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Characterization of trihalomethanes (THM) and their precursors patterns in a drinking water conveyance network in Tunisia

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ABSTRACT

The objective of this study is to characterize the spatial and temporal distribution of trihalomethanes (THMs) in a drinking water network in Tunisia and to propose treatment guidelines for improvement. The presence of THM was studied in the raw water treatment plant and during the transfer through the network. Monitoring was done over three 10-day periods, corresponding to three seasons, to search for THM species and their main precursors. The average concentration of THMs at the end of the water conveyance network during the three study periods was estimated at 95.5 μg/l. The results showed that at the end of the network, chloroform was the species predominantly formed during the warm season. Dichlorobromomethane was the compound found mostly during the cold and temperate seasons. Dibromochloromethane and bromoform only accounted for a small percentage of the total THMs during all three study periods. Better management of the treatment plant and the chlorination are proposed as keys to reduce THMs formation.

Keywords: Drinking water; Chlorination; Precursors; By-products; Trihalomethanes; Tunisia

1. Introduction

In drinking water distribution networks, water disinfection is generally done by applying doses of chlorine at the water sources (water treatment plants, drill boreholes, wells, etc.), allowing the entire network to be protected. However, this chlorination does not ensure steady levels of chlorine in extended networks. Free residual chlorine appears in high concentrations at the start of the network, accompanied by a bad taste and smell. In general, at the ends of the network, chlorine concentration has very low levels or sometimes none at all when this method of chlorination is used [1].

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Organic matter (OM) in water reacts with free residual chlorine (Cl_2) and causes the formation of chlorination by-products (CBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs) [2–6]. Several studies have shown that the formation of CBPs mainly depends on the dosage of Cl_2, water temperature (T), water pH, OM, bromide ion concentration (Br^-), and the amount of time that the free residual chlorine is in contact with the OM [7–16]. The water pH defines the characteristics of the chemical reactions causing the CBPs formation [17–20].

The World Health Organization (WHO) has set guidelines for maximum admissible limits of THMs concentration in drinking water [21]. These maximum admissible values are 200 μg/l for chloroform ($CHCl_3$), 100 μg/l for bromoform ($CHBr_3$), 60 μg/l for bromodichloromethane ($CHBrCl_2$), and 100 μg/l for dibromochloromethane ($CHBr_2Cl$). In addition, in order to take into account the simultaneous presence of these substances and their probably additive toxicity, it is considered that the sum of the ratios between the measured concentration of each contaminant and its guideline value must not exceed 1 [21]. Some countries have imposed standards concerning the presence of disinfection by-products in drinking water networks. Canadian [22] and European [23] regulations have set a maximum admissible concentration of 100 μg/l for all the THMs. American regulations [20] set this maximum value at 80 μg/l.

Several studies have pointed out that CBPs are suspected to have negative effects on consumer health [24–29]. Epidemiological studies have shown both an increase in the risk of cancer of the bladder and of the rectum linked to the consumption of affected drinking water and the existence of ties between chlorinated drinking water and incidences of colon cancer in individuals aged 60 and older [30–33]. Other authors have revealed a link between the mother's exposure to CBPs and the newborn's birth weight, delayed growth, malformations of the neural tube and a cleft lip, and palate [34,35]. A relatively strong relationship between several types of congenital anomalies and THMs is described in [34]. Other studies were able to show a correlation between exposure to THMs and miscarriage [36,37]. Epidemiological proof cited by [38], showed that the main groups which cause risks of cancer are THMs and HAAs. A link between consumption of water having a high level of CBPs and cancer of the colon, rectum, and bladder was noted in [39].

Most parts of urban towns in the north of Tunisia get their water from surface water, generally rich in OM when untreated. In order to comply with drinking water standards, raw water usually goes through stages of treatment: prechlorination, coagulation and flocculation, filtration followed by a final disinfection stage before reaching the network. To this day, there has been no study done in Tunisia evaluating the risk of the consumers' exposure to CBPs through tap water. Studies done on similar drinking water networks in terms of source, temperature, or nature of the network [2,40–45] have shown the formation of CBPs after treatment. Due to this lack of information, the present study was carried out with the objective of characterization of THMs patterns, as well as their precursors in a water conveyance network in Tunisia.

Even if it seems to be a classical study, the outputs of this research are fundamental for the drinking water producers to characterize the performances of their processes, to adapt the treatment, and to try to enhance the economic profitability of their industry. The findings of the present study will be also very useful for water quality control strategic planning of the Tunisian Ministry of Health. It is planned to install wireless network for drinking water quality in Tunisian main cities. The locations of control stations and water quality parameters need to be efficiently chosen. This study will bring detailed information and will help making the right decisions.

2. Materials and methods

The drinking water network studied here is made up of a raw water treatment plant and a water conveyance pipeline 28 km long, it has a 1,600 mm of diameter made of reinforced concrete and characterized by an average of water age or residence time of 25 h. The average flow is about 2 m^3/s. This pipeline provides drinking water to seven tanks along the way (R1, R2, R3, R4, R5, R6, and R7) as shown in Fig. 1. Each of the seven tanks supply water to consumers in the north of Tunisia city through looped pressurized networks.

At the water treatment plant, the raw water first undergoes a prechlorination step with a concentration between 1.5 and 2.0 mg/l of free chlorine. The second step is a physical and chemical treatment based on flocculation and coagulation. In the last step, water undergoes sand filtration in order to retain suspended matter. The clear water is thus disinfected by chlorine until it maintains a free residual chlorine level between 1.5 and 2.0 mg/l in the main tank of the water conveyance network (ST). This set point is

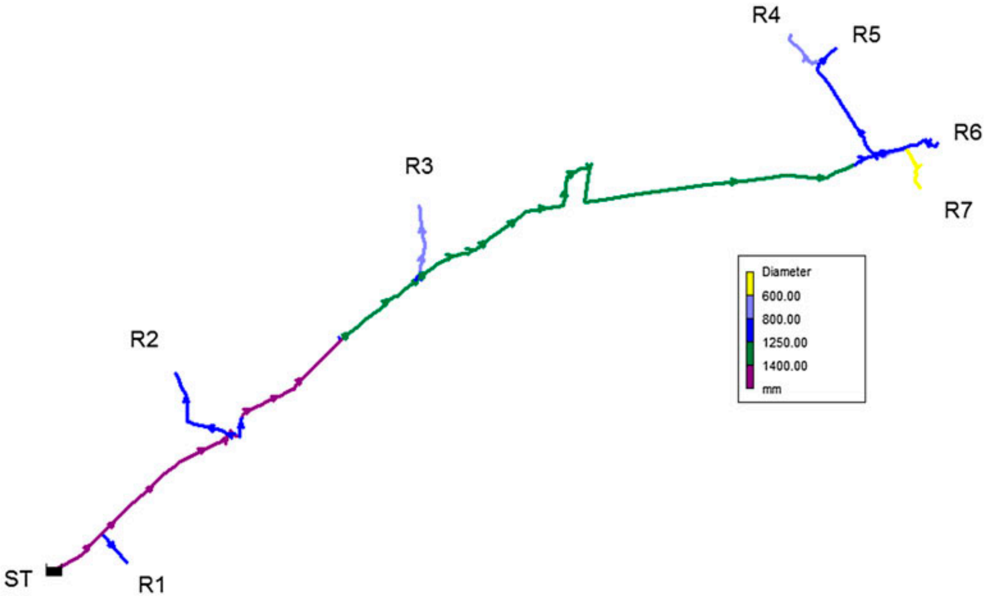

Fig. 1. Diagram of the studied water conveyance network.

calculated in order to ensure chlorination of the entire water conveyance network.

In order to characterize the temporal change in THMs and their precursors in the studied network, sampling was done during three 10-day periods in order to cover the three typical seasons of the region. The first group of samples (C1) was taken during the hot season (from 28 July to 8 August 2008); the second, C2, was taken during the cold season (from January 19 to 30 2009); and the third, C3, during the temperate season (from May 11 to 27 2009).

The following measurements were taken in order to analyze both THMs as well as their precursors: Cl_2, absorption of ultraviolet radiation with a wavelength of 254 nm (UV254), Br^-, water pH, and T. The water samples were taken from five monitoring points. The first represents the raw water that feeds into the water treatment plant. The second point is the raw water after prechlorination. The third sample is taken after the water is treated and the fourth sample is from the treated and chlorinated drinking water before it reaches the water conveyance network. The last sampling point is at the end of the water conveyance pipe, in the tank (R6), characterized by the largest contact time: water age (Fig. 1).

Given the evidence of a strong correlation between the total organic carbon and UV254 [46–48] and with the aim of proposing an approach which can be generalized, UV254 was considered as an indicator of the presence of OM and a precursor to THMs formation.

The Cl_2, T, and pH parameters were measured at the time of sampling. UV254, Br^-, and THMs were measured in the laboratory. Cl_2 was measured with a digital colorimeter using the titrimetric (DPD) method. Bromide ions were determined using the ion chromatography method. UV254 was measured with a visible spectrophotometer UV, with 1-cm path length, whereas THMs were determined by gas chromatography with electron capture detection (GC-ECD) following the 551.1 method [49]. The samples used to analyze UV254 were put into 125-ml plastic flasks which had been previously washed with nitric acid 10% in order to destroy any trace of OM, and rinsed with ultra pure water. A sodium sulfite solution (1.5 ml of a solution at 10%) was then added to the sample to suppress the excess of free chlorine and prevent reaction with the natural organic matter after the sample was taken. For THMs analysis, water samples were put into 250-ml glass bottles, which had been previously washed with a phosphate-free detergent then rinsed in deionized water and ultrapure water. The bottles were then dried for 30 min at 400˚C. Before sampling, a solution of sodium thiosulfate (1.5 ml of a solution at 10%) was added to the bottles in order to get rid of the free chlorine and prevent the formation of THMs in between sampling and laboratory analysis. In order to prevent air bubbles from forming, the bottles were completely filled during sampling as specified in the USEPA method 551.1 [49].

For the THMs analysis, water samples were heated to laboratory temperature. A volume of 60 ml was taken in 100 ml glass bottles, where 1 g of a mixture of sulfite of sodium and phosphate tampon solution was added. Each bottle was then agitated for 4 min and left

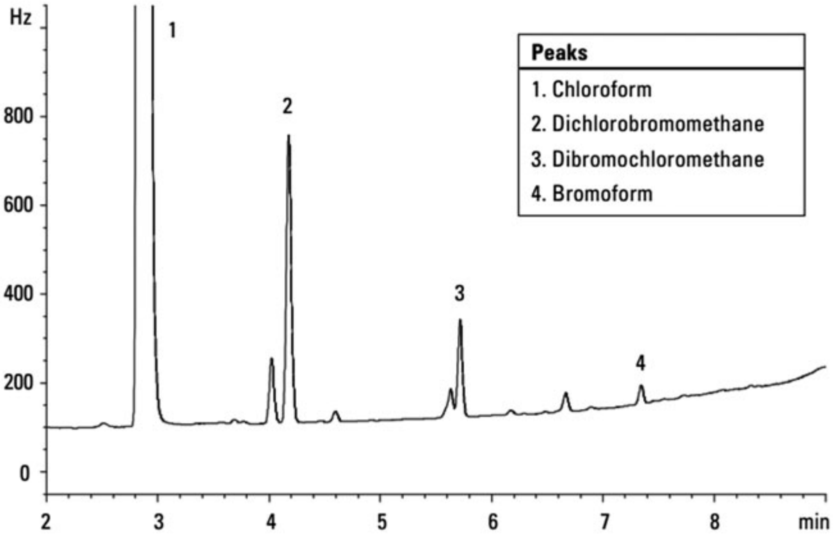

Fig. 2. Typical chromatogram of THMs species in water samples [50].

to rest for 2 min. pH verification was done on 10 ml/samples to ensure values between 4.5 and 5.5.

To encourage the coefficient of sharing of THMs between water and the solvent, 5 ml of pentane and 20 g of sulfate of sodium (Na_2SO_4) were added. The solution was then agitated for 4 min and left to rest for 2 min to facilitate the separation of the liquid and organic phases. The organic phase was transferred with a pipette pastor to an "Autosample" vial that was then sealed and preserved in the refrigerator until the THMs analysis.

Before THMs analysis, the GC-ECD was calibrated. For every THMs species, five known concentrations of standard solutions were injected in the GC-ECD. Standard solutions were prepared from a concentrated solution ($CHCl_3$: 5,000 µg/l, $CHBrCl_2$: 1,000 µg/l, $CHBr_2Cl$: 1,000 µg/l, $CHBr_3$: 1,000 µg/l). Results demonstrated that the determination coefficients (r^2) between injected and measured concentrations of the THMs species were 0.996, 0.999, 0.998, and 0.999 for $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$, respectively.

The THMs analysis was done by injecting 2 µl of the solution in the GC-ECD. The components were separated using a J&W, HP1 column: 0.25 mm DI × 30 m and 1.0 µm film thickness, fused silica capillary with chemically bonded methyl polysiloxane phase. Detection was done by electron capture (µECD). The vector gas was nitrogen and the injection technique was split/splitless. The vector gas flowed at a rate of 1.6 ml/min. The oven temperature of the GC-ECD was first maintained at 35°C for 22 min. In the second step, the temperature was raised to 145°C, at a rate of 10°C/min, and thus maintained for 2 min. The third step involved increasing the oven temperature to 225°C, at a rate of 20°C/min, and thus maintaining it for 15 min. In the last step, the temperature was increased to 260°C, at a rate of 10°C/min, and maintained for 30 min. The resulting chromatogram was then analyzed and quantified by ChemStation GC-ECD management software. Fig. 2 is a typical chromatogram of THMs species.

The quantification limit values of the analysis method of the THMs and their standard deviations were (µg/l) 0.31 ± 0.07, 0.21 ± 0.06, 0.30 ± 0.02, and 0.01 ± 0.005 for the $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$, respectively. In order to ascertain the reliability of the results obtained, the quality control procedures specified in norm 551.1 [49], Section 9.0 were respected.

In order to study the effect of chlorine and bromide ions on THMs speciation, correlations will be computed between the ratio "Cl_2/Br^-" and concentration of each THMs species measured during the experimental three study periods. We chose in this study to assess the strength of the linear relationship between the above variables using the Pearson correlation coefficient.

3. Results and discussion

The experimental methodology outlined in the previous paragraph made it possible to compile a database of the THMs in the studied drinking water network during the three seasons characteristic of the region. Here, the results of the spatial and temporal distribution of the THMs and their precursors in the water treatment plant and in the studied water conveyance network are presented.

3.1. Quality of the treated water and effectiveness of the treatment

At the water treatment plant, the precursors of THMs formation had a large temporal variability. Table 1 sums up their minimum, maximum, and average values as well as the standard deviation. The measurements were done on samples taken from four origins: raw water feeding the water treatment plant, prechlorinated, treated, and chlorinated water.

From these results, it was clear that, on one hand, the water temperature did not vary to any significant degree due to treatment. The temperature of the raw water varied between 10.9 and 27.0˚C, with an average of 19.3˚C. For the treated water, the minimum, maximum, and average values were 11.1, 26.5, and 18.8˚C, respectively. On the other hand, treatment of the raw water lowered pH and brought it closer to neutral. Table 1 clearly shows the effect of prechlorination on raw water treatment. In fact, the level of Cl_2 at the end of the treatment reached a maximum value of around 0.98 mg/l. The average concentration of Br^- measured during the three periods was estimated at 1.74 mg/l. During the three study periods, the average concentrations recorded were 1.81 (±0.05) mg/l, 1.66 (±0.10) mg/l, and 1.75 (±0.22) mg/l for periods C1, C2, and C3, respectively.

In terms of OM, the average concentration of UV254 at the inlet of the water treatment plant was much greater in the winter (C2) at 0.15 (±0.10) and in the spring (C3) at 0.18 (±0.06) than in the summer (C1) at 0.08 (±0.01). This can be explained by the increase in frequency and quantity of surface water inflow during the two periods C2 and C3. Water OM during these times is usually high. For all three sampling periods, the average decrease in Br^- concentration through treatment is estimated at 20.5% and that of UV254 is estimated at 63.2%. Non-negligible quantities of these two THMs precursors still remain in the treated water. In these conditions, the addition of chlorine could generate the formation of THMs, especially when the water temperature is favorable [50], which was the case during the C1 and C3 sampling periods. This hypothesis will be checked during the presentation and interpretation of the results of the THMs analyses.

According to first results, it is possible to conclude that water treatment process is favorable for THMs formation. Manager is advised to prospect possibilities of Br^- and UV254 concentrations reduction and to study the possibility to eliminate pre-chlorination phase.

3.2. Formation of THMs in the water treatment plant and in the water conveyance network

This paragraph presents the results from the three monitoring periods of the formation of the four main species of THMs: $CHCl_3$, $CHBr_3$, $CHCl_2Br$, and $CHClBr_2$. Fig. 3 shows the spatial variations in the average concentration of THMs measured at the five monitoring points.

The first important result to emphasize is that, the raw water already contained more than 20 μg/l of THMs. There were continuous increases in the concentration of THMs in the water treatment plant and the water conveyance network during the C2 and C3 sampling periods. During the C1 period, a large formation of THMs was observed during prechlorination, which was later reduced by the physical and chemical treatment.

The average concentrations of THMs at the end of the water conveyance network were 149.9 (±23.5) μg/l, 46.0 (±14.5) μg/l, and 90.6 (±41.9) μg/l for periods C1, C2, and C3, respectively. The maximum concentration of THMs, observed again at the end of the network, were 186.7, 73.8, and 210.0 μg/l for periods C1, C2, and C3, respectively. Similar values were found in the drinking water networks of 53 municipalities in Canada, fed by 50 different sources of raw water, which underwent 3 types of treatment [50], and in 3 drinking water networks in Quebec (Canada), fed by different surface waters which underwent different physical and chemical treatments [13,51].

Concentrations of THMs were 2.0–4.0 times higher in the summer (C1) than in the winter (C2). This confirms the results found in other studies: in three networks in Greece fed by three different sources (dam, drill hole, and well) after having undergone treatments [12]; in a distribution network in Canada characterized by considerable seasonal variation in temperature and surface water quality [40]; in three distribution drinking water networks in Quebec [13]; in a distribution system in Istanbul (Turkey) fed by a surface water treatment plant [42]; and in three reservoirs fed by the largest surface water treatment plants in Istanbul [44]. The highest concentrations of THMs were measured during the first period (C1) characterized by elevated temperatures. When T reached 25.0˚C, the concentration of THMs at the end of the network was 1.3–4.0 times higher than that measured at the water treatment plant. However, when T was less than 15.0˚C, THMs concentration did not exceed 100 μg/l. This result confirms that shown by [13,52].

During the "Chlorinated water—end of the network" phase, THMs continued to be formed despite

Table 1
Minimum, maximum and average values of the THMs precursors measured at the water treatment plant in raw, prechlorinated, treated and chlorinated water during study periods C1, C2, and C3

		Raw water						Prechlorinated water						Treated water						Chlorinated water					
		T	Cl_2	pH	Br^-	UV_{254}	THMs	*T*	Cl_2	pH	Br^-	UV_{254}	THMs	*T*	Cl_2	pH	Br^-	UV_{254}	THMs	*T*	Cl_2	pH	Br^-	UV_{254}	THMs
C1	Min	25.7	0.00	7.87	2.02	0.07	10.7	25.3	0.03	7.64	1.89	0.06	33.9	25.0	0.00	7.78	1.74	0.03	10.9	24.5	1.00	7.83	1.57	0.02	32.9
	Max	27.2	0.00	8.27	2.17	0.09	62.2	27.1	1.20	8.18	1.99	0.10	147.1	26.5	0.98	7.98	1.91	0.08	101.9	26.2	1.56	8.07	1.79	0.08	135.1
	Av	26.5	0.00	8.18	2.09	0.08	26.4	26.4	0.31	7.94	1.94	0.07	67.6	25.7	0.33	7.88	1.81	0.05	44.1	25.3	1.26	7.92	1.69	0.05	77.5
	σ	0.5	0.00	0.11	0.05	0.01	19.6	0.5	0.37	0.14	0.03	0.01	41.7	0.5	0.40	0.05	0.05	0.01	31.9	0.6	0.22	0.07	0.06	0.01	33.6
C2	Min	10.9	0.00	7.88	1.88	0.01	0.8	11.0	0.07	7.94	1.78	0.14	0.9	11.1	0.00	7.40	1.52	0.05	0.8	10.5	0.80	7.38	1.52	0.02	10.1
	Max	12.3	0.00	8.12	2.15	0.34	5.4	11.4	0.08	7.99	1.89	0.19	1.2	11.5	0.07	7.71	1.76	0.06	10.5	12.1	1.48	7.93	1.91	0.06	32.6
	Av	11.5	0.00	8.01	1.98	0.15	1.8	11.2	0.08	7.97	1.84	0.17	1.1	11.3	0.04	7.52	1.66	0.05	7.1	11.3	1.22	7.66	1.72	0.04	23.1
	σ	0.4	0.00	0.07	0.07	0.10	1.3	0.2	0.01	0.02	0.06	0.03	0.2	0.2	0.03	0.13	0.10	0.00	4.4	0.5	0.21	0.17	0.13	0.02	8.7
C3	Min	19.2	0.00	7.83	1.97	0.10	0.2	19.2	0.00	7.84	1.70	0.11	0.7	17.8	0.00	7.27	1.48	0.01	13.6	17.7	0.95	7.31	1.21	0.02	21.3
	Max	21.7	0.00	7.97	2.93	0.30	5.5	21.4	0.10	7.96	2.81	0.34	8.0	21.7	0.11	7.50	2.33	0.07	51.7	20.8	1.50	7.49	2.10	0.06	147.8
	Av	20.1	0.00	7.91	2.49	0.18	2.3	20.0	0.01	7.90	2.09	0.20	2.1	19.3	0.01	7.39	1.75	0.05	25.1	19.1	1.25	7.41	1.51	0.04	52.4
	σ	0.7	0.00	0.04	0.37	0.06	1.5	0.6	0.03	0.04	0.32	0.07	2.1	1.1	0.03	0.08	0.22	0.02	10.1	0.9	0.17	0.05	0.24	0.02	34.0

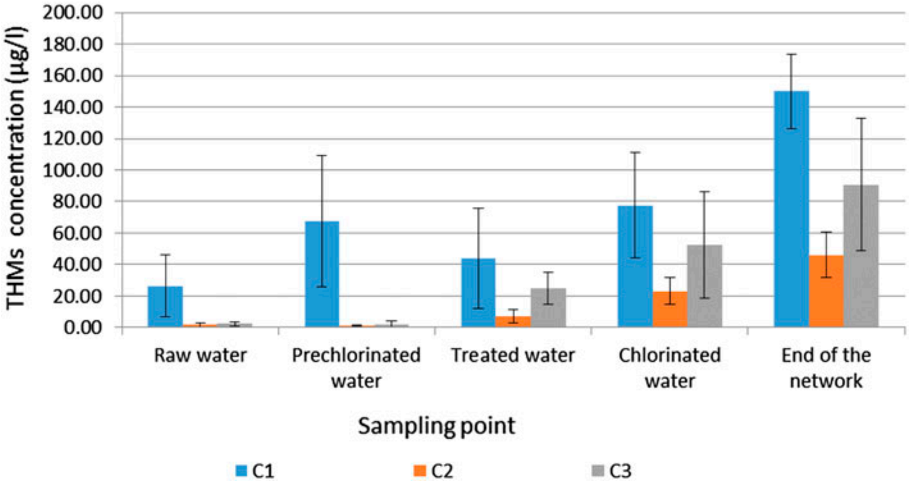

Fig. 3. Spatial evolution of the average concentration of THMs in the water treatment plant and in the water conveyance network during the sampling periods C1, C2, and C3.

the fact that no chlorine was injected. During the hot (C1) and cold (C2) periods, the average concentration of THMs almost doubled. Increases in the average values were 93 and 99%, respectively. The C3 period was characterized by a 73% increase in the average concentration of THMs.

As in the first phase, increases in THMs concentrations in the water conveyance network can be attributed to the presence of high concentrations of Cl_2 when the water penetrated the water conveyance network. In addition, the kinetics of the chemical reactions of THMs formation was controlled by both the presence of OM and Br^- as well as by T and contact time [43].

Interactions between THMs formation and changes in the concentrations of their precursors will now be examined. Fig. 4 shows that, for the three sampling periods, maximum values of Cl_2 were reached following chlorination. In fact, during the three periods, the level of Cl_2 measured after the final chlorination varied between 0.93 and 1.56 mg/l, with an average of about 1.26 mg/l. During the water's transit through the network, the level of Cl_2 decreased with the formation of THMs. At the end of the water conveyance network, the average level of Cl_2 was measured at 0.11 mg/l. The decrease in the average Cl_2 rate in the network was estimated at 91, 93, and 89% for periods C1, C2, and C3, respectively.

Analysis of the spatial distribution of Br^- showed a continuous decrease in concentration during the treatment and transfer phases, parallel to THMs formation (Fig. 5) and decrease in Cl_2 rates. During the three periods, the average went from 2.18 mg/l in the raw water to 1.33 mg/l at the end of the water conveyance network. From the "Treated water" phase, Br^- concentrations decreased with the formation of THMs. Br^- reduction rates from the "Raw water" phase to the end of the conveyance network were estimated at 34, 30, and 51% for periods C1, C2, and C3, respectively. The reduction rate of Br^- along the water conveyance network was around 19% for the respective sampling periods. [5,53] explained the Br^- decrease by the formation of brominated by-products.

A continuous decrease in the concentration of UV254 was also observed, parallel to THMs formation (Fig. 3) and to decreases in Cl_2 (Fig. 4) and Br^- (Fig. 5) concentrations.

The average concentration of UV254, during the three periods went from 0.135 (unit) in the raw water to 0.035 (unit) at the end of the water conveyance network. The UV254 reduction rates from the "Raw water" phase to the end of the conveyance network were estimated at 48, 81, and 80% for periods C1, C2, and C3, respectively. Along the water conveyance network, the reduction rates of UV254 were estimated at 16, 25, and 13% for the respective periods. The decrease in UV254 concentrations can be explained by the oxidation, by the Cl_2, of the OM in the treated water (Fig. 6).

It should be noted that both UV254 and Br^- were still present in the drinking water provided by the water conveyance network. This water was carried through the distribution networks where chlorine was added. Therefore, when the conditions were favorable, increased *T* and Cl_2 led to a possibility of much greater THMs levels [20,54].

These last results clearly show that THMs formation depends on Cl_2 levels and on concentrations of both Br^- and UV254. It would be interesting in this

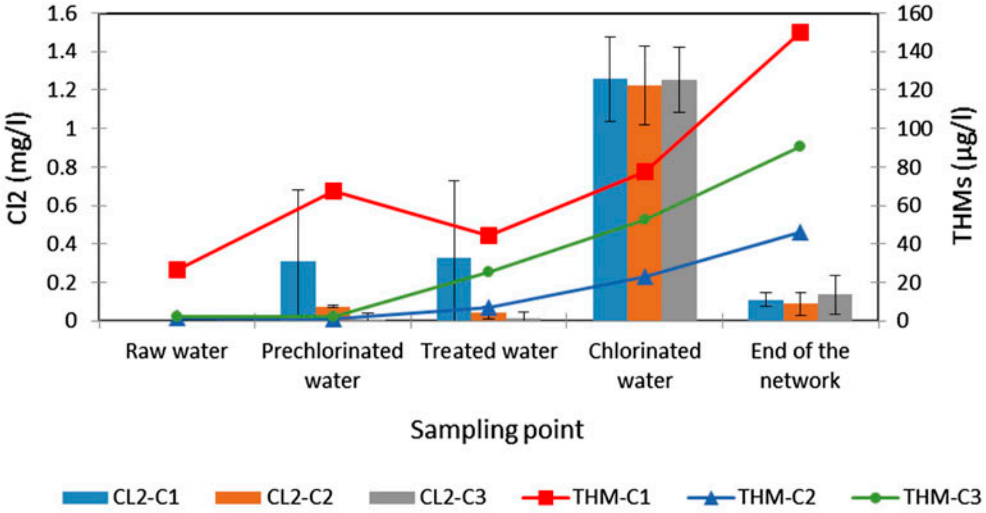

Fig. 4. Spatial change in the mean level and standard deviation of free residual chlorine (CL-C1, CL-C2, and CL-C3) in the water treatment plant and in the water conveyance network during the three sampling periods C1, C2, and C3.

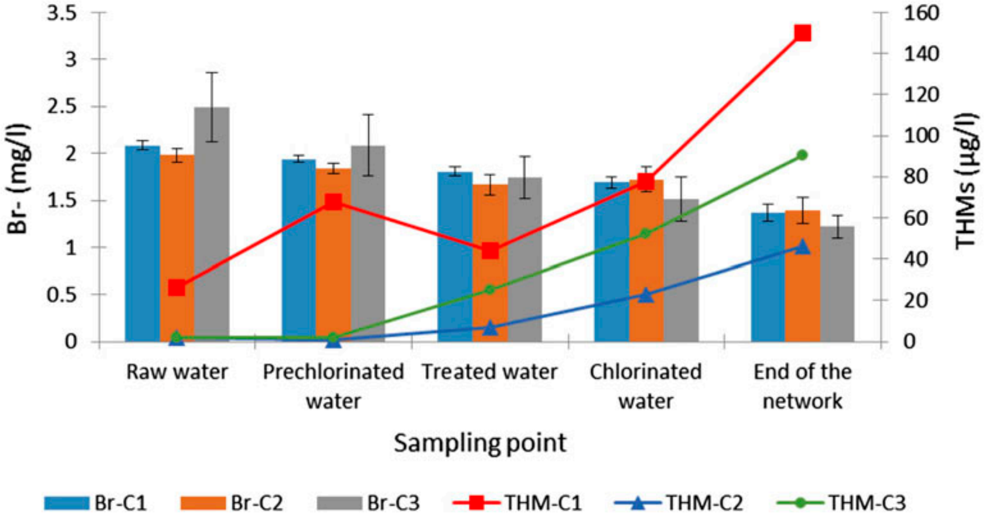

Fig. 5. Spatial evolution of the mean concentration and standard deviation of Br^- ions (Br-C1, Br-C2, and Br-C3) in the water treatment plant and in the water conveyance network during periods C1, C2, and C3.

step to evaluate the general contribution of each precursor in forming THMs and, more specifically, in forming its species. This phase provides a research perspective in order to have better control over THMs formation in drinking water networks.

The formation of THMs species in the studied system essentially depends on the season and the place within the network. Fig. 7 presents the spatial and temporal distribution of these compounds during the three sampling periods. $CHCl_3$ was the compound most often found during period C1, characterized by water high in *T* and UV254. This result was noted at the three monitoring points: in raw water, in chlorinated water, and at the end of the network. However, $CHBrCl_2$ was the compound most often found during periods C2 and C3 both in chlorinated water and at the end of the network.

The presence of chloroform in raw water can be attributed to pollution coming from diffuse focal points, such as industrial discharges, urban water, and accidental spills as these compounds may be present in many products and processes (i.e. paints, fuels, petroleum products, raw materials, solvents, etc.) [55]. This hypothesis is supported by the large size of the

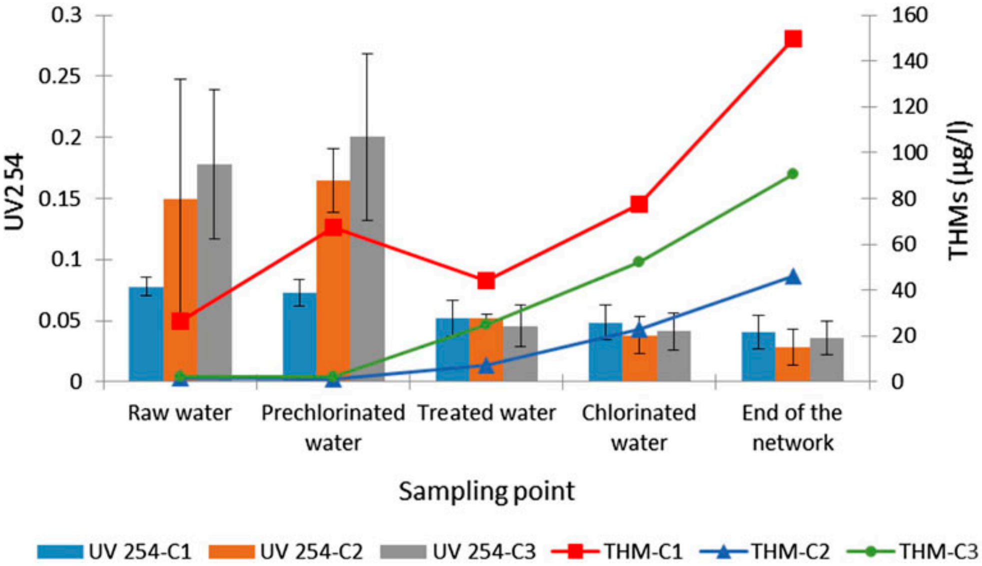

Fig. 6. Spatial evolution of mean and standard deviation of UV254 absorbance (UV254-C1, UV254-C2, and UV254-C3) in the water treatment plant and in the network during periods C1, C2, and C3.

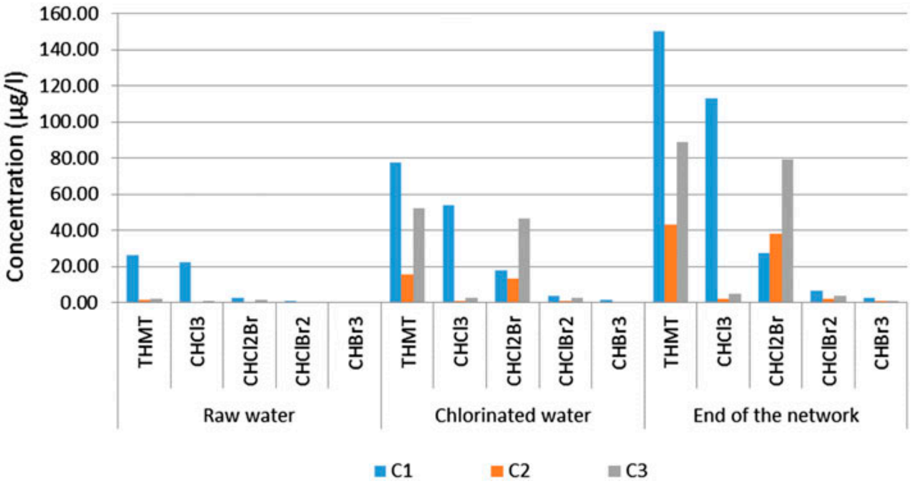

Fig. 7. Distribution of the average concentrations of THMs species during the three measurement periods along the three monitoring points.

river basin (transboundary) in which the used surface water is harvested, and therefore the height pollution probability.

Fig. 7 shows that, during water treatment and chlorination, there was a large formation of $CHCl_3$ during sampling period C1. The average $CHCl_3$ concentration was about 54.1 µg/l. During periods C2 and C3, measurements of $CHCl_3$ concentrations were found to be very low, with averages of 1.0 and 2.5 µg/l, respectively.

In the water conveyance network, the formation of $CHCl_3$ was also very high during sampling period C1. The average measurement at the end of the network was 113.2 µg/l, representing 75% of the THMs. The average concentrations of $CHCl_3$ at the end of the water conveyance network during sampling periods C2 and C3 were 2.2 and 4.6 µg/l, respectively. In terms of spatial evolution, the concentrations of $CHCl_3$ increased around 109, 122, and 83% for periods C1, C2, and C3, respectively, between the water treatment plant and the end of the network. The maximum concentration of $CHCl_3$ (140.9 μg/l) was measured during period C1. This value was found to be less than the maximum admissible limit of 200 μg/l set by the WHO directives.

$CHBrCl_2$ was the compound most often formed after the treatment phase and during sampling periods C2 and C3. The average concentrations at the end of the treatment were estimated at 13.3 and 46.7 μg/l for C2 and C3, respectively, representing 84 and 89% of the THMs formed during those respective periods. In sampling period C1, 18.5 μg/l of $CHBrCl_2$ was formed, representing only 23% of the THMs. In the water conveyance network, evolution of the average concentration of $CHBrCl_2$ was estimated at 52, 187, and 70% for sampling periods C1, C2, and C3, respectively. The maximum value measured of $CHBrCl_2$ was 188.1 μg/l taken during sampling period C3. This value is greater than the maximum admissible value of 60 μg/l set by the WHO directives.

The THMs speciation described in the Tunisian case study was also demonstrated in numerous recent studies of CBPs [56]. In order to understand the THMs speciation, their concentrations are transformed in "μmol/l" and reported to the total concentration of all species and the ratio "Cl_2/Br^-" is calculated. The Pearson correlation study demonstrates that there is a relationship between the ratio "Cl_2/Br^-" and the species $CHCL_2Br$ ($r = 0.72$), $CHClBr_2$ ($r = 0.61$), and $CHBr_3$ ($r = 0.63$). $CHCl_3$ presents the lowest correlation coefficient ($r = 0.15$).

Fig. 7 also shows that $CHBr_2Cl$ and $CHBr_3$ were formed during treatment and conveyance of the water in the studied system. However, they only made up a small percentage. The average concentration of $CHBr_2Cl$ measured at the end of treatment was around 3.9, 1.0, and 2.5 μg/l for sampling periods C1, C2, and C3, respectively. They represented 5, 6, and 5% of the THMs for the three periods, respectively. Although the concentrations at the end of the treatment were small, the evolution of the concentration of $CHBr_2Cl$ in the water conveyance network was significant. The change in average concentration was calculated at around 70, 114, and 45% for sampling periods C1, C2, and C3, respectively. The maximum value of $CHBr_2Cl$, measured during period C1, was 9.6 μg/l, less than the maximum admissible value of 100 μg/l set by the WHO directives [21].

At the end of treatment, the average concentration of $CHBr_3$ was estimated at 1.4, 0.4, and 0.6 μg/l for the C1, C2, and C3 sampling periods, respectively, representing 2, 3, and 2% of the THMs for the same periods, respectively. During the conveyance phase, measurements showed that the increase in concentrations of this THMs species was around 84, 84, and 24% for study periods C1, C2, and C3, respectively. The average concentrations calculated at the end of the network for these same periods were 2.6, 0.8, and 0.8 μg/l, respectively. The maximum concentration of $CHBr_3$ in the network was 3.3 μg/l, measured during sampling period C1. This value is less than the maximum admissible value of 100 μg/l set by the WHO directives [21].

The lower $CHBr_2Cl$ and $CHBr_3$ concentrations observed over the three sampling periods were consistent with the literature findings. In [57], while Br^- and Cl_2 tested higher in concentration, $CHBr_3$ was found lower than the detection limit. In [58], $CHBrCl_2$ and $CHBr_2Cl$ were formed in lower concentrations while using higher Br^- and Cl_2 concentrations: 10.0 μM and 5.0 mg/l, respectively. In the latter study, an increase in $CHBr_3$ formation was obtained with Br^- and Cl_2 concentration values up to 50.0 μM and 12.0 mg/l. The major species of THMs formed during water chlorination was chloroform (more than 70% of total THMs).

In order to better understand THMs speciation due to chlorination, additional work is required to study the effect of water pH and temperature and other precursor's concentrations, bromide and UV254 in particular. This is a research perspective that can highly improve drinking water treatment process.

From the presented results, it is possible to underline that surface water characteristics, the treatment process, and the chlorination approach used by the manager of the drinking water system were favorable circumstances for THMs formation. The drown schematic will be certainly more critical if chlorination booster stations will be used to control free chlorine rate in storage tanks supplying final consumers, what is really done by the network manager.

Results show clearly that the treatment process is not efficient and need to be revised in order to improve drinking water quality, by reducing THMs precursors in particular. In order to protect the consumer's health against the possible effects of THMs, manager need to revise the treatment process. As practical recommendation, it is urgent to eliminate the prechlorination of raw water before reducing the amount of OM and bromide ions. In addition, in order to reduce THMs formation, treatment process before chlorination need to be improved to reduce more OM and bromide ions. Final chlorination of treated water has to be optimized to reduce the used chlorine mass while ensuring the chlorination of the hole network.

Based on the presented results, and seen the importance of the studied supply system, Tunisian

Ministry of Health designed and installed an on line wireless control system for drinking water quality in Tunis City. The new system is now used to control THMs precursors and to forecast THMs concentrations mainly on the exit of the treatment plant, using regression models.

4. Conclusion

This analytic study highlighted the presence of a family of CBPs in a drinking water conveyance network in Tunisia: trihalomethanes (THMs). The average concentration of THMs measured at the end of the water conveyance network was estimated at 95.5 μg/l, less than the maximum admissible value according to the WHO directives. This study showed that the formation of THMs is always accompanied by decreases in Cl_2 levels and in concentrations of OM and Br^- ions. The species of THMs predominantly found in treated and distributed drinking water were $CHCl_3$ and $CHBrCl_2$.

Results showed that the distribution of THMs species mainly depends on the presence of precursors and water temperature. During the hot season, $CHCl_3$ was the most predominantly formed at the end of the water conveyance network and represented about 75% of the THMs. The other species were formed in much smaller percentages. The maximum value of the concentration of $CHCl_3$ was recorded during the hot season and reached 140.9 μg/l. During the cold and temperate seasons, $CHBrCl_2$ was predominant at the end of the water conveyance network, representing 88 and 90% of the THMs for the two seasons, respectively. The maximum concentration of $CHBrCl_2$ was measured during the temperate season and reached 79.5 μg/l. $CHBr_2Cl$ was formed in small amounts in all three seasons and represented an average of 4% of the THMs. Its maximum concentration (6.68 μg/l) was measured during the hot season. $CHBr_3$ was the least-predominant species in the drinking water network studied. It represented less than 2% of the THMs on average, with a maximum concentration (2.6 μg/l) measured during the hot season. The THMs species distribution was explained by the ratio Cl_2/Br^-.

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