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Evaluation of trace-metal concentrations in water consumption of streams near Guajira (Colombia)

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Abstract. The spatial distribution of metals in the water for consumption in the different supply sources, natural sources, family storage tanks and deep wells were studied. 16 samples were made for different municipalities belonging to the department of La Guajira upper part. The water samples were analyzed in 2016 and analyzed physically and chemically and microbiologically. The results were compared with national standards and those established by the WHO. The results found show some traces of metals in some of the sampling sites. The concentrations of Calcium, Magnesium exceeded the concentrations established by the standards. The results reinforce the need for better control of the physicochemical and microbiological parameters of the water consumed by the population.

1. Introduction

The analysis of the water resource is of great importance for human health [1,2] as well as concentrations of metals in surface and groundwater has been of great research interest [3-5]. Various studies have shown that metals can reach the bottom of water bodies causing alterations in ecosystems and communities. Therefore, the metals in the basins will contaminate the drinking water system, can cause impacts on human health, on the soils and on the aquatic biota [5]. The effects of metals in drinking water have been reported by different researchers [6-11]. According to the WHO, most consumers do not have the means to judge for themselves the safety of the water they consume, but their attitude towards drinking water and their water providers will be greatly affected by aspects of water quality that you are able to perceive with your own senses. Additionally, different studies have been carried out in order to evaluate the quality of groundwater, especially from the United States, through the evaluation of water quality, which is designed to evaluate water quality conditions, determine spatial trends and



temporal, and to identify the Physical, chemical and biological factors that affect the underground resource (Gilliom., et al 1995). In some cases, the spatial and temporal focus of metals is analyzed, including an integrated water evaluation that includes a combination of physicochemical, biological and microbiological analyzes with chemical aspects [3]. Similarly, Abraham J et al. [5] analyzes some of the main factors that affect the metal cycle and the dynamics in hydrographic basins such as forest fires, soil and water pH, hydrology, biological processes, events of precipitation, organic matter in the soil and water. Finally, another important aspect in the analysis of drinking water is hardness. According to Dahl, C et al. [12], drinking water provides small doses of calcium and other essential minerals for bones throughout life. When a water is referred to as "hard" water it simply means that it contains more minerals than normal water. There are especially calcium and magnesium minerals. The presence of calcium and magnesium in very high proportions in the water, generates what is known as hard water [1]. For these reasons, it has been considered of great importance to carry out a study of the concentration of metals, chemical parameters that determine hardness, and microbiological parameters in order to determine if the concentrations may represent a risk for daily use and consumption in the area. study.

2. Materials and methods

2.1. Study area

The Guajira peninsula, which corresponds to the northernmost part of the country, made up of a series of low hills of marine origin, extensive plains and, in the extreme north, a more prominent relief with heights of up to 864 meters above sea level (masl) in the Macuira mountain range. In a department where the least rainfall occurs in relation to the other departments of the country with annual totals of 500 mm or less. The mangrove precipitation ranges from 150 mm per year in La Guajira. The highest values of the average air temperature are between 28 °C and 32 °C, which occur in the high and medium Guajira. In relation to runoff, the plain of La Guajira in contrast presents values ranging from 25 mm (in the middle and high Guajira) to 200 mm in the foothills of the Sierra Nevada. Finally, it has one of the largest populations of indigenous communities [13]. It is the department in which it has the largest number of ecosystems from perpetual snow to the sea, and in Manaure the largest exploitation of sea salt in the country is carried out.

La Guajira is home to the Cerrejon mines that make up the largest open pit coal mine in the world, likewise it owns 36% of the Sierra Nevada de Santa Marta territory where the highest elevation in the country is located with 5775 masl, (Depto del Magdalena) considered the highest coastal mountain in the world [14]. The department of La Guajira has 15 municipalities [14]. Municipalities such as San Juan del Cesar, Albania, Barrancas and Fonseca are considered with ecoepidemiological conditions [15].

The present study was designed to evaluate the temporary concentration of the metals Aluminum, Arsenic, Boron, Barium, Beryllium, Calcium, Cadmium, Cobalt, Chromium, Copper, Iron, Lithium, Manganese, Molybdenum, Nickel, Phosphorus, Lead, Antimony, Selenium, Tin, Titanium, Thallium, Vanadium and Zinc, as well as microbiological analyzes at 16 sampling points in the waters that are used for consumption by the inhabitants of the communities located in the municipalities of Papayal, Chancleta, Patilla, Hato Nuevo, Guairmarito, Albania, Cuestecias and Matitas (Figure 1).

The study area constituted Media Guajira which is uniform, straight and regularized, with alternation of sectors of erosion that cut the central plain in low cliffs, and sectors of coastal accumulation that isolate salty or brackish lagoons, in addition to the Ranchería river that builds a delta cut by coastal drift and lower Guajira made up of gallery forests, pastures and crops, main urban centers and coal mining [14].

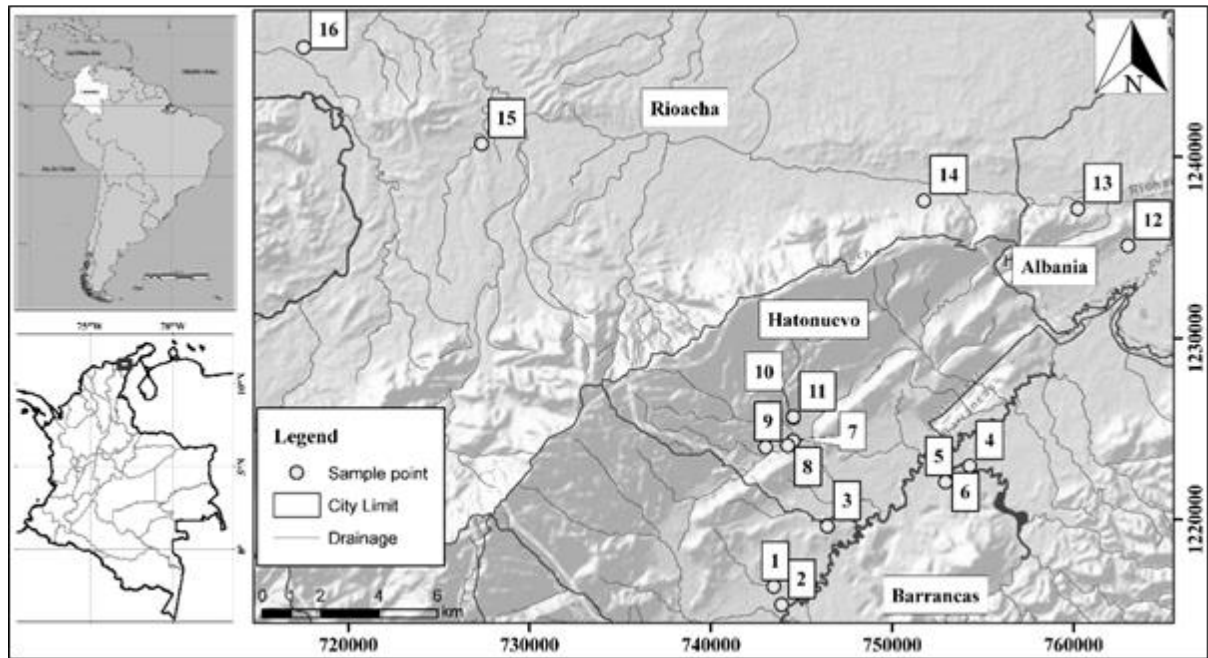


Figure 1. Location of the study area and sampling sites in the Department of La Guajira.

2.2. *Sampling and analysis method*

2.2.1. *Sampling.* A total of 16 water samples collected for chemical and microbiological analysis in June 2016 from supply sources, see Table 1.

Table 1. Location of study sites near Guajira State.

Site	Municipality	Sample point	Longitude	Latitude		
1	Papayal	Underground storage tank	743471,08	1216302,16		
2	Papayal	Rancheria River	743912,55	1215301,79		
3	Papayal- Serrito 2 Sector	Deep well	746426,38	1219630,64		
4	Chanqueta	Cerrejoncito River	754284,89	1222953,11		
5	Patilla	Storage tank	752943,92	1222066,24		
6	Patilla	car tank	752943,92	1222066,24		
7	Hatonuevo	kitchen faucet restaurant	744540,37	1224334,85		
8	Hatonuevo	wellspring " El Pozo"	kitchen faucet family home	744247,16	1224081,47	
9	Hatonuevo	wellspring " El Pozo"	Hatonuevo	wellspring " El Pozo"	743027,19	1223999,70
10	Guaimarito	Storage tank open	744551,52	1225616,33		
11	Guaimarito	Storage tank open	744551,19	1225660,59		
12	Albania	kitchen faucet family home	763012,79	1235099,67		
13	Cuestecitas	Hosepipe	760242,41	1237151,15		
14	Homestead "La Isla"	Deep well	751753,22	1237589,48		
15	Homestead "Villa Martin"	Deep well	727368,32	1240724,30		
16	Matitas	Deep well	717546,04	1246050,00		

The sampling period corresponded to June where the sea breeze and the northeast trade winds act during most of the year and influence the climate regime in this area of the country, with rainy periods

when their intensity decreases (June-November and periods dry when it increases (December-May). The climate in the department of La Guajira is warm and dry at sea level, where the annual average temperature is 29 °C, with maximums of 39 °C in the desert area from Uribia [14]. All the material, including the sampling bottles, used for the determination of heavy metals, were subjected to washing with neutral soap and then immersed in HNO₃ diluted to 10%. In the field, the pH parameters were determined and temperature for each of the samples.

2.2.2. Chemical analysis. The analyzes of the reported metals were carried out on an optical emission spectrometer by Inductively Coupled Plasma (ICP-OES), brand VARIAN VISTA-MPX, with a water recirculation system, argon gas cylinder, extractor for vapors and fumes generated by the plasma, located approximately 30 cm above the plasma generating chamber, Schott Ceran heating plate, Thermolyne Cimarec 2 or equivalent.

The elements analyzed were Silver, Aluminum, Arsenic, Barium, Beryllium, Calcium, Cadmium, Cobalt, Copper, Chrome, Iron, Potassium, Lithium, Magnesium, Manganese, Molybdenum, Sodium, Nickel, Phosphorus, Lead, Antimony, Selenium, Silicon, Tin, Strontium, Titanium, Thallium, Vanadium, Zinc and Sulfur. Argon gas AP grade 4.8. Ultrapure water. Nitric acid, HNO₃, 65% ultrapure. Acidulated water: Dissolve 2.5 mL of ultrapure 65% nitric acid in 2 L of ultrapure water. Hydrogen peroxide, H₂O₂, 30%. Standard solutions traceable to SRM of 1000 mg / L of the analyzed metals.

2.2.3. Microbiologic analysis. Aliquots of water were collected in 15 of the 16 sampling points in 250 ml capacity amber plastic bottles contained with a volume of water of approximately 200 ml with an air chamber corresponding to a volume of 50 ml. The samples were kept in refrigeration from their origin and until the moment of analysis. The microbiological parameters evaluated were total Coliform count (CT) and Fecal or thermotolerant Coliforms (CTT) by two methods; (I) Most Probable Number method (NMP per 100 / ml of water) according to the protocols of the (American Public Health Association) APHA29 and in accordance with Decree 1594 of 1984 of the Colombian Ministry of Health. (II) membrane filtration with a 0.45 micron pore and subsequent seeding in Cromocult Agar according to the protocols established by IDEAM. In both cases the strain used for quality control of the protocols was E. coli ATTC 25922.

The reference values According to decree 1594/1984, the microbiological quality of the water intended for primary contact activities, such as swimming and diving, allows a maximum count of 200 NMP / 100 mL of thermotolerant Coliforms and 1000 NMP / 100 mL Total coliforms; for secondary contact activities such as fishing, the total Coliform count should not exceed 5000 NMP / 100 mL. And According to Decree number 1575 of 2007 "By which technical standards of drinking water quality are issued." ARTICLE 25. The water for human consumption must comply with the following values admissible from the microbiological point of view by the MEMBRANE FILTRATION method: Total coliforms 0 CFU / 100mL and E. coli 0 CFU / 100mL [16].

3. Results and Discussion

3.1. Chemical parameters

Figure 2 presents the concentrations obtained in the laboratory for different metals analyzed and according to this, the most impacted points. Most of the monitored points presented higher values than those stipulated by the drinking water standard for Calcium (60 ppm) in points 2, 3, 10, 13 and 14 that correspond to the townships of Papayal, Guaimarito, Cuestecitas and the sidewalk of "the island" with an average value of (52.60 ppm) in 16 samples an interval of (4.1 to 105 ppm), see Figure 2a and Magnesium (36 ppm) were found an average of 13.8 and an interval in the 16 samples (1.8 to 56.6 ppm), see Figure 2b. In the study area (5) points exceed the norm for Calcium and 1 point the norm for Magnesium. Kipler M et al. [17] evaluated and found mean calcium concentrations of 44 ± 24 in 40 samples an interval of (12 - 86 ppm) and magnesium an average of 24 ± 4 in 22 samples (96.1 and 46

ppm), in drinking water in Bangladesh. This indicates that the water has characteristics of hardness, derived from the presence of calcium and magnesium, which is generally evidenced by the precipitation of soap residue and the need to use more soap to achieve the desired cleaning (WHO 2006) [16]. Studies have shown the relationship between calcium and magnesium on mortality from stroke and ischemic diseases. This relationship is stronger in cerebrovascular disease than in ischemic heart disease, is more pronounced for women than for men, and is more evident with magnesium than with calcium concentration levels [18]. Other studies indicate a relationship of the thyroid size by waters with high calcium content [19]. Chandra et al. [19] conclude in their study that chronic exposure to high calcium content progressively modify the activities of the thyroid hormone by synthesizing enzymes, possibly acting on the cellular and molecular levels that are reflected in the altered profile of the thyroid hormone.

This situation is also conditioned by factors of acceptability of drinking water for consumers, which is subjective and can be affected by various components, that is, the concentration of these components that is unpleasant for consumers is variable, and depends on individual factors. and local, such as the quality of water to which the community is accustomed and various social, environmental and cultural considerations (WHO 2006) [16]. In the case of the study area and in the same way, tourism, trade and exploitation of mining-energy resources have also been considered some of the main drivers of population concentration in the coastal area of La Guajira (Corpoguajira and Invemar 2012, [14]) as factors in the increase of the population and its location in areas that have little guarantee in the access of drinking water.

For the studied regions, high concentrations were found with respect to the levels accepted by Resolution 2215/07 of the following metals: calcium (Ca), strontium (Sr), silicon (Si), Sodium (Na) and potassium (K). In particular cases, concentrations over the norm value of the following metals were found: Barium (Ba) Figure 2c, Lithium (Li). Figure 1e shows the concentration values per sampling point with respect to the accepted average value for Silicon are the corregimientos denoted by the numbers 2, 3, 4, 6, 14, 15 and 16.

Metals also alter the health of the environment, in fact, the increase in heavy metals due to industrial activity has seriously unbalanced and polluted many natural ecosystems. Once these heavy metals are released by human action, they can remain in the environment for hundreds of years [1]. Likewise and according to Corpoguajira and Invemar [14] during 2009, the four main rivers of La Guajira (Cañas, Jerez, Palomino and Ranchería) released nearly $60 \text{ m}^3 / \text{s}$ of water loaded with various pollutants, which allowed calculating how About $26,215 \text{ t} / \text{a}$ of solids, $212 \text{ t} / \text{a}$ of inorganic nitrogen, $67 \text{ t} / \text{a}$ of phosphates and about 918 MPN of microorganisms with faecal contamination. Where the main polluting sources are Mining, agriculture, livestock, industries, port activity and transportation of fuels and domestic origin (wastewater and solid waste).

According to Abraham J et al. [5], the water resources and watersheds contaminated with metals have the potential to represent a significant risk for downstream communities and ecosystems due to the effects of these metals on the health of ecosystems and human beings. The use of deep wells has been reported as a protection factor against some diseases including diarrhea (Wistons et al 2013), however this situation shows the high concentrations of metallic elements such as Manganese. The townships of Papayal, Chancleta, Patilla, Guaimarito and Cuestecitas mostly impacted by high levels of metals are those denoted by numbers 2, 3, 4, 6, 10, 14 and 15, which is a worrying finding for the health of the communities that are supplied from the water resource. In the study area, the highest concentrations of Potassium were found at the sampling points: 2, 3, 4, 6, 14 and 15. Strontium (Sr): 2, 3, 4, 6, 10, 11, 12, 13, 14 and 15. Sodium (Na): 2, 3, 4, 6, 10, 11, 12, 13, 14 and 15. Barium (Ba): 2, 3, 4, 6, 10, 11, 12 and 13.

The highest concentrations of lithium were found at points: 3, 7, 12, 13 and 14. Harari F et al. [10] conducted a study of exposure to lithium through drinking water during pregnancy, the authors suggest that exposure A high lithium through drinking water during pregnancy can affect calcium homeostasis, particularly vitamin D. The danger of metals is that, once they enter the body, they accumulate and are not easily self-eliminated. These compounds are very dangerous for human health and negatively affect vital organs. We are continually exposed to metals, whether through food, water, or the air we breathe.

The main organs highly impacted by the accumulation of heavy metals in the body are the kidneys, liver, lungs and also the nervous system (central and peripheral). According to Kippler M et al. [17] iron-rich water can cause an unpleasant taste or odor, as well as brown precipitation in stored water before use. An advantage with such precipitation is that arsenic can be co-precipitated with it, resulting in less than estimated exposure from the concentration in the sampled water. When relating the sampling points with the water supply sources to the population of the study area, it was observed that the points that presented the values above the norm correspond to underground wells, domestic storage tanks that do not have protection (without cover) and surface sources such as the River of Rancheria.

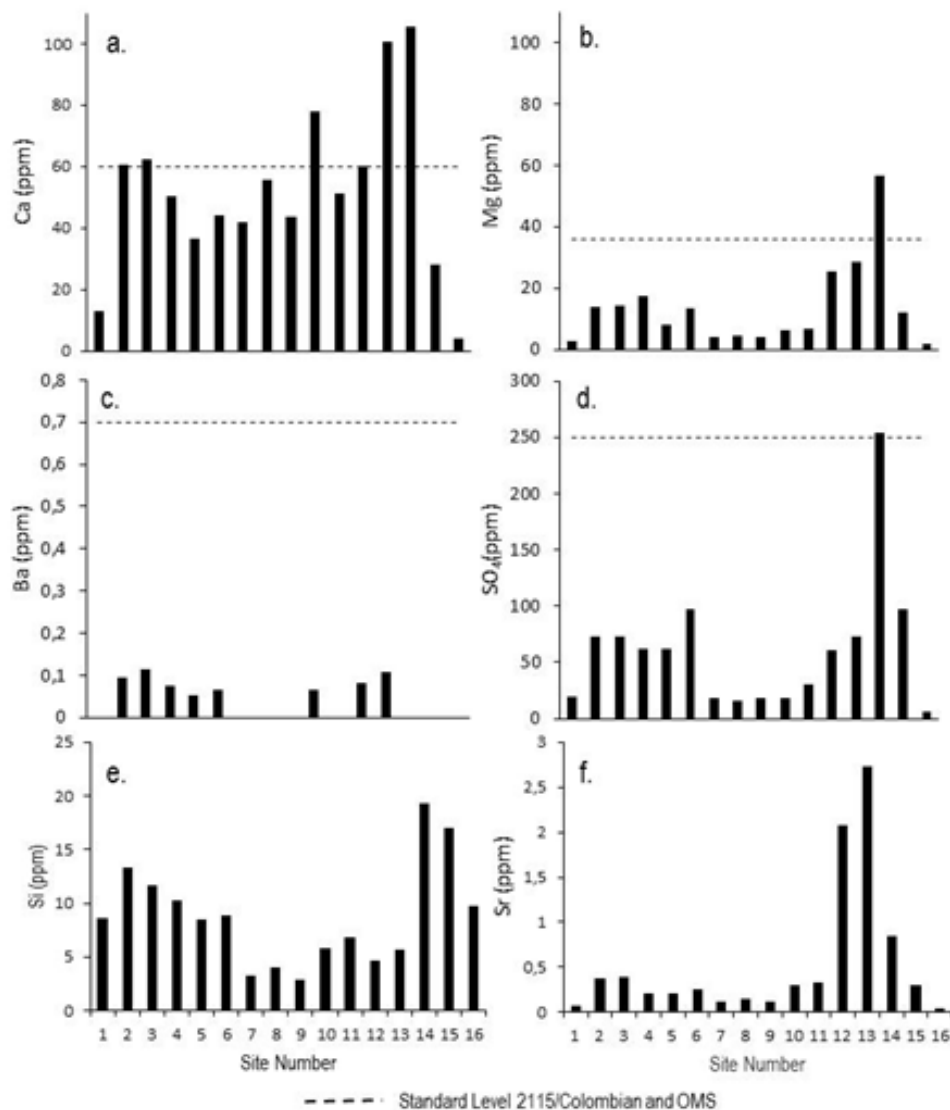


Figure 2. Concentration of metals: Ca, Mg, Ba, SO₄, Si and Sr in parts per million per sampling point

The high reactivity and therefore retention of metals in any biological matrix, is due to the favourable acid-base properties of the metallic elements, which allows it to interact strongly with any organic and inorganic electro-donor or electro-acceptor species. This property causes the metallic elements to be almost irreversibly retained in complex molecular structures, such as proteins and nucleic acids. In most cases, when a metal enters the internal structure of proteins, these structures lose or change their

physiological functionality, altering the vital processes for which they were designed. Therefore, metals have a highly toxic effect on vital systems and the concentrations allowed in water for human consumption allowed by current legislation should be very low, for the preservation of public health.

The most common sources of aluminum in drinking water are naturally occurring aluminum and aluminum salts used as coagulants in water treatment. Sampling point 6 is the only point that presents higher values of aluminum 0.532 ppm, this sampling point corresponded to the sample taken in a tank car which is supplied from the Rancheria River. This can be attributed to the fact that (WHO) the final water can be contaminated with chemicals used in water treatment and substances from materials in contact with water. This indicates the need for mechanisms to deliver water to the population so that water access guarantees its quality.

3.2. Microbiologic analysis

The determinations of Total Coliforms (CTT) and Thermotolerant Coliforms (CT) evaluated by the NPM / 100 mL method, were below the maximum limit allowed for primary contact (200 NMP / 100 mL for CTT and 1000 NMP / 100 mL for CT), but not in all cases the potability conditions established in Decree number 1575 of 2007 (0 UFC / 100mL for CT and CTT) are met, see figure 3.

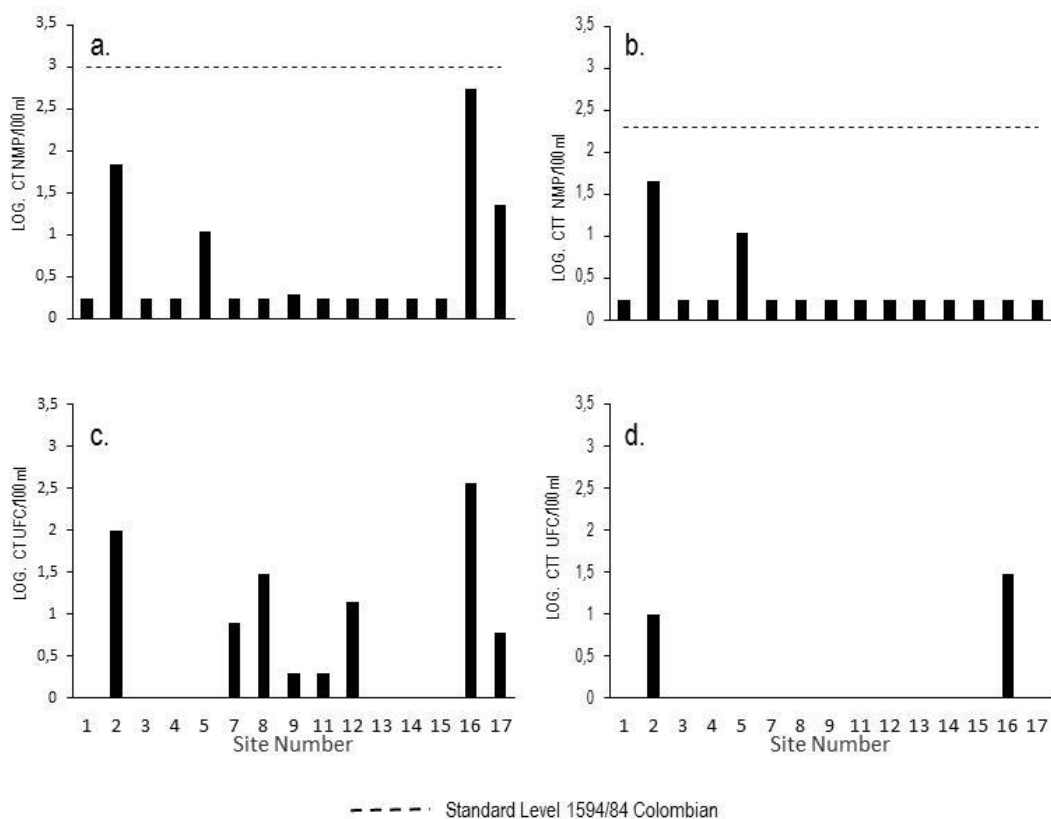


Figure 3. Determinations of Total Coliforms (CTT) and Thermotolerant Coliforms (CT) in the sites tested.

4. Conclusions

Assessment and monitoring of metals in local drinking water could provide effective regional prevention programs including mitigation strategies and prevention of contamination of the water resource. It is essential that additional mitigation strategies are implemented and effectively evaluated in the long term

for water monitoring throughout the Guajira region. Additionally, the need to assess the exposure of the population by biomarkers is established, reflecting the exposure of all sources, not just drinking water.

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