Investigation of geochemical quality of water from public fountains of Salvador

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Palavras-chave:
Hidroquímica.
Fontes de água.
Qualidade de água.

Resumo
Este estudo objetiva caracterizar, em termos de parâmetros físico-químicos, bacteriológicos e concentração de metais, a qualidade da água das fontes públicas da cidade de Salvador (Bahia, Brasil), a fim de identificar sua potencialidade para os usos atuais, contribuindo para o diagnóstico ambiental da qualidade das águas de acesso público da população. Para tanto, realizou-se campanhas nos meses de julho e novembro dos anos de 2017 e 2018 em quatro fontes (Fonte Nova, Estica, Pedrinhas/Pedreiras e Via Expressa), as quais foram georreferenciadas e analisados parâmetros físico-químicos (pH, condutividade, temperatura, oxigênio dissolvido, turbidez e sólidos totais dissolvidos, salinidade, sulfato, nitrato, cloreto e alcalinidade), bacteriológicos (coliiformes termotolerantes) e metais (Cd, Pb, Ni, Co, Cr, Cu, Zn, Fe, Mn). Os chafarizes apresentaram valores em desacordo com as portarias Conama 396/2008, 357/2005, e 274/2000 principalmente quanto os parâmetros pH, Oxigênio Dissolvido, Nitrato e Coliformes Termotolerantes, apontando, portanto, inadequação para os usos a que se destinam. Estas informações devem servir de amparo para tomadas de decisão e medidas mitigadoras que minimizem a degradação ambiental das fontes urbanas da cidade de Salvador (BA), a partir da adoção de medidas de recuperação, revitalização e monitoramento que possibilitem eficaz gestão destes recursos hídricos.

Keywords
Hydrochemistry.
Water fountains.
Water quality.

Abstract
This study aims to characterize, in terms of physicochemical, bacteriological and metal concentration parameters, the water quality of public fountains in the city of Salvador (Bahia, Brazil), in order to identify its potential for current uses, contributing to the diagnosis of water quality on the public access. Therefore, campaigns were conducted in July and November of 2017 and 2018 in four fountains (Fonte Nova, Estica, Pedrinhas/Pedreiras and Express way), which were geo-referenced and analyzed physical-chemical parameters (pH, conductivity, temperature, dissolved oxygen, turbidity and total dissolved solids, salinity, sulfate, nitrate, chloride and alkalinity), bacteriological (thermotolerant coliforms) and metals (Cd, Pb, Ni, Co, Cr, Cu, Zn, Fe, Mn). The fountains showed values in disagreement with the CONAMA Ordinances 396/2008, 357/2005, and 274/2000 mainly about the pH, Dissolved Oxygen, Nitrate and Thermodeterlant Coliforms parameters, indicating inadequacy for their intended uses. This information should support decision making and mitigation measures that minimize the environmental degradation of urban fountains in the city of Salvador (BA), from the adoption of recovery, revitalization and monitoring measures that enable the effective management of these water resources.

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1. INTRODUCTION

Due to the growing water deficit registered in many regions, (MEKONNEN, 2016), in Brazil and especially in the Northeastern region, the trend of consumption of water from alternative water sources has been increasing, among them, spouts, fount and public fountains. (TOURINHO, 2008).
Natural fountains are the emergence of groundwater stored in underground reservoirs. In general, the water quality of the aquifer systems that feed the fountains is adequate for several uses, and it may present some restrictions locally (Zobby, 2008), so that waters that are used for human supply, even secondarily, need to be constantly monitored.

The existence of fountains along the slopes and beaches of Salvador is conditioned by the geological constitution of the city, characterized by precambrian rocks of the crystalline basement partially covered by the cretaceous sediments, of Barreiras Formation, which leans discordantly on crystalline rocks. The most of Aquifers are shallow and highly vulnerable and are mostly from waters draining the municipality land allowing the fountains emerge from the water contained in the porosity of rocks (Alves et al., 2016).

Urban fountains of public access, in general, are considered rare resources and of great vulnerability, weak connection with society, part of this is a result of negligence in the management of these environments. In Salvador, it can be said that fountains that have resisted time and omission and are still being used as a secondary supply system in the daily life of the city, but there is no official and regular information of the physicochemical and bacteriological conditions of their groundwater (Tourinho and Beretta, 2010).

The urbanization process increase added to the significant population growth make it indispensable to know about the conduct of water quality, not only for use and management planning, but mainly to control environmental impacts, allowing adaptation to the many uses of this resource, especially those in greatest demand for quality in order to reduce the health risks of consumers.

Groundwater monitoring is fundamental to support environmental pollution control and management actions (Dias et al., 2008). According to National Council of Environment - CONAMA Resolution 396/2008, which deals with the classification and environmental guidelines for groundwater placement, the minimum parameters required for monitoring groundwater quality include pH, turbidity, electrical conductivity, total dissolved solids, nitrate and thermotolerant coliforms.

The input of trace metals to aquatic bodies can occur naturally through geochemical processes and weathering of the origin material or as a result of anthropic activities (Melô et al., 2012). Changes in biological, physical and chemical conditions, such as pH and redox potential, also promote the mobilization of metals naturally contained in soil or rocks, such as aluminum, iron and manganese. Therefore, the geological context may act as a fount or sink, depending on its nature and environment (Lima, 2001).

Organic fountains of groundwater contamination are generally related to industrial and domestic effluent disposal, urban and agricultural diffuse discard, and manure from landfills that can contaminate groundwater with pathogenic microorganisms. In addition, they are also potential source of nitrate and organic substances potentially toxic to man and the environment (Freitas et al., 2009).

Concentration and distribution of groundwater pollutants can be influenced by several factors, including atmospheric deposition, chemical dissolution and/or hydrolysis processes in the aquifer and mixture with sewer and/or saline water by intrusion (Gomes, 2009), factors which not only modify the qualitative and quantitative characteristics of underground fount but also represents a risk to public health (Silva et al., 2018).

This study has shown the physicochemical quality of water of four fountains located in the city of Salvador (Fonte Nova, Estica, Pedrinhas/Pedreiras and Express way), evaluating physicochemical parameters (pH, electrical conductivity, temperature, dissolved oxygen, turbidity, total dissolved solids, salinity, sulfate, nitrate, chloride and alkalinity), bacteriological (thermotolerant coliforms) and metals (Cd, Pb, Ni, Co, Cr, Cu, Zn, Fe, Mn) and compared to the CONAMA resolutions 396/2008, 357/2005, and 274/2000 that regulate environmental guidelines that certify the water quality.

2. MATERIALS AND METHODS

Water samples were selected from four public access fountains in Salvador (BA), having as a criterion of choice the presence of continuous moderate flow, multiple use by the community (consumption, hygiene, ingestion) and not used for religious purposes. Table 1 shows the identification of each sampling point, followed by their location and georeferencing.

| Identification | Name            | Latitude (s)    | Longitude (W) |
|----------------|-----------------|-----------------|---------------|
| 1              | Pedrinhas or Pedreira | 12°57′38.01″    | 38°30′3.63″   |
| 2              | Estica           | 12°56′44.96″    | 38°30′14.00″  |
| 3              | Express way      | 13°0′38.74″     | 38°30′0′′00″  |
| 4              | Fonte nova       | 12°58′38.01″    | 38°30′3.63″   |

Source: Own author.

The samples were collected in 4 sampling campaigns, in the months of July (rainy season) and November (dry season) of 2016 and 2017 and performed according to the National Guide for Collection and Preservation of Samples, published by the National Water Agency (ANA, 2011).

Washing of materials and containers designated for collection and analytical procedures was carried out in HNO₃ (10%) nitric acid solution and subsequently washed in ultra-pure water (Milli-Q). For water collections, reusable 1,000 mL bottles were used, cleaned and properly identified, and about 750 mL per sample were collected.
For each fountain, the bottles were set prior to collection to ensure the adequacy of the water properties, at Fountain 4 (Fonte Nova) water was collected at about 15 cm depth. For the metal analysis, previously acidulated bottles with concentrated HNO₃ were used, and after the collection procedure, the plastic bottles were packed in styrofoam boxes containing ice (-4°C) and immediately transported to the laboratory, not exceeding the minimum period of 24 hours stipulated for analysis security.

Physicochemical measurements were also performed on site using a multiparameter lead-line (Horiba 104 U-54 Multiparameter Water Quality Checker). CONAMA Resolution No. 357/05 establishes a legal limit for both measured parameters and conducting field analysis with the aid of a portable probe enables greater data consistency, considering the local climate at the exact time of collection (BRANDÃO, 2011).

For the pre-treatment for metal analysis, the samples were digested and treated with 5 mL of 20% concentrated HNO₃ and then diluted to 2% and the subsequent reading carried out using inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies, model 720 series) according to the methodology 3120B of the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

The analytical procedures were performed by the Plasma laboratory and the Environmental Studies Center (IGEO/UFBA) and microbiological analysis by the Laboratory of the Environmental Engineering Department (Polytechnic School/UFBA), according to the standards described at Standard Methods for the Examination of Water and Waste Water (APHA, 2012) (Table 2). Sixteen samples were analyzed totaling 160 determinations.

### Table 2 - Techniques, reference methods, quantification limits and wavelengths for the determination of metal concentrations in water by inductively coupled plasma optical emission spectrometry (ICP-OES).

| Analysis   | Technique | Reference methods | Quantification limits | Wavelengths (nm) |
|------------|-----------|-------------------|-----------------------|------------------|
| Thermol. Colif. | Filtering Membrane | SM-9222D | 1 UFC/100mL | N.A. |
| Cadmium (Cd) | ICP-OES | SM-3120B | 0.005 µg/L | Cd 228.802 |
| Lead (Pb) | ICP-OES | SM-3120B | 0.010 µg/L | Pb 220.353 |
| Nickel (Ni) | ICP-OES | SM-3120B | 0.02 µg/L | Ni 221.648 |
| Cobalt (Co) | ICP-OES | SM-3120B | 0.02 µg/L | Co 228.615 |
| Chrome (Cr) | ICP-OES | SM-3120B | 0.02 µg/L | Cr 267.716 |
| Copper (Cu) | ICP-OES | SM-3120B | 0.01 µg/L | Cu 324.754 |
| Zinc (Zn) | ICP-OES | SM-3120B | 0.005 µg/L | Zn 213.857 |
| Iron (Fe) | ICP-OES | SM-3120B | 0.10 µg/L | Fe 259.940 |
| Manganese (Mn) | ICP-OES | SM-3120B | 0.01 µg/L | Mn 257.610 |

Source: Own author.

During the campaigns, the geographical coordinates with GPS were determined and the conservation conditions and current uses were observed. Informal interviews were also accomplished with the local population aiming at diagnosing activities such as water use, time and frequency of use of the fountain, flow conduct during the year and whether a shortage period or recent history of water-borne diseases were noted.

### 3. RESULTS AND ANALYSIS

The results of laboratory analysis on water samples from the four public fountains are shown in Table 3. Table 4 shows results from previous work by Silva et al. (2013), Tourinho and Costa (2012), Tourinho and Beretta (2010) and Alves et al. (2016) for Pedrinhas/Pedreira fountain, Estica fountain and Fonte Nova. No previous research was found that worked with the geochemical water patterns of the Express way fountain. In both tables, the values found were compared with the parameters stipulated by CONAMA Resolutions 396/2008, 357/2005, 274/2000, according to the verified uses (secondary consumption, bath and car wash), and highlighted when not in conformity.

The results for the metal analysis have shown that, except for manganese in three of the four fountains, all other metals presented values below the detection limit. Concentrations found for Cd, Pb, Ni, Co, Cr, Cu, Zn and Fe are below the limit of detection, therefore within the maximum level allowed by regulation norms (BRASIL, 2008, 2005, 2000).

At Pedrinhas fountain (Fountain 1) the manganese was only below the detection limit (0.01 µg/L) in the water sample collected in July 2018 (rainy season), in the dry period of the same year (November) the concentration was 0.11 mg/L repeating the conduct of the same period of the previous year (0.19 mg/L), that is, above the limit recommended by CONAMA Resolution 357/2005 (0.10 mg/L). In the rainy season of 2017, the value found was 0.03 mg/L, which is in accordance with the established values by Brazilian law.

At Estica fountain (Fountain 2), manganese concentration was below the detection limit in 2017 and 2018 during the dry season (July). In the rainy season, values of 0.015 mg/L and 0.02 mg/L were found. Both in accordance with the values established by CONAMA.

Manganese was below the detection limit in all collection periods at the Express way Fountain (Fountain 3). At Fonte Nova (Fountain 4), values were found within the limits allowed by the legislation in both years, being 0.014 mg/L (July/2017), 0.01 mg/L (November/2017),
The presence of dissolved manganese ions influences strongly the parameters related to color, turbidity and transparency (POHLING et al., 2007; BRASIL, 2014). In other studies, done in different locations in Brazil, manganese values have also been reported that are higher than that allowed by the legislation in fountains, with emphasis on increase in the rainy season (BEZERRA et al., 2017; COSTA et al., 2012). The origin of manganese in these environments is related to the natural occurrence in mineral rocks which dissolution, by local, creates waters with concentrations of metals above the drinkability pattern, therefore being in a dependence relation with the soil organic composition and capacity of cation exchange (ZOBY, 2008; WHO, 1999).

Thermotolerant coliforms were present in two of the four fountains, Estica fountain and Fonte Nova, which presented values above the limit established by Resolution CONAMA 396/2008 that determines the absence of coliforms in NMP/100 mL as a determinant of groundwater quality Class 1 for human consumption. However, all fountains are within the limits established by CONAMA 274/00 and 357/05, which establish suitability for primary contact recreational use (bathing).

| Parameters | Fountains/Season | Fountain 1 2017 | Fountain 2 2018 | Fountain 3 2017 | Fountain 4 2018 | CONAMA 396/08 | CONAMA 274/00 | CONAMA 357/05 |
|------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| pH         | Rainy Dzy       | 5.51 5.82 5.83 | 5.75 5.87 6.01 | 5.38 5.36 6.71 | 5.43 5.43 5.53 | 6 9 6 9        | -              | -              |
| Conductivity (mS/cm) | Rainy Dzy       | 0.58 0.60 0.57 | 0.65 0.65 0.66 | 0.65 0.65 0.66 | 0.65 0.65 0.66 | 0.65 0.65 0.66 | -              | -              |
| Temperature (°C) | Rainy Dzy       | 27.17 28.25 28.53 | 28.65 27.35 27.57 | 27.57 28.57 29.57 | 29.57 27.57 28.57 | -              | -              | -              |
| Dissolved oxygen (mg/L) | Rainy Dzy       | 7.39 8.65 5.00 | 7.27 7.21 3.79 | 4.98 5.07 4.98 | 4.98 5.07 4.98 | 4.98 5.07 4.98 | 4.98 5.07 4.98 | 4.98 5.07 4.98 |
| Conductivity (g/L) | Rainy Dzy       | 0.37 0.416 0.363 | 0.415 0.412 0.414 | 0.413 0.413 0.413 | 0.373 0.373 0.373 | 0.373 0.373 0.373 | 1.000* | -              | -              |
| Turbidity (NTU) | Rainy Dzy       | 0.39 0.3955 0.389 | 0.389 0.413 0.413 | 0.383 0.383 0.383 | 0.383 0.383 0.383 | 0.383 0.383 0.383 | -              | -              |
| ORP/Eh (mv) | Rainy Dzy       | 24.0 25.3 26.3 | 255 255 255 | 255 255 255 | 255 255 255 | 255 255 255 | <100           | <100           |
| Sulphate (mg/L) | Rainy Dzy       | 4.1 6.5 4.1 | 6.5 6.5 6.5 | 6.5 6.5 6.5 | 6.5 6.5 6.5 | 6.5 6.5 6.5 | 6.5 6.5 6.5 | 6.5 6.5 6.5 |
| Nitrate (mg/L) | Rainy Dzy       | 21.4 21.4 21.4 | 21.4 21.4 21.4 | 21.4 21.4 21.4 | 21.4 21.4 21.4 | 21.4 21.4 21.4 | 21.4 21.4 21.4 | 21.4 21.4 21.4 |
| Chloride (mg/L) | Rainy Dzy       | 1.1 1.1 1.1 | 1.1 1.1 1.1 | 1.1 1.1 1.1 | 1.1 1.1 1.1 | 1.1 1.1 1.1 | 1.1 1.1 1.1 | 1.1 1.1 1.1 |
| Total alkalinity (mg/L) | Rainy Dzy       | 0.31 0.31 0.31 | 0.31 0.31 0.31 | 0.31 0.31 0.31 | 0.31 0.31 0.31 | 0.31 0.31 0.31 | 0.31 0.31 0.31 | 0.31 0.31 0.31 |

Source: Own author. Subtitle: * Organoleptic effect

Other authors (TOURINHO, 2008; TOURINHO and COSTA, 2012; TOURINHO and BERETTA, 2010; ALVES et al., 2016), had already identified the presence of coliforms in these two fountains, highlighting their inadequacy, mainly for human ingestion (drinkability) according to MS ordinance 2.914/11 (BRAZIL, 2011). It is important to note that the Fonte Nova samples were collected in the stagnant space of the water, ever since the sewer undermines the structure built to keep this water accumulated. Fish and turtles, strong urine odor, visible organic and inorganic residues, as well as intensive car-washing activities are found on the local. It was observed the presence of sanitary sewage at Estica fountain, which can interfere as a source of contamination, being present in the collected samples.

Table 4 - Physicochemical parameters and thermotolerant coliforms in the studies of Silva et al. (2013), Tourinho and Costa (2012), Tourinho and Beretta (2010) and Alves et al. (2016). The data in bold show values not in conformity with the ones allowed.
Samples from all fountains presented pH below the limits recommended by CONAMA Ordinances 274/00 and 357/05 for Class 1 freshwater, indicating that the freshwater from these fountains are more acidic than recommended for their current use. Earlier research (Table 2) also reported similar or lower pH levels than those found in this study, suggesting that this change may have a natural origin (from the dissolution of rocks that make up the aquifer system, absorption of atmospheric gases, or influence of vegetal cover) or anthropogenic (domestic and industrial dumpings from the urban context).

The alteration in pH values in the rainy season represents a bigger dilution of dissolved compounds, conditioned by the increased runoff of water from the rain (POHLING, 2009). The expression of acidity in these environments, however, is not considered harmful to public health, making exception for extremely acidic or alkaline values (e.g. 3.69 found in the 2018 rainy season at Fountain 4, which due to the unique conditions, the origin is controversial) and may cause skin or eye irritation (BEZERRA et al., 2017).

Observing the values found for D.O. (Table 1), one can see that Fountain 3 (Express way) and Fountain 4 (Fonte Nova) do not comply with the values of D.O. of CONAMA Resolution 357/05 for class 1 (> 6 m/L). The same problem was also found at Pedrinhas/Pedreira fountain (Fountain 1) quite accentuated in previous works (Table 2), not observed in this research. At Fountain 2 (Estica fountain), this conduct was only observed in the rainy season of 2017. Tourinho and Costa (2012) and Tourinho and Beretta (2010) found similar values to those of this study.

The dissolved oxygen concentration changes with temperature, solubility, atmospheric pressure and salinity (ALVES et al., 2016). The absence of vegetation around the fountains studied may have an influence on the values of D.O., since higher temperatures predominate in very urbanized areas, with higher incidence of solar radiation and very small presence of vegetation in the surroundings. In addition, sampling at strong solar times may have caused a decrease in oxygen solubility, influencing low D.O. values (TOURINHO and BERETTA, 2010).

Most of the nitrate values were not in accordance with the contents of CONAMA resolutions 274/00 and 357/05. For all fountains, in the dry season, values were found above the limits in all years. And in the rainy season, only in 2017, the levels were in accordance with the standards (which for human consumption should not exceed 10 mg/L). In the previous analyses by Tourinho and Costa (2012), Tourinho and Beretta (2010) and Alves et al. (2016), nitrate levels above the recommended in the fountains Estica and Pedrinhas/Pedreira were also found. Silva et al. (2013) also obtained close values in this work at Fonte Nova, exceeding five times the limit recommended by regulatory standards.

Nitrate concentration represents the last oxidation state of organic material, therefore its existence in water corps is indicative of eutrophication of water founts. The presence of nitrate in drinking water causes damage to public health and is mainly associated with two adverse health effects: induction of methemoglobinemia, especially in children, and the potential formation of carcinogenic nitrosamines and nitrosamides (FREITAS et al., 2001).

Nitrate ion usually occurs at low levels in surface waters, but it can reach high concentrations in deep waters (FREITAS et al., 2001). Concentrations above 10 mg/L demonstrate inadequate sanitary conditions (TOURINHO and COSTA, 2012). In regions without agricultural influence the main source of nitrate is human dumping and animal waste. At Fonte Nova, however, whose collection conditions described previously shows the probable existence of animal waste, and it is worth highlighting the values that exceed by more than six times that recommended, in this case, the presence of contamination by high nitrate concentrations is also proved with the results of the bacteriological analyses.

4. CONCLUSIONS

The results of geochemical and microbiological analyses indicate the inadequacy of the fountains studied for their intended uses, showing the negligence of management and determining a social and public health problem.

The fountains presented values in disagreement with the CONAMA Ordinances 396/2008, 357/2005 and 274/2000, specially about parameters pH, Dissolved Oxygen, Nitrate and Thermotolerant Coliforms. Regarding the metals studied, only the presence of Manganese ions was observed in three of the four fountains, but still within the stipulated limits.

Therefore, the development of new studies is recommended, as well as management interventions that allow frequent and effective monitoring, aiming at preventing waterborne diseases and conserving the quality of these founts, in addition to awareness actions for maintenance and preservation by users.
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