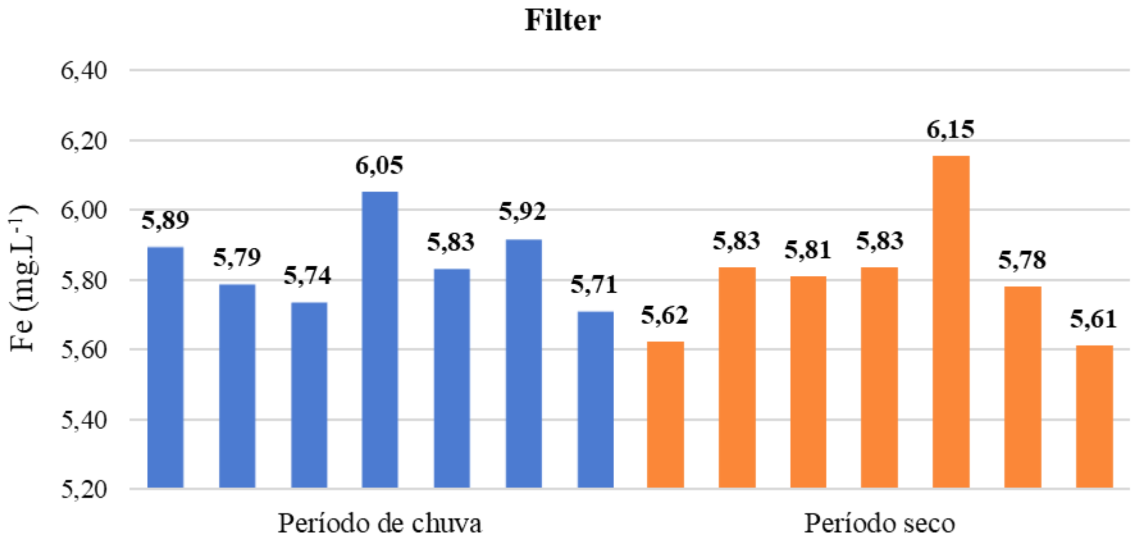
It can be observed that the highest total iron content found was in the 1st collection, carried out on January 25, 2018 (Table 5), referring to the season with the highest intensity of rain. While the lowest concentration of total iron was found in the 14th collection, alluding to the period with the lowest rainfall.

It is important to note the trend line showing a lower concentration of iron as it progresses to the period with less rainfall, taking into account that point 1 is the only one to which the water characteristics are directly linked to the natural environment, undergoing changes in according to the season, which may be the reason for the decline. This phenomenon can be explained by leaching, a process common in tropical climates, which occurs when the surface layer of the soil is washed away due to heavy rains, leading to the runoff of surface water loaded with waste into the groundwater (Ribeiro, 2017).

Point 2

The second collection point was the filter, where the first stage of water treatment should take place, the results obtained are described in Figure 10.

Figure 10 - Total iron concentration of samples collected on the filter.



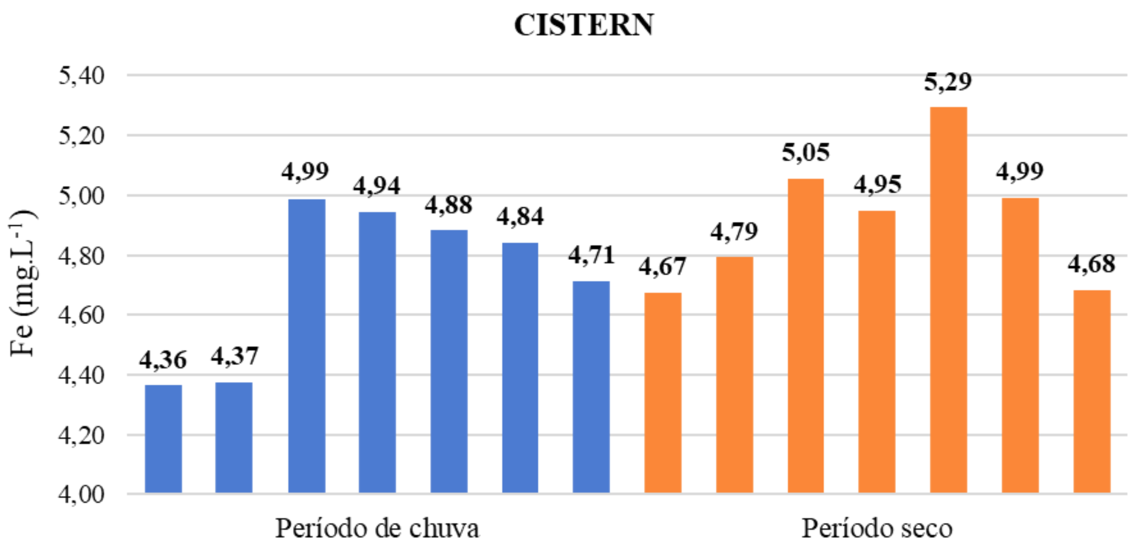
Source: Authors (2019).

Observed the data in Figure 10 regarding the filter, it is noted that the highest (collection 12- 6.15 mg.L^{-1}) and lowest (collection 14-5.61 mg.L^{-1}) total iron concentration found was in the period with the lowest rain intensity. In relation to the 12th collection carried out on August 23, 2018 (Table 5), where the highest peak of iron found in the filter occurred, compared to the previous point regarding the same collection, there was an increase of 0.83 mg.L^{-1} iron, that is, in the place that should promote the filtration of elements, if it had the internal coating for its adequate performance, ended up adding, probably due to the lack of maintenance in the structure, which accumulates sediments on the walls to its limit, where break up and mix with water.

Point 3

The third collection point was the cistern, where the second and final stage of removing solid waste from the water would take place.

Figure 11 - Total iron concentration of samples collected in the cistern.



Source: Authors (2019).

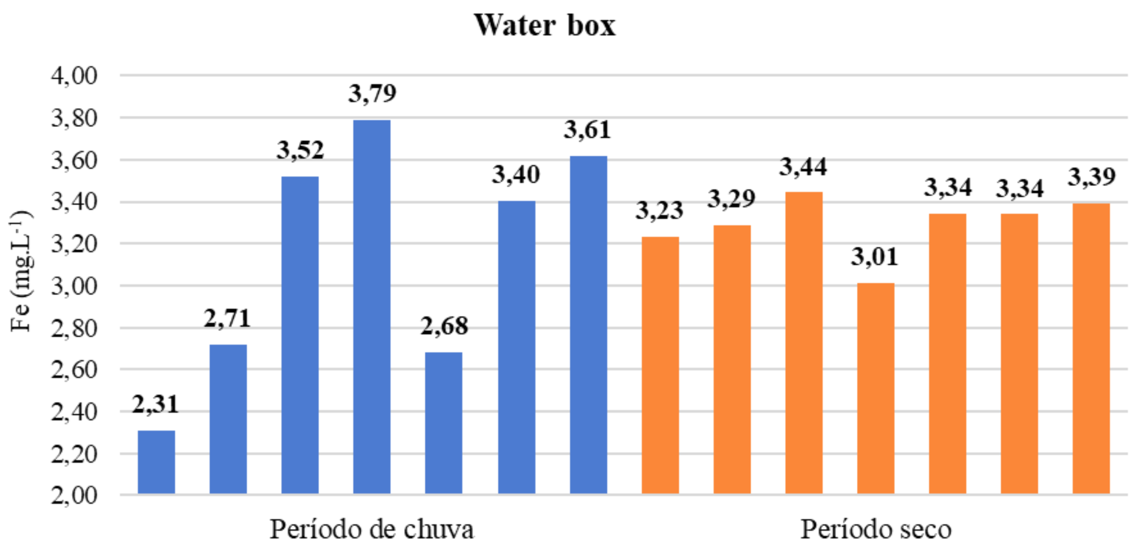
Based on the results of the analyzes carried out on the cistern water, as illustrated in the graph presented in Figure 11, it can be observed that the lowest concentration of total iron found was in the 1st collection carried out on January 25, 2018 (Table 5) referring to to the rainy season, causing a significant drop, but not efficient in relation to the previous points and the highest iron content found was in the 12th collection, carried out in the second period of the year, still a consequence of the peak of the previous point of the same date.

The cistern should be treated with chemical products, as there is no such treatment, the results are not significant, resulting in low quality water with high iron content.

Point 4

The fourth collection point is the reservoir, the last collection point inside the WTP. Place where it had the lowest levels of total iron concentration, taking into account the average between the points.

Figure 12 - Total iron concentration of the samples collected in the water reservoir of the supply station.



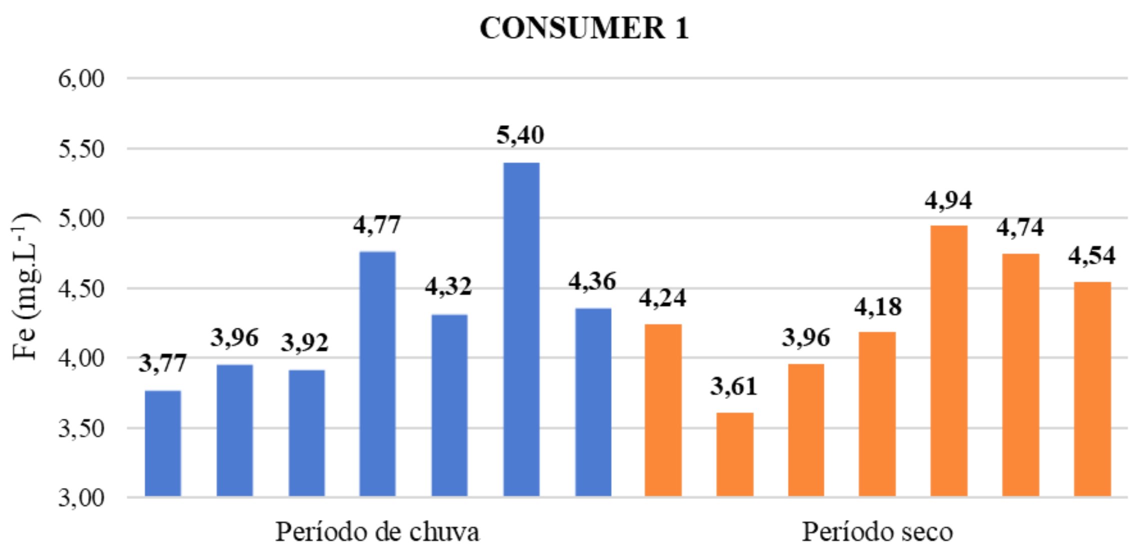
Source: Authors (2019).

Point 5

In the water reservoir, as can be seen in Figure 12, the lowest iron content was found among all the collections, located in the 1st collection of the period with the highest rainfall, in this same period there is also the highest concentration of the point referring to the 4th collection carried out on February 15, 2018.

The lower total iron levels for this point are probably due to the suction of only the supernatant part of the water from the cistern, leaving most of the iron sedimented in the bottom body of the previous point, thus reducing the total iron contents.

Figure 13 - Total iron concentration of samples collected at consumer 1's residence (near the station).

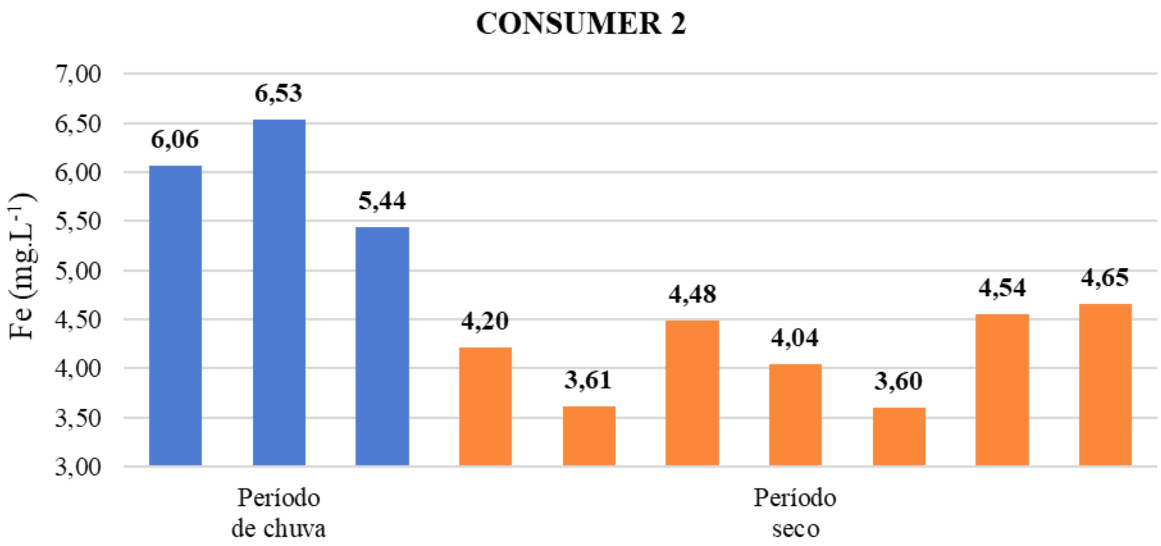


Source: Authors (2019).

Point 6

As consumer 2 was the last point established, there were fewer samples in relation to the previous points, however its results were relevant to the investigation.

Figure 14 - Total iron concentration of the samples collected at the residence of consumer 2 (distant from the station).



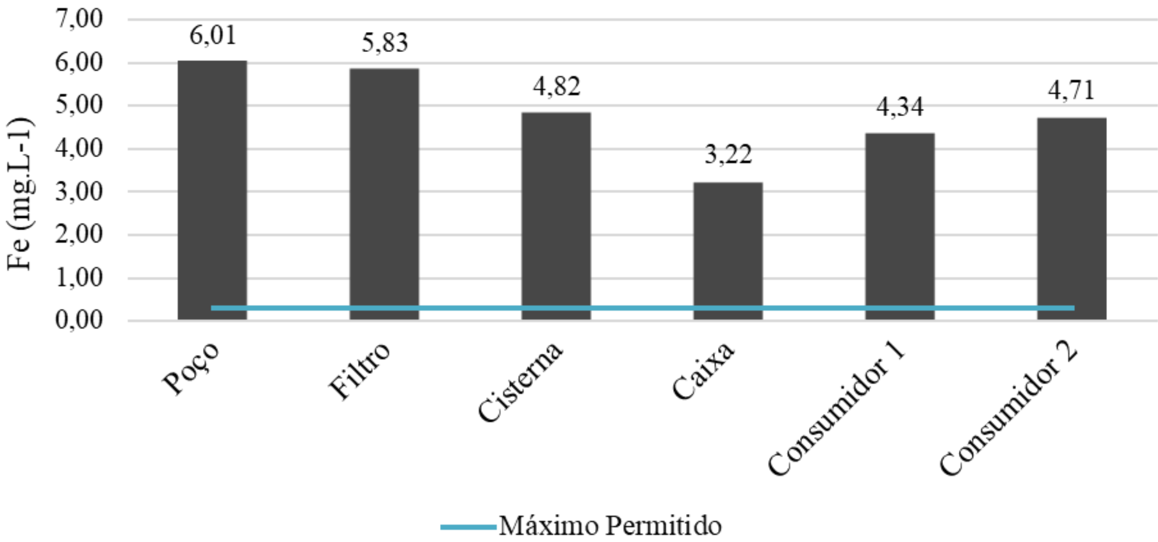
Source: Authors (2019).

Based on the data in Figure 14, in consumer 2, which is at the end of the distribution network, there is an increase in relation to the average result of consumer 1, probably generated by the same problems found in the previous point. However, the increase occurs due to the further distance that the water travels to reach point 6, taking into account the precariousness of the hydraulic network, the greater the distance, the greater the number of cracks in the pipes, consequently, the greater the concentration of total dissolved solids, including the iron.

3.2 Average of results obtained

All samples are outside the average value allowed by the Ministry of Health, some are more than 20 times above the value.

Figure 15 - Average results obtained from total iron concentration in water samples.



Source: Authors (2019).

From the graph illustrated in Figure 15, it is possible to observe the average results for the 14 analyzed collections, referring to the well, filter, cistern, box and consumer 1, and for the 10 analyzed collections referring to consumer 2. there is a decrease in the concentration of Iron found in the water, which passes from the well to the filter, possibly associated with the tray aerator together with the filter itself, although according to NBR 12.216/1992, as mentioned earlier, for better oxygenation of the water, consequently increasing the percentage of Fe^{+3} withdrawal through precipitation, the aerator must have at least 4 overlapping platforms. However, the aerator in question contains only a single platform, which resulted in a small rate of precipitation inside the filter, which can be observed by the sediments in Figure 5B.

There is also a decrease in the concentration of total iron when it passes from the filter to the cistern, a decay of 10.4% is observed, probably attributed to the time in which the water is at rest, facilitating the "precipitation" or bottom body of material. solid “rust”.

Still based on the analysis of the graph, it is observed that there is an increase in the concentration of Iron found in the water collected in consumer 01 and 02, respectively. The increase observed in the concentration may be related to the water transmission system (piping), which, according to the ETA employees themselves, is composed of PVC tubes, being in a bad state of conservation with several cracks, facilitating the entry of contaminating material between the supply periods, when the internal pressure in the pipe decreases due to the interruption of the supply, leading to an increase in the concentration of iron as the water travels through the pipes, consequently the consumer 2, for this in a greater distance, is more harmed.

4. Conclusions

The results obtained for all collection points showed that the concentration of total iron is above the maximum allowed by current legislation, which is equal to 0.3 $mg.L^{-1}$, making the water unsuitable for both consumption and use. domestic due to the high concentrations found. These results are probably associated with a deficient water treatment procedure, due to the incorrect use of the present structures and the lack of adequate infrastructure, as well as equipment and reagents to assist in the water purification process and trained workers, a since, employees do not have any specific qualification to work in water treatment processes.

Furthermore, the lack of resources prevents workers from carrying out any type of more elaborate technique for the treatment of water for consumption, since there is no type of collection from consumers for the maintenance and improvement of the internal structures of the station, being the water distribution carried out free of charge, but of poor quality.

A possible solution or mitigation of the water problem would be if the beneficiaries of the distribution system contributed with a small, non-mandatory amount, in cash per month for each residence, because with good management of these resources, the purchase of products and improvements in the structures, leaving the process functional and raising the quality of the water that reaches the consumer. For this, it would need the support of the local residents, through a meeting, where they would verify if they would be in agreement with the proposal, leaving to the municipal government only the expenses with the employees and eventual reforms of larger proportions, however this proposal still needs more studies and an equivalent budget.

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