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Analysis of Haloacetic Acids (HAA5) in Waters of Public Schools and Residencies in Maringá-Brazil

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Abstract

For water to become suitable for human consumption in most water treatment plants this occurs by making use of the chlorination process where the organic matter is destroyed by the action of chlorine. Chlorine is a disinfectant that at low concentrations meets requirements such as not being toxic to humans and inactivating microorganisms. The reaction of chlorine with organic compounds results in chlorination byproducts, many potentially harmful to human health, such as trihalomethanes, haloacetic acids, among others. The present work aimed to collect and analyze samples of treated water from reservoirs from public schools in the city of Maringá, Brazil. Analyses of haloacetic acids (HAA5: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid and dibromoacetic acid), natural organic compounds and free residual chlorine were performed (the latter analysis, in loco). The water collection points were chosen in order to maximize the concentration of haloacetic acids that characterize network distant points from treatment station and also samples near the water treatment plant. With the results, the formation of haloacetic acids between the entrance water of the school and the water of the reservoir of the collection points were compared, where higher values were obtained in the reservoirs. Furthermore, the haloacetic acid levels of water supplied to the population close to the treatment station and distant points of the treatment station were compared, resulting in larger values at the distant points. The value of 0.170 mg/L in haloacetic acid (the maximum value allowed by the legislation is 0.080 mg/L) was obtained at a point distant in the network from the treatment plant. The Consolidation Ordinance n.5/2017, current legislation for treated water in Brazil, was used in relation to the maximum allowable values for free residual chlorine and haloacetic acids.

Keywords

Chloro, Disinfection, Natural Organic Compounds, Byproducts

1. Introduction

In the process of purifying water intended for human consumption, Water Treatment Plant (WTP) analyzes the parameters of raw water such as turbidity and organic matter to regulate the concentration of chemicals to be added (for example, chlorine concentration). Thus, water with higher concentrations of organic matter will require higher dosages of chlorine or other chlorine-based disinfectant, increasing the production of disinfection byproducts, DBPs [1] [2] [3].

Large amount of organic matter from surface water is removed by the treatment process. But even so large finely dissolved portion reacts with free chlorine used as a disinfectant. This leads to the production of many halogenated compounds or by-products of disinfection [4].

The Ordinance n. 2914/2011 [5] incorporated into the Consolidation Ordinance n.05/2017 [6], which is the current legislation, presents guidelines for the control and monitoring of water quality for human consumption purposes and its potability. It also mentions permissible maximum values for the by-products of disinfection: for trihalomethanes (THMs) at 0.100 mg/L and haloacetic acids (HAA5) at 0.080 mg/L. The term HAA5 indicates the sum of five haloacetic acids: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid and dibromoacetic acid [6]. These molecules are formed when natural organic compounds react with chlorine in two points of WTP in Maringá city: at the pre-chlorination and post-chlorination [2].

According to [1] studies indicate that trihalomethanes, haloacetic acids and other halogen compounds have high potential for toxicity and carcinogenicity. Human exposure to these harmful agents is not limited to the intake of chlorinated water. Exposure also occurs in any other activity that uses treated water, such as pool and shower baths.

The responsibility of the water supply company that supplies water to the city of Maringá-Brazil ends when water from the distribution network enters the home through the water consumption control register. From this point (record of consumption) the user is the one who responds by the quality of the water of its residence. It occurs that many times the user does not pay attention to the periodic cleaning of the water reservoir every six months, which contributes to the increase of the concentration of natural organic matter in this reservoir and, consequently, to the formation of haloacetic acids.

Regarding the effect of time on the formation of THMs, the study [7] report that under natural conditions formation does not occur rapidly. In some circumstances the formation of THMs may end in less than an hour. In others, it may take several days before the maximum THM production occurs. The same

authors also show that among many other aspects, pH and water temperature also influence the production of THMs so that the higher the increase in these variables, the higher the formation in THMs.

Based on this context, we have the following questions: do haloacetic acid levels increase when the treatment station is compared to distant points in the distribution network? In the path from the consumption control register to the user's water reservoir, do haloacetic acid levels also increase? These are the objects of study of this work. In addition, analyses of natural organic compounds (NOCs) and residual chlorine were carried out.

2. Materials and Methods

In order to carry out this research, six sampling points in the city of Maringá-Brazil were chosen for the collection of water samples, according to **Figure 1**. Analyses of haloacetic acids (HAAc), free residual chlorine and natural organic compounds (NOCs) were carried out at each sampling point. Of the six points, five of them are the furthest possible from the treatment plant, within the urban perimeter. They were classified in A, B, C, D, E and F. The point D is the sample point near the WTP. The samples come from public schools and homes.

Water samples were taken from the register of water consumption (water from the distribution network) and the user's water reservoir. The samples were collected and preserved according to Brazilian Standard n. 9898 [8] and the Guide of Collection and Preservation of Samples of the Environmental Company of the State of São Paulo [9].

Nomenclatures were given for all the samples collected at the six points, as exemplified in point A: A-HAAc-CAV; A-HAAc-RES; A-Cl_2-CAV; A-Cl_2-RES; A-NOC-CAV and A-NOC-RES. The term "CAV" refers to the sample collected in the water consumption register. The term "RES" refers to the sample collected in the water reservoir. The term "Cl_2" refers to the analysis of free residual chlorine and "NOC" refers to the analysis of natural organic compounds.

Free residual chlorine analysis was performed locally by the colorimetric analysis DPD (N, N-diethyl-p-phenyl phenylene diamine) quoted by Standard Methods, method 4500 Cl-A [10]. The analysis of natural organic compounds (NOCs) consists of the indirect method of determining the concentration of organic matter dissolved in accordance with Standard Methods n. 5910 B [10] based on UV absorption at 254 nm. The analytical method used to quantify total haloacetic acids occurred by gas chromatography with electron capture detector (CG-DCE) cited by the United States Environmental Protection Agency [11]. The chromatographic analyses were performed on Agilent equipment with Agilent HP-5MS UI column with 5% phenyl methyl siloxane phase (30.0 m × 250 μm d.i. × 0.25 μm film thickness). For optimum separation of the analytes in the system, optimum oven temperature programming was used: initial temperature of 92˚C maintained for 2.5 min, then ramp of 15˚C min^{-1} to 175˚C maintained for 13 min, and ramp of 20˚C min^{-1} to 280˚C and maintained for 15 min.

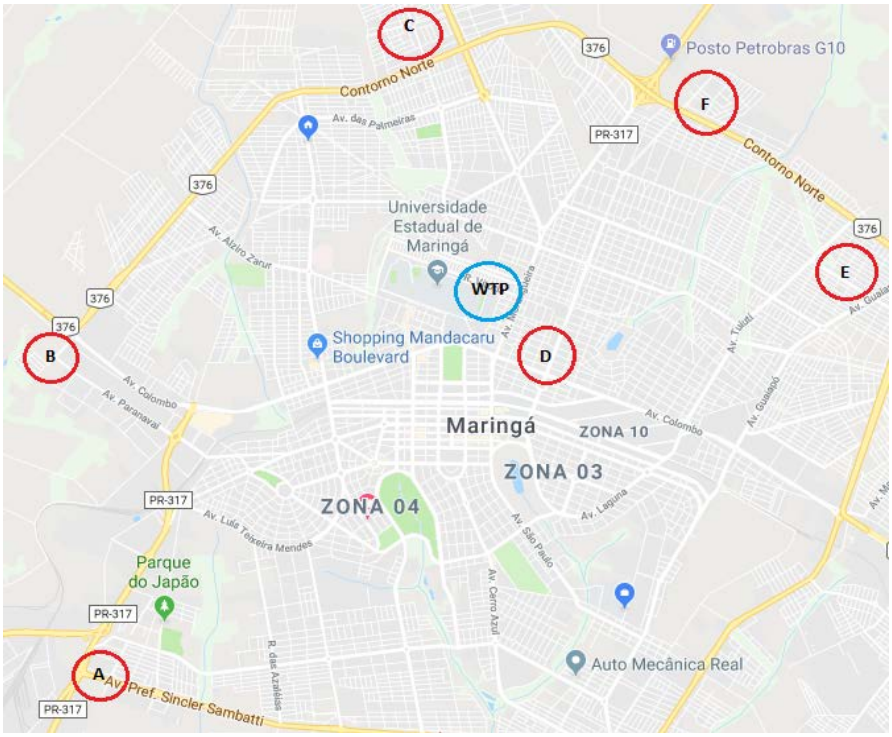

Figure 1. Location of six sampling points: A, B, C, D, E, F in Maringá city, Brazil. Source: Google Earth, 2018.

3. Results and Discussion

The results in Table 1 show the total haloacetic acid analyses of the samples taken in the water consumption register and in the reservoirs. The minimum limit of detection for this analysis reported by the method used was 0.050 mg/L.

A higher concentration of HAAc is expected in all samples in the water consumption register relative to the consumption register in sample D, close to the WTP because of the time provided to the reaction for the formation of HAACs. In relation to the value of HAACs in the consumption register D (close to WTP) for the values of water consumption register A, B, C and F, there was an increase in values, except for point E. Below 0.050 mg/L it does not have the exact value of the concentration of HAACs, so it was not possible to infer the comparison for the register of water consumption in E.

Although the value obtained in the consumption register of the D point (near the WTP) had a value lower than 0.050 mg/L, in the other samples of the consumption register, except for the analysis at point E, higher values were obtained. These results are in agreement with the affirmation of the authors in [7] regarding the reaction time.

With respect to the magnitude of the values obtained in the analyses in HAAc of the water consumption register, of the six sampling points only three (points C, D and E) are below the maximum permissible value of 0.080 mg/L as stated in Consolidation Ordinance n.05/2017 [6]. Regarding the magnitude of HAAc values in the reservoirs, only two points presented values below 0.080 mg/L (points

Table 1. Analytical results of HAA5 in the consumption register (CAV) and water reservoirs (RES) at the sampling points.

Sampling Point	CAV (mg/L)	RES (mg/L)
A	0.094	0.128
B	0.170	0.085
C	0.066	0.052
D	<0.050	0.095
E	<0.050	0.139
F	0.136	<0.050

C and F). Possibly due to the variable cleaning period of the reservoir, the concentration of HAAc increased from the consumption register to the reservoir at three points (A, D and E) and decreased by three points (B, C and F).

At the points where HAAc values greater than 0.080 mg/L were found, it is important to highlight the concern about the health of the people who use this water because studies relate the incidence of cancer and the ingestion of disinfection byproducts such as THMs and HAACs [1] [12].

In **Table 2**, the decrease in free residual chlorine concentrations between the water consumption register and the reservoir can be observed. This decrease occurs due to the reaction of natural organic compounds present in the water with chlorine, as well as its natural tendency to volatilize.

It is observed that in the analysis of the F point the lowest concentration of free residual chlorine was obtained when it decreased from 0.4 mg/L to 0.2 mg/L. Even so, the value of 0.4 mg/L is above the minimum value recommended by Consolidation Ordinance n.05/2017 [6] which is 0.2 mg/L. In the analysis of point B, the concentration of free residual chlorine in the consumption register (0.8 mg/L) was higher than the other samples, when the maximum permissible value was 2.0 mg/L. This value of 0.8 mg/L indicates possibly point chlorination. For the values found in the reservoirs, only the value of 0.2 mg/L was found in the F point reservoir, being the lowest value, but still satisfying the legislation.

Table 3 shows that the values in natural organic compounds (NOCs) of analyses A, B, E and F were higher in the reservoir than in the consumption register. This may have occurred due to contamination entering the water reservoir or due to microbiological activity. For samples C and D, there was a decrease in NOCs values between the consumption register and reservoir, when this decrease can be understood as a result of the cleaning of the reservoir or consumption of organic matter by chlorine.

The arithmetic mean of the temperature values of the samples in the consumption register resulted in 20.5˚C and in the reservoir 18.2˚C. All measured values were within the range of 18˚C to 25˚C as required by free residual chlorine analysis.

Table 2. Values obtained from free residual chlorine in the water consumption register (CAV) and reservoir (RES).

Sampling Point	CAV (mg/L)	RES (mg/L)
A	0.6	0.4
B	0.8	0.4
C	0.6	0.4
D	0.6	0.4
E	0.6	0.4
F	0.4	0.2

Table 3. Arithmetic mean of the values obtained in triplicate of absorbance for Natural Organic Compounds (NOCs) at each sampling point.

Sampling Point	CAV (mg/L)	RES (cm^{-1})
A	0.7	0.4
B	0.8	0.4
C	0.6	0.4
D	0.7	0.4
E	0.6	0.4
F	0.4	0.2

4. Conclusions

With the results found it is possible to conclude that:

1) The levels of HAACs in the water consumption register increased as the collection point moved away from the WTP, which characterizes the points farthest from the distribution network with the highest values in HAAc. Several sampling points in the consumption register showed values above the allowed (0.080 mg/L).

2) The analyses of points A, C, D and E of the reservoirs have an increase in the levels of HAAc in relation to their respective water consumption registers.

3) Free residual chlorine had higher levels in the water consumption register at all sampling points in relation to the respective values in the reservoir, that is, there was no increase of free residual chlorine in relation to the maximum point D, close to WTP.

4) The analysis of the C point presented the highest level in natural organic compounds (NOCs), even when compared to the consumption register in point D, near the WTP. This shows contamination by organic matter in the distribution network.

5) A continuation of the present study is suggested by deepening the relationship between time of disinfection of the reservoir and levels of HAAc.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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