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Monitoring the trihalomethanes concentrations in drinking water

Monitoramento das concentrações de trihalometanos na água potável

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Tuany Natana SCHÄFER[1], Beatriz BOGER[1], Ingryd Isabelle Maia de SOUZA[1], Marilene da Cruz Magalhães BUFFON[2], Rafael Gomes DITTERICH[2], Milene Zanoni da SILVA[1], Yanna Dantas RATTMANN[1]*

*Correspondence to: [1]Laboratory of Public and Environmental Health, Department of Collective Health, Federal University of Paraná, Av. Lothário Meissner, 632, Jardim Botânico, Curitiba, PR, Brazil, zipcode: 80210-170. Tel: +55 41 3360 4166 / +55 41 3360 4073. E-mail: yannadr@gmail.com

[2]Department of Collective Health, Federal University of Paraná, Curitiba, PR, Brazil

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ABSTRACT

The reduction of the incidence of water-borne diseases is achieved with the diffusion of the use of chlorination techniques. However, in spite of the benefits of this disinfection method, the reactions of chlorine with the natural organic matter occurring in the water induce the production of disinfection by products such as trihalomethanes. These products have already been associated with the incidence of some cancers types. Considering that in the Brazilian legislation, it is not mandatory measuring and controlling the occurrence of trihalomethanes at the exit and during the water distribution to the consumer**.** This study aimed at analyzing the relationship between chlorination and its by products**.** Thus, this project evaluated the concentrations of trihalomethanes in water collected at different points of supply in the municipality of Colombo, Paraná, Brazil, during the period from November 2015 to February 2016. Chromatographic methods were employed, besides the spreadsheets provided by the Health Surveillance of Colombo for comparison. The found values were tabulated and they were compared with the limits established by the Brazilian Ministry of Health**-** Ordinance Nº 05/2017**.** The results confirmed that the values of those provided by the concessionaire responsible for the city water treatment and supply, and being within the standards determined by the legislation.

Keywords. trihalomethanes, chlorine, disinfection by products, drinking water, Brazil, gas chromatography.

RESUMO

A redução da incidência de doenças transmitidas pela água foi alcançada com a difusão do uso de técnicas de cloração. Apesar dos benefícios desse método de desinfecção, as reações de cloro com a matéria orgânica natural presente na água levam à formação de subprodutos de desinfecção como trihalometanos. Esses produtos já foram associados à incidência de alguns tipos de câncer em animais, e muitas vezes podem ser detectados em água tratada e fornecida para o consumo. Pela legislação brasileira não é obrigatório efetuar o monitoramento de trihalometanos após o tratamento e distribuição de água. Frente a este problema, este estudo teve como objetivo avaliar as concentrações de trihalometanos em água coletada em diferentes pontos de abastecimento no município de Colombo, PR, Brasil, durante o período de novembro de 2015 a fevereiro de 2016. Utilizou-se método cromatográfico para as análises, além de planilhas fornecidas pela Vigilância Sanitária de Colombo. Todos os valores foram comparados com os limites estabelecidos na Portaria de Consolidação Nº 05/2017 do Ministério da Saúde. Os resultados confirmaram que os valores de trihalometanos fornecidos pela concessionária, responsável pelo tratamento e fornecimento de água na cidade, atendem aos parâmetros legais.

Palavras-chave. trihalometanos, cloreto, produtos da desinfecção, água potável, Brasil, cromatografia a gás.

INTRODUCTION

No other resource that nature comes to offer to earth, none is so abundant as the water. It is estimated that 70% of the earth's surface is covered by water, however, only a small fraction of this volume is valuated as available for human consumption [1].

Increasing industrialization and demographic explosion occurred over the past XVII century in the European continent, and these events brought up the need to invest in the water and sewage collection and supply systems; with the main aim to sterilize water and make it available for consumption. The significant increase of life expectancies in the developed countries during the XX century is due to this, whereupon today it's known as the conventional treatment of water [2,3].

Among the chemical agents that can be used for disinfecting the water for human consumption, chlorine is still the most utilized, due to its efficiency and its low cost[4]. The expressive presence of natural organic matter (NOM) in the raw water promotes the formation of trihalomethanes (TTHM) compounds since the NOM tends to react with free chlorine within its midst[5,6].

The use of chlorine as a disinfection agent in water treatment is associated with the traditional sanitary measures and has brought undeniable benefits to society, as the decline of morbid-mortality resulting from pathogens of hydric propagation[3,7].

Nonetheless, a control for regulating the concentrations of chlorine in the water outlet is needed, and in the distribution networks by the companies, liable for the water supply. These strategies aim at maintaining the water chlorination at a safe and effective level, as well as to minimize the formation of TTHM and their harmful consequences to the health when exposed to the large concentrations or over a long period of time[3].

The risk of forming TTHM is, they act as potential carcinogenic and mutagenic substances in some animals[8,9]. These occurrences have already been associated with some epidemiological studies with cancer, and they are cited in journals using search engines ScienceDirect and PubMed, the search results having an average of 119 articles.

In Brazil, the current legislation on the drinking water establishes the value of 100 $\mu g.L^{-1}$ as the maximum contents of TTHM, and 5 $mg.L^{-1}$ for free residual chlorine in the water from the distribution networks[10]. The Ordinance nº 05/2017 states to monitor the TTHM concentrations in the treated water, but unlike those required by other countries, this category of monitoring established by the Brazilian governmental agencies[10] is not compulsory.

Due to the scarcity of studies concerning the quality of the water that reaches the taps for Brazilian consumers, the present investigation aimed at evaluating the TTHM concentrations in samples collected at different points in the city of Colombo, state of Paraná - Brazil, for evidencing the possible risks to the health of the local population.

METHOD

The study consisted of monitoring for four months, from November/2015 to February/2016, the water samples collected for measuring the chlorine concentrations, and to evaluate the formation of water disinfection by products (trihalomethanes) in the water supply distribution system of the city of Colombo, Paraná-Brazil.

According to the Census of the Brazilian Institute of Geography and Statistics (IBGE), in 2015, the population of Colombo was estimated to have 227.220 inhabitants[11]. The higher percentage of inhabitants resides in the urban area at the southern region of the municipality.

Collection points

Water samples were collected in triplicate at five specific points, all of them located in the Basic Health Units (BHU) in the city of Colombo. The criterion adopted for choosing the sites was justified by the regular territorial distribution, and because they are regions that cover the greater part of the population of the municipality.

Samples were collected in 45 mL glass bottles, equipped with teflon caps and silicone septums, containing 3 mg of sodium sulfite. The flasks were completely filled with the water samples, and they were kept under refrigeration at 4 °C.

Reagents

Water free of organic matter (HexiS) was diluted in a volume of 500 mL, as the TTHM non-forming control under the laboratory conditions.

Samples evaluation

Colorimetric assay

Samples were firstly evaluated at the Laboratory of Public and Environmental Health of the Pharmacy course of the Federal University of Paraná. A colorimetric assay was performed using the reagent kit for detecting trihalomethanes (TTHM Plus®-HACH). The detected absorbance values were compared to the positive and negative patterns for the specific chemical substance. The results from this colorimetric method were not quantitative, and they were discarded.

Gas Chromatography

The samples were submitted for extraction using purification and trapping (purge and trap method) and analyzed by gas chromatography with mass spectrometry detection (CG-MS).

Shimadzu gas chromatograph, model 2014, with electron capture detector was used; separations were performed on Rtx-5MS, Restek capillary column (30 m x 0.25 mm d.i and 0.25 mm film thickness). The chromatographic conditions are summarized in **Table 1** below.

A detector, containing an electron ionization source (EI-70 eV) and a quadrupole mass analyzer, operated at 40-500 m/z linear scanning mode, were used for the detection by mass spectrometry and for compounds identification. The interface was maintained at 310 °C and the source of ions at 200 °C.

Table 1. Experimental conditions

Inlet temperature	250° C
Injection volume	1 µL
Split ratio	1:5
Furnace temperature	40° C (2 min), with a heating ramp of 20° C/min to 200° C, followed by ramp from 4° C/min to 290° C
Detector temperature	300° C
Carrier gas	Helium gas
Flow rate	1.2 mL min^{-1}

The linearity of the method was studied in ten different concentrations of analyte, in triplicate. The proposed method showed good linear range between 0,1 - 100 μL^{-1}, with excellent coefficients of determination (R>0.9933) for analyte. The limit of detection (LOD) and the limit of quantification (LOQ) were 0,03 μL^{-1} and 0,1 μL^{-1}, respectively.

Data provided by the Colombo Health Surveillance

The monthly average of chlorine concentrations in the municipal water supply networks was monitored since the excess of free residual chlorine was predisposes to a higher formation of TTHM.

The Health Surveillance agency for the city of Colombo, that controls the heterocontrol for the parameters of chlorine concentrations, provided the value of concentrations for comparing with the data informed by the concessionaire, which is responsible for treating and for distributing water, the Sanitation Company of Paraná (SANEPAR).

Data on the TTHM concentrations in the water supply system, reported by SANEPAR were provided by the Health Surveillance of the municipality of Colombo, which were used as a pattern for comparing the results from the present study.

The data were tabulated by using the GraphPad Prism® program. The results were evaluated according to the limits allowed by the Brazilian Ministry of Health - Ordinance nº 05/2017, which stipulates a maximum of 5.0 $mg.L^{-1}$ chlorine in the water, and the permitted maximum value of 0.1$mg.L^{-1}$ (=100 $\mu g.L^{-1}$) of TTHM in the treated water and distributed for consumption.

RESULTS

SANEPAR is responsible for the water treatment and distribution in Colombo, and for analyzing the total TTHM concentrations at two points in the trial system time.

Concentration of trihalomethanes

Figures 1 and **2** represent the values of TTHM found in the water after the treatment (**Figure 1**) and at the distribution points (**Figure 2**), at different points of the supply system, during the years of 2015 and 2016. These data were provided by both the SANEPAR and the Health Surveillance.

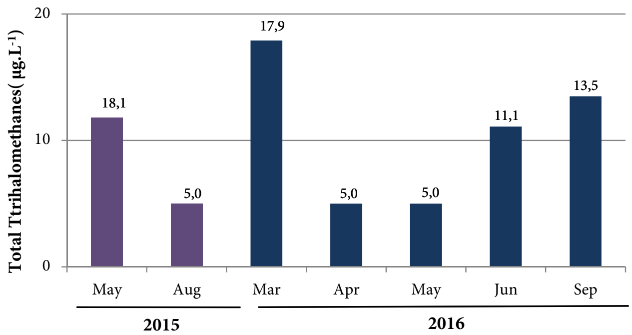

Figure 1. Values of total trihalomethanes (TTHM) in µg.L^{-1} at the end of treatment

Source: SANEPAR and Health Surveillance of the city of Colombo

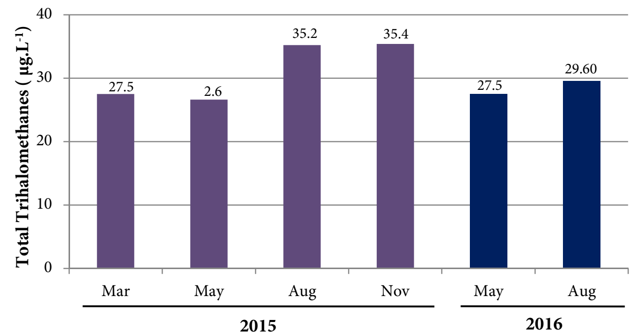

Figure 2. Values of total trihalomethanes (TTHM) in the water supply system at distinct periods.

Source: SANEPAR and Health Surveillance of the city of Colombo

A higher variation in the TTHM concentration was observed in **Figure 2**. In **Figure 1** the values remained constant only during the months of August 2015, April and May 2016; at the same time, a significant variation between the months of March and April of 2016 was observed (12.9 µg.L^{-1}). **Figure 1** illustrates the increasing occurrence of TTHM along the water supply system, besides indicating certain invariability on the values over the investigated periods. Although, there was no possibility of establishing a direct relationship between the values since some of them indicated one of the variables only, the output value or the value in the distribution network.

Mean value of TTHM at the exit of treatment was established as 9.9 ± 5.0 µg.L^{-1}, with the lowest value of 5 µg.L^{-1}and the highest value of 17.9 µg.L^{-1}. The concentration of TTHM in the distribution network was established as 30.3 ± 3.9 µg.L^{-1}. This indicates an approximate increase of 206% in the concentration of TTHM in the water, which leaves the treatment site until reaching the tap of the consumer.

Table 2 shows the mean concentrations of TTHM detected by means of gas chromatographic analysis in water samples collected at five specific points in Colombo city, from November 2015 to February 2016.

On average the present study found the following TTHM concentration values: 33.1 ± 3.7 µg.L^{-1}; 31.3 ± 5.5 µg.L^{-1}; 30.7 ± 5.1 µg.L^{-1}; 27.3 ± 5.7 µg.L^{-1}; 32.3 ± 0.7 µg.L^{-1} for the collection points located in Jardim Monza, Atuba, Maracanã, Guaraituba and São José, respectively. November was the month, in which the highest TTHM contents were detected, on average 32.74 ± 4.4 µg.L^{-1}.

Table 2. Mean values (± standard deviation) to total concentrations (µg.L^{-1}) of trihalomethanes (TTHM) in the supply drinking water at the Basic Health Units (UBS) that serve some of the most populous neighborhoods of Colombo, Paraná during November of 2015 to February of 2016

Mean and standard deviation to Total Concentrations of TTHM (µg.L^{-1})								
Collection point in Colombo (UBS)	**Nov**		**Dec**		**Jan**		**Feb**	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
Jardim Monza	36.6	2.0	28.2	3.1	32.3	2.3	35.3	1.3
Atuba	36.1	1.9	26.5	2.2	36.1	1.5	26.7	0.6
Maracanã	25.6	1.3	36.3	0.9	27.3	2.0	33.8	1.4
Guaraituba	32.1	1.8	22.1	1.7	22.7	0.7	32.3	0.8
São José	33.3	2.0	32.3	2.0	32.3	2.1	31.6	1.3

The data corresponding to mean concentration and standard deviation (SD). Water samples were collected in triplicate at five specific points, located in basic health units in Colombo-PR

Otherwise, a mean of 29,0 ± 5,4 μg.L^{-1} was found in December, the lowest mean concentration. The means of 30.1 ± 5.2 μg.L^{-1} and 31.9 ± 3.2 μg.L^{-1} were recorded in January and February, respectively. The overall mean for all of the monitored months was 30.9 ± 4.5 μg.L^{-1}.

Chlorine concentration

Figure 3 shows the monthly average concentrations of chlorine obtained from heterocontrol worksheets provided by the Health Surveillance of Colombo, which delivered the values comprising the period from January to December 2015.

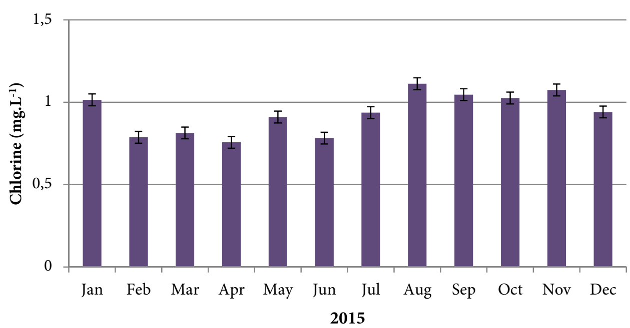

Figure 3. Concentration (mg.L-1) of chlorine in the supply drinking water at the Basic Health Units (UBS) of Colombo, between January and December of 2015

Source: Health Surveillance of Colombo

Values of this parameter are concentrated in the range from 0.5 mg.L^{-1} to 1.2 mg.L^{-1}, and the highest variation being between 1 mg.L^{-1} and 1.8 mg.L^{-1} in January. A lower concentration of chlorine was detected during September, being circa 0.7 mg. L^{-1} of residual chlorine in the drinking water.

DISCUSSION

Due to the technical limitations, the Health Surveillance of the city of Colombo does not perform the heterocontrol of TTHM concentrations in the water of the municipality. Therefore, this was the proposal of the present study, and seeing that, it strategically selected the sample collection sites in the basic health units, which serve some of the most populous districts (Guaraituba, Atuba, Monza) in Colombo[11].

Since they were detected for the first time in the early 1970s in treated water[4], some epidemiological studies have suggested the possible relationship between the long-term exposure to these disinfection by products from the chlorination method and the increased risk of cancer and other health-related ills[12-14].

By means of the ScienceDirect search system (strictly using the keyword "trihalomethanes"), it may find about 1,108 papers referring to study on TTHM since the 1970s when these by products began to be investigated.

Several of these studies are still focused on the new testing (or already known) techniques for detecting and removing the TTHM and NOM from drinking water[15]. Though, in the last decade, a significant increase in papers regarding the study of these compounds and their association with the induction of some neoplasms can also be found.

Studies on related cases have been reported in several countries: Canada, Spain and Italy[12,16,17]. These surveys analyzed the quality of the incoming water to the population, concerning the presence of TTHM in drinking water for ingestion or inhalation. In Brazil, this kind of monitoring has still been scarce[18,19]. In Brazil, the majority of the researchers working on TTHM and disinfection by products investigate the methods for detecting or removing these compounds from the drinking water[15, 20], are made under laboratory conditions.

As shown in **Figures 1** and **2**, the obtained data were not directly correlated. Therefore, it cannot accurately assert the type of parameters that should be evaluated to detect what caused the TTHM increase throughout the treatment from the exit (particularly in August 2015) to the collection points. Although it is implied that the reactions of TTHM occurred during the distribution, as reported[4,9].

Higher production of TTHM might be associated with: (a) the higher availability of organic precursors[4,6,9,18,21,22] which may originate from the humus derivatives (common in the water medium) or even from the sewage contamination on the way, or (b) high concentration of residual chlorine in water[4,3,21,23].

It is important to consider that when talking about the supply of treated water at each stage, the abstraction of water from springs, rivers and other sources, before their distribution, they have to go through a rigorous supervision process.

Heterocontrol is the process of monitoring the quality of goods or services, whether it involves risk or it represents a protection factor for public health. In general terms, in addition to the control that must be exercised by the producer on their production, distribution and consumption rocedure, and the state institutions also having to exercise these controls [24].

The control of the chlorine concentrations in water, treated by the SANEPAR, is performed by the concessionaire.

In contrast, the Health Surveillance of the Municipality is responsible for the heterocontrol, which compares the detected values and passes them on to the Information System for Surveillance of Water Quality for Human Consumption (SISÁGUA), of the Ministry of Health. Nevertheless, the same Brazilian standard that establishes the maximum values of TTHM for the consumption, the periodic measurement of the TTHM concentration at the exit of the treatment and along the supply networks are not obligatory.

The Brazilian legislation establishes that the analyzes for TTHM determination have to be done in accordance with the methods described in the "Standard Methods for Water and Sewage Examination"[25] published in 1905, and periodically updated by the American Public Health Association (APHA). Among the methods proposed by APHA, the "purge and trap" extraction technique with GC/MS (gas chromatography/mass spectrometry) detection was adopted to quantify the TTHM in this project.

The present study did not aim at individually quantifying the TTHM produced such as: chloroform ($CHCl_3$), bromodichloromethane ($CHClBr_2$), dibromodichloromethane ($CHBr_2Cl$), bromoform ($CHBr_3$) and other components such as haloacetic acids (HAA). Although, it is important to note that other similar studies indicated the higher presence of chloroform and haloacetic acids[15] as being the principal compounds contained in drinking water.

Knowledge of the maximum permissible value of the TTHM concentrations in drinking water varies greatly according to the drinking water standards of each country. The World Health Organization (WHO) establishes the maximum permissible values of up to 100 $\mu g.L^{-1}$ for TTHM[23] (WHO 2008). However, some countries such as Germany, Switzerland and other regulatory agencies such as the United States Environmental Protection Agency (USEPA) have lower values than WHO (10 $\mu g.L^{-1}$, 25 $\mu g.L^{-1}$ and 80 $\mu g.L^{-1}$, respectively) for the occurrence of these compounds in the water for consumption[4,26].

The values of the TTHM concentrations at the exit stage of the treatment procedure, as well as those found in the distribution network (**Figures 1** and **2**), were below the limit established by Brazilian and Paraná legislation, that is 100 $\mu g.L^{-1}$ [4,6,18,27] and 80 $\mu g.L^{-1}$, respectively[6]. The results found in this study corroborated the information provided by the SANEPAR and the Health Surveillance.

Monitoring the NOM concentrations was not performed in the present study, but it is essential to analyze it at the collection and distribution points, especially during the periods of high temperature and rainfall[28]. The amount of NOM present in the collection and supply reservoirs may be changed, and this will directly interfere in TTHM contents, pH value and water turbidity constants[25].

Analyzing **Figure 1**, a considerable variation can be observed in the TTHM concentration during the period from March and April of 2015. This difference could be attributed to the high rainfall recorded in these months in this region[29]. In fact, the peaks of the highest concentration of TTHM recorded at the end of treatment (March and September 2016), coincided with the times when the rainfall measurements for the Curitiba region were above the normal range. For this reason, in addition to the presence of TTHM at this time during the treatment withdrawal, the amount of NOM and turbidity of the water should be reasonably altered because of the rainy season.

Although TTHM concentrations are below the limits established by Ordinance Nº 05/2017, the free residual chlorine concentrations in municipal water were also monitored. For this parameter, the concentrations are within the safe limits established by Brazilian legislation, that is, from 0.2 $mg.L^{-1}$ to 5 $mg.L^{-1}$ [10]. The concessionaire responsible for water distribution discloses the number of samples of residual chlorine, which it annually performed. In 2014, 185 analytical assays for determining the concentrations of this disinfectant agent were carried out montlhy[29]. Currently, the free residual chlorine content for the last monthly analysis was 1.2 $mg.L^{-1}$ [30].

The concentration of free residual chlorine is vital for inhibiting the proliferation of pathogens, which possibly still can be found in the water distribution network. However, it is also essential that the chlorinated water receives the addition of ammonia compounds[10]. Since chloramines (structures more stable than free residual chlorine) act as a secondary source of chlorine to other possible oxidants that arise in the network, they might cause the recontamination[4,9], the corrosions to the distribution system[5,6].

CONCLUSION

The concentrations of TTHM and the free residual chlorine found in drinking water of the city of Colombo, Paraná, during the evaluated period were within the standards determined by the Brazilian legislation.

Although some aspects that might interfere, the increase of the chlorination by products formation have not been analyzed or considered in this study. The obtained results are important to ensure the monitoring of water supply in the community so that they comply with required safety limits.

Little is discussed the importance and relevance of TTHM to the public health provided by the Brazilian government agencies, which stress the seriousness of the data and information to be brought to the public knowledge. Therefore, numerous water disinfection techniques could be developed, ensuring the product quality, and increasing the human and environmental health safety.

Given the high public health relevance of the topic, further research is needed to draw strong evidence about the risk of TTHM in drinking water. In comparing to other countries, the maximum level proposed for TTHM in Brazil is high and should be revised and better regulated.

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