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ORIGINAL ARTICLE

Formation of disinfection by-products within the drinking water production system and distribution network of a real case study

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Abstract

This work presents a collaboration between the so-called Gasset Service Association (responsible for providing drinking water to 100,000 inhabitants from a surface water reservoir) and researchers from the University of Castilla-La Mancha (Spain). The main aim of this work was providing a comprehensive characterization of the formation and removal of disinfection by-products in a real drinking water treatment plant (DWTP) and water distribution network. According to the results obtained, it can be stated that bromate is formed on the pre-oxidation stage and it is not eliminated throughout the DWTP; meanwhile, total organic carbon is partially removed on the clarification process. Moreover, it demonstrates the key role of the residence time and the type of water storage throughout the distribution network (either in pipes or in tanks) due to the combined effect of, at least, four overlapped mechanisms: THMs chemical generation, air stripping, hydrolysis and biological removal. This comprehensive view of the drinking water production and distribution network represents an excellent framework for allowing the improvement in the drinking water quality for a very common water production case study: a medium-size city fed by a surface water source.

Keywords Drinking water production · Disinfection by-products · Trihalomethanes · Bromate · Real case study

Introduction

Droughts and overpopulation have increased the value of high-quality water resources, converting a common action as opening the tap to obtain quality water into a difficult task in many parts of the world (Water 2017). Also, legal regulations have become more restrictive due to a better knowledge of the effect of a wider spectra of contaminants on human health (Tröger et al. 2021). In Spain, drinking water regulation is established in Royal Decree 140/2003. For all that, water purification processes are becoming more exhaustive in recent years and their different stages must be optimized to obtain a greater volume and a higher quality of drinking water, turning them more versatile and effective (Qiu et al. 2021).

Water pollutants can be divided into three different groups: physical (taste, color, suspended solids, temperature, etc.), chemical (nitrates, bromates, trihalomethanes, etc.) and biological (bacteria, virus, protozoa, etc.) (Srivastav et al. 2020). They have a great impact in water quality and must be analyzed frequently. Some of these contaminants may be problematic for the purification process if they are in high concentration. The presence of higher or lower concentration of contaminants depends mainly on raw water (surface or ground water) and on the treatment scheme of the drinking water treatment facility. In drinking water treatment facilities, disinfection stage is without doubt the most important basic operation as it is compulsory to guarantee that tap water is secure (Isidro et al. 2018). Chlorine derivatives (mainly chlorine gas or hypochlorite or, in less extent, chloramines or chlorine dioxide) are the chemicals most commonly used to disinfect a water effluent due to their effectiveness in disinfection and its persistence (Degrémont 2014).

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Due to the use of these disinfectants and to the presence of bromide ions in surface water bodies, trihalomethanes (THMs) are one of the group of disinfection by-products whose presence causes a major concern regarding the quality of tap water (Ding et al. 2019). Chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) are the four trihalomethanes that could be produced in drinking water due to disinfection procedures (use of chlorine) and the presence of bromide in water sources. Some studies have established a relation between the exposure to these disinfection by-products with adverse reproductive outcomes and cancers (Shi et al. 2020). For this, it is a crucial task to control the concentration of THMs in drinking water, being the maximum concentration allowed in Spain 100 $\mu g\ L^{-1}$ for the sum of these four trihalomethanes.

As previously stated, bromide (Br^-) is an ion commonly present in natural water bodies (Watson et al. 2012). Bromide can be oxidized by disinfectants (O_3, Cl_2, NaClO) and may react with organic matter, increasing the concentration of brominated THMs (Soyluoglu et al. 2020), which are more cytotoxic and genotoxic than the chlorinated ones (Plewa et al. 2004). Furthermore, bromate (BrO_3^-) formation could become a problem if bromide concentration in raw water is significant (above 50 $\mu g\ L^{-1}$) and ozonation is used in the purification process (Jahan et al. 2021). The formation of bromate, which maximum allowed concentration for Spanish regulation is 10 $\mu g\ L^{-1}$, is influenced by natural organic matter concentration, pH, temperature and competing inorganics in raw water (Yang et al. 2019).

There are few studies which have conducted such a comprehensive analysis of the drinking water supply and purification process of a drinking water treatment plant (DWTP). The existing literature is mainly focused on specific topics, as it is the case of looking for a model to predict THMs formation (Lin et al. 2018; Godo-Pla et al. 2021), THMs elimination applying different techniques (Zainudin et al. 2018) or evaluating the kinetics of different by-products formation in natural water (Nikolaou et al. 2004).

Based on this background, the main aim of this study was providing a comprehensive view of the evolution of trihalomethanes, bromide, TOC and bromate under real conditions within the production and distribution of drinking water in a very common case study: a medium-size city fed by surface water. The study is focused on the DWTP and distribution network of the Gasset Service Association (GSA) that provides drinking water of high quality to around 100,000 inhabitants of nine surrounding towns located 200 km at the south of Madrid, the capital city of Spain. A deep examination of the different stages of the purification process and the water network was performed. Based on this, kinetics tests were proposed in order to present a simple model for the formation and removal of disinfection by-products. The results presented here can be the base for any further action that aims to improve the quality of the drinking water produced in DWTP of similar characteristics.

Materials and methods

All experiments were performed between April and June 2021. All water samples were taken from the GSA purification process stages or distribution network. No synthetic solutions were employed for any experiment. For ease of understanding, the list of dates on which the sample measurements were taken is summarized in Table S1. For the historical record of THMs ("Purification process and water supply system characterization" section, Fig. 5), 92 samples taken during the year 2020 (from February to December) from the different points of the drinking water distribution network were considered: 6 for DWTP, 9 and 7 for Town 1 (Locations 1 and 2, respectively), 17 for Town 2, 7 for Town 3, 7 for Town 4, 12 for Town 6, 9 for Town 7, 10 for Town 8 and 8 for Town 9. All samples were measured in less than a week since collected by the GSA analytical staff, and THMs samples were measured before 48 h. These installations are prepared to make all types of analysis of drinking water established by legislation and are recognized with ISO 9001:2015 quality certification and compulsory authorization from the Department of Health of the Castilla-La Mancha Government for making sanitary analysis to substances connected with environmental and alimentary health as established in Royal Decree 43/2003. All methods of analysis are validated in compliance with the criteria of accuracy, precision and uncertainty indicated in RD 902/2018, so the quality of the equipment results can be assured.

Sodium hypochlorite (NaClO) was used to maintain the free chlorine concentration between 0 and 0.4 $mg\ L^{-1}$ for the kinetics experiments. Free chlorine was measured with a kit based on a colorimetric method. A packet of N-N′-diethyl-p-phenylenediamine (DPD) was added to 10 mL of water sample and was analyzed on site quickly based on the fast coloring when the reactive is added.

Bromide was measured with the ion chromatograph DIONEX ICS-1000. Five milliliters of each sample was introduced in the automatic sampler without any previous treatment step. The same ion chromatograph was used for bromate determination. In this case, samples must be filtered (Filters OnGuard II Ag/H 2.5 mL c/12 from THERMO DIONEX were used) initially in order to eliminate chloride, which cause interference for the bromate ion measure. It is recommended to add ethylenediamine for immediate ozone elimination and avoid any further bromate generation. The detection limit of the method for bromates is 3 µg L^{-1}, and the uncertainty in the measurement is 12%.

TOC was analyzed with an Analytik Jena 2100S TOC analyzer without any further pre-treatment (detection limit is 1.5 mg L^{-1} and its uncertainty is 12.4%). Lastly, THMs were measured by gas chromatography and mass spectrometry detection (THMs extraction was achieved along the headspace) with an Agilent 8860 GC System. THMs extraction was performed through the headspace. Samples were collected in 125-mL amber bottles with 0.5 mL of sodium thiosulfate (3%). Adding this reactive helps to neutralize the free chlorine which remains in the sample, stopping subsequent THMs generation. Ten milliliters of homogenized sample with 100 µL of methanol and 100 µL of internal standard was stored in 20-mL vials for its analysis. The detection limit of the method for THMs measurement is 5 µg L^{-1}. Uncertainty in the measurements for chloroform and dibromochloromethane is 17.5%, while that for bromoform and bromodichloromethane is 17.4%.

For the characterization of the purification system ("Purification process and water supply system characterization" section), concentration of bromides, bromates, TOC and THMs was measured at different stages of the purification process: (A) raw water, (B) ozonation, (C) ozonation + $KMnO_4$, (D) after clarifiers and (E) after granular activated carbons (GAC). All samples were taken when ozone was used at pre-treatment and NaClO for post-chlorination.

Additionally, a test was carried out using chlorine as tracer along the water supply system for residence time estimation. Although chlorine is not an ideal tracer (because it is not inert), it is precise enough to obtain an estimation of the approximate residence times of the different water delivery points along the distribution network. To do this test, chlorine dose was increased at ST1 and ST2 water tanks re-chlorination (to get a free chlorine concentration close to 1 ppm at this point, the maximum legal threshold), while the remaining re-chlorinations (closer to towns) at different points of the water network were stopped. The test was carried out for 48 h, taking samples of free chlorine during the next hours in different target places within the distribution network. Chlorine concentration was expected to decrease initially (re-chlorinations stopped close to towns) and increased afterward (when water with a higher free chlorine concentration arrives from ST1 and ST2), allowing to calculate an estimated residence time.

Kinetics experiments consist of storing tap water at 2-L opened beakers and adding a sodium hypochlorite solution to maintain free chlorine concentration between 0 and 0.4 mg L^{-1} in order to simulate the free chlorine conditions along the water supply system. When it was observed that the concentration fell, a dose of this sodium hypochlorite solution was added to increase it near to 0.4 mg L^{-1}. Tests were performed under controlled conditions at 20, 25 and 30 °C. These are typical water temperatures on spring and summer seasons when THMs concentration is higher along the water network. Water was stored within 72 h, and samples of disinfection by-products were taken at increasing sampling times.

Drinking water treatment plant and water supply system description

Drinking water treatment plant description

Before presenting the results obtained in the present work, it is important to describe the process that takes place in the DWTP and the water supply system of the GSA to tackle the objective of THMs concentration reduction and process improvement.

A simplified scheme of the DWTP is represented in Fig. 1. The sludge treatment line has been omitted due to its null importance for the study.

As shown in Fig. 1, approximately 70–80% of raw water comes into a pre-oxidation stage that is performed by the addition of ozone or active chlorine (depending on the season of the year). This chemical oxidation process is commonly used for organic matter removal and microorganisms' inactivation. Ozonation could be used to reduce the addition of active chlorine throughout the treatment process and thus controlling THMs formation along the water supply system (Liu et al. 2021). For this reason, it is applied in hotter seasons when it is more common to register higher concentration values of these compounds. However, it also generates bromate in the presence of bromide ions (Srivastav et al. 2020), so its addition should be carefully controlled in order not to exceed the very restrictive parametric value (10 µg L^{-1}). The rest 20–30% of raw water enters the treatment without being submitted to the pre-oxidation stage.

After the pre-treatment stage, the purification process divides into two different lanes. The one above in Fig. 1 is called 'old lane,' while the one below is called 'new lane.' As it can be observed, potassium permanganate ($KMnO_4$) is mixed with the entire water flow in the old lane. After the $KMnO_4$ addition, water divides into three different clarifiers: One of them is a Densadeg type (DSDG) and the two remaining clarifiers are Accelator type (D2 and D1). The Densadeg clarifiers use external sludge recirculation and combine the principle of lamellar settling with an integrated thickener, while the Accelator clarifiers employ the principle of internal slurry recirculation to accelerate the dense particle growth. Regarding the new lane, $KMnO_4$ is mixed with all the water flow, but then, water divides into two different clarifiers, both lamellar type. In both lines, aluminum sulfate ($Al_2(SO_4)_3$) is applied as a coagulant and starch is applied as a flocculant prior to the decanters stage.

After the coagulation–flocculation and settling process, water goes to the filtration stage. On the one hand, 11 GAC filters are used in the old lane for this purpose. On the other hand, six sand filters and four GAC filters are employed in

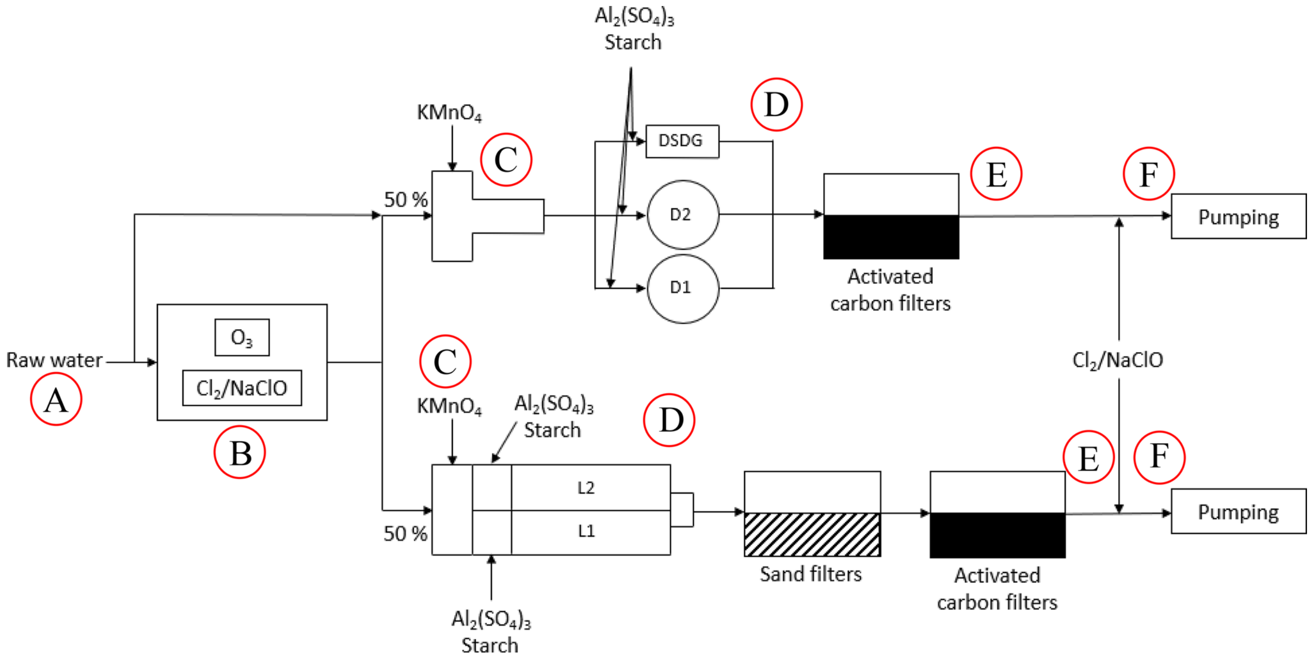


Fig. 1 Drinking water treatment plant purification processes and reactive addition. DSDG, D2, D1, L2 and L1 are three different types of clarifiers. 'Old lane' is represented above and 'New lane' is represented below

the new lane. As it is well known, GAC filters remove dissolve organic matter, thus reducing the concentration of this precursor for the formation of THMs (Gibert et al. 2013).

The last step in water purification is the post-chlorination for both lanes. It is usually used Cl_2 gas as reactive, but it is also used NaClO for this purpose. Finally, the treated water is pumped into two water tanks located near the DWTP, called storage tank 1 (ST1) and storage tank 2 (ST2), with capacities of 27,500 m^3 and 18,000 m^3, respectively. From there, water is supplied to all the towns that take part in the GSA with a total population of approximately 100,000 inhabitants: Towns 1–9.

Water supply system description

There are several studies that link higher THMs concentration at the point of use compared to the water obtained at the end of the purification process (Toroz and Uyak 2005). This can be explained because of the existence of THMs precursors such as chlorine, organic matter and bromine reactive species combined to the presence of biofilm along the pipe distribution system (Abokifa et al. 2016). Therefore, THMs concentration behavior at the point of use at the towns of the GSA must be included in this study to have a comprehensive view of the complete production and distribution scheme. Figure 2 represents the pipe distribution system from the water source to the points of consumption. Pressure reducing valves, pumping stations and water tanks are included too.

Surface water from the reservoir flows to the DWTP where the purification process takes place. Then, the produced drinking water is stored at ST1 and ST2, as previously explained, from where it is supplied to the different places of the GSA. There are other smaller storage tanks near certain towns: two at Town 9 (300 and 250 m^3), two at Town 8 (300 and 200 m^3) and one at Town 6 (500 m^3). Chlorine addition is the last step in the purification process of the DWTP as explained before, but this reactive is also added in further re-chlorinations near to every town, either in water tanks or directly in pipes.

Results and discussion

Purification process and water supply system characterization

Initially, a chemical characterization of the different streams involved in the DWTP is needed to understand the set of reactions that are taking place along the purification process and when they are happening. Investigation is focused on the generation and destruction of different compounds that contribute to the THMs formation, but also in other disinfection by-products formed along the process. Thus, bromide, total organic carbon, trihalomethanes and bromate concentration are selected as the most important parameters to characterize.

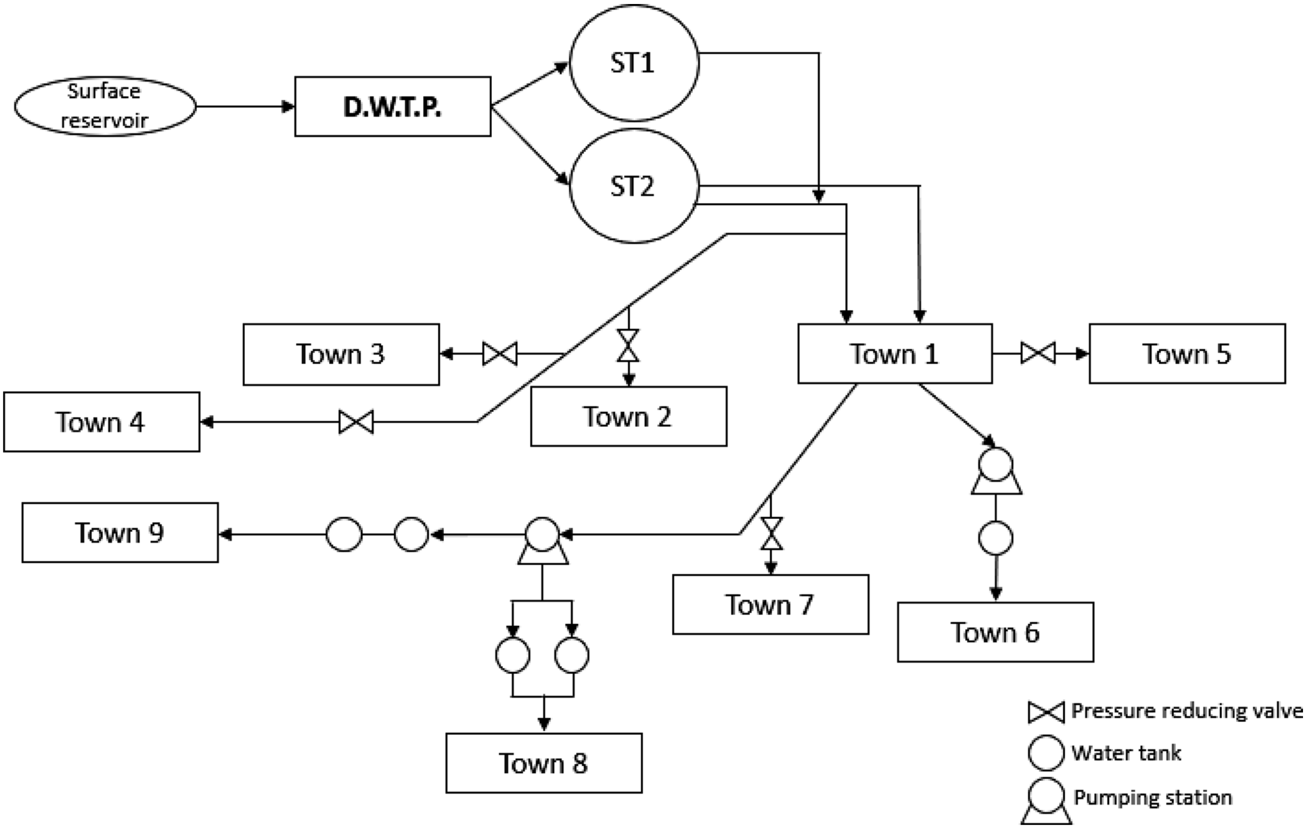


Fig. 2 GSA water supply system. Unscaled

Bromide and bromate

The evolution of both bromide and bromate concentration throughout the purification process is shown in Fig. 3.

As observed in Fig. 3a, bromide concentration along the purification process slightly decreases from its initial concentration (around 0.2 mg L^{-1}) after the ozonation process due to the formation of bromate, as it will be explained later.

Apart from this slight initial decrease, the variation observed in the concentration of bromide throughout the process can be considered negligible. This means that there is no

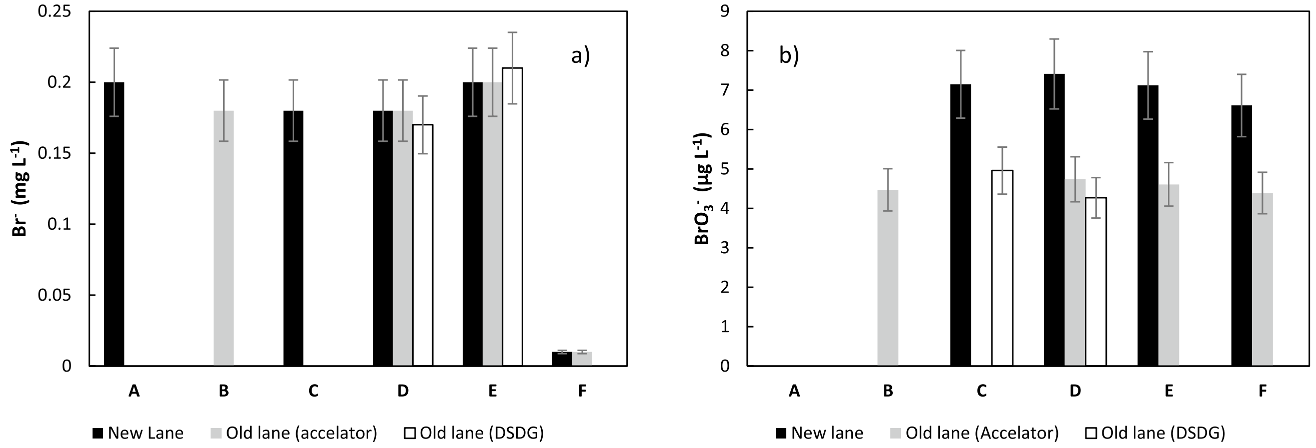


Fig. 3 **a** Bromide and **b** bromate concentration along the DWTP. A: Raw water; B: ozonation; C: ozonation + KMnO$_4$; D: after clarifiers; E: after granular activated carbon filters; F: before pumping. Letters correspond to those encircled in Fig. 1

process at the DWTP able to remove the dissolved bromide existing at the initial raw water. However, bromide concentration decreases suddenly close to 0 mg L^{-1} at the end of the plant when chlorine is added for the post-chlorination step and the treated water is ready to be pumped to ST1 and ST2 (F).

According to this result, active chlorine reacts quickly with bromide in line with studies performed before (Li et al. 2008). When chlorine is added to water that contains bromide, hypobromous acid and hypobromite are generated immediately following reactions (1–3) (Myllykangas 2004):

$$HClO + Br^- + H^+ \rightarrow 1/2Br_2 + H_2O + Cl^- \quad (1)$$

$$Br_2 + H_2O \rightarrow HBrO + H^+ + Br^- \quad (2)$$

$$HBrO \leftrightarrow BrO^- + H^+ \quad (3)$$

Hypobromous acid (HBrO) and hypobromite (BrO^-) react quickly with organic matter producing brominated products, such as trihalomethanes. To provide context, the halogen substitution for trihalomethanes formation is 25 times stronger for HBrO than for HClO (Chang et al. 2001).

Moreover, as shown in Fig. 3b, bromate appears immediately when ozonation process takes place at the pre-treatment stage. The mechanism of bromate formation by ozone is quite complex, but it can be summarized with three main reactions during the ozonation process (Reactions 4–6) (Yang et al. 2017):

$$Direct: Br^- \overset{O_3}{\rightarrow} HBrO/BrO^- \overset{O_3}{\rightarrow} BrO_2{}^- \leftrightarrow Br_2O_4 \rightarrow BrO_3{}^- \quad (4)$$

$$Direct - Indirect: Br^- \overset{O_3}{\rightarrow} HBrO/BrO^- \overset{\cdot OH}{\longrightarrow} BrO\cdot \rightarrow BrO_2{}^- \overset{O_3}{\rightarrow} BrO_2\cdot \leftrightarrow Br_2O_4 \rightarrow BrO_3{}^- \quad (5)$$

$$Indirect - Direct: Br^- \overset{\cdot OH}{\longrightarrow} \cdot Br \overset{O_3}{\rightarrow} BrO\cdot \rightarrow BrO_2{}^- \overset{O_3}{\rightarrow} BrO_2\cdot \leftrightarrow Br_2O_4 \rightarrow BrO_3{}^- \quad (6)$$

Due to physical restrictions related to the configuration of the plant, the sampling point was different in new and old lanes. In the former, both ozone and $KMnO_4$ were added; meanwhile, in the latter only ozone was added to raw water. As can be seen, this represents a big difference in bromate concentration: When only ozone is added (B), bromate concentration grows to 4.47 µg L^{-1}, while when $KMnO_4$ is added straight after ozone (C), BrO^{3-} concentration grows to 7.41 µg L^{-1}. This means that not only ozone generates bromate, but $KMnO_4$ does too. This oxidant increases bromate concentration yield by approximately 60%.

Apart from this, new lane keeps always greater bromate concentration than old lane (D, E, F). This is because part of flow from the old lane does not enter the ozonation stage and goes directly to the mixing chamber where $KMnO_4$ is added, decreasing BrO^{3-} concentration. An additional conclusion that can also be observed from Fig. 3b is that bromate is not eliminated at any stage of the purification process.

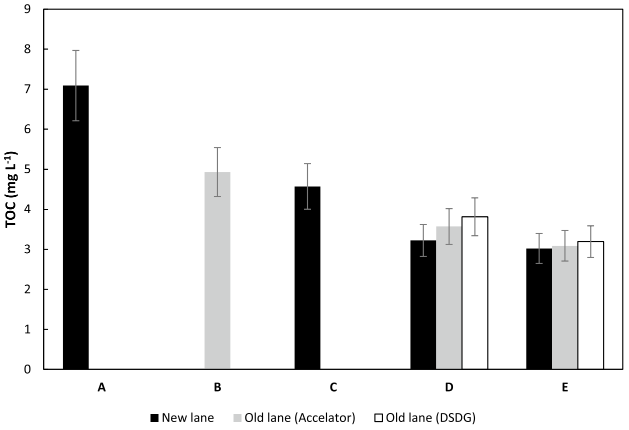


Fig. 4 Total organic carbon (TOC) concentration along the DWTP. Old lane is divided into two separate lanes depending on the type of clarifier. A: Raw water; B: ozonation; C: ozonation + $KMnO_4$; D: after clarifiers; E: after granular activated carbon filters

Total organic carbon

Following DWTP characterization, natural organic matter is another parameter studied due to its key role in THMs generation. THMs formation potential raises when TOC concentration is higher. Nevertheless, when TOC concentration is 4 mg L^{-1} or higher, the THMs formation potential does not change remarkably. If TOC concentration is less than 4 mg L^{-1}, THMs formation potential follows a first-order reaction, meaning that a higher TOC concentration will result in greater THMs concentration whether residual chlorine is left (Ramavandi et al. 2015).

The results of TOC concentration throughout the DWTP are shown in Fig. 4.

As observed in Fig. 4, TOC concentration is reduced in all treatment steps, passing from an initial concentration around 7 mg L^{-1} (the historical TOC concentration ranges from 5 to 9 mg L^{-1} depending on the natural water reservoir level) to a final value of 3 mg L^{-1}. Ozone and coagulation–flocculation in clarifiers are the processes with most remarkable impact on TOC elimination. Ozone reduces 30% TOC concentration present in raw water, while coagulation–flocculation reduces another 30% of the remaining TOC concentration in water ozonized with $KMnO_4$ added. The impact of coagulation on reducing the formation of disinfection by-products such as THMs has been highlighted in previous works (Ghernaout 2014; Sillanpää et al. 2018) which confirm the reduction in THMs concentration by decreasing natural organic matter with coagulation. Granular activated carbon filters perform a final reduction in TOC of 10% in the old lane and a 6% in the new lane (percentages calculated from clarifiers outlet water).

Trihalomethanes

Finally, THMs concentration was also monitored throughout the DWTP. New lane had a concentration of 4.92 μg L^{-1}, while old lane had a concentration of 7.21 and 2.26 for the Accelator and DSDG paths, respectively. Samples were taken after (B), (C) and (D) too, but THMs concentration was negligible at these points. These disinfection by-products only start appearing after granular activated carbon filters and its concentration was very low (2–7 μg L^{-1}), being even lower than the measurement error.

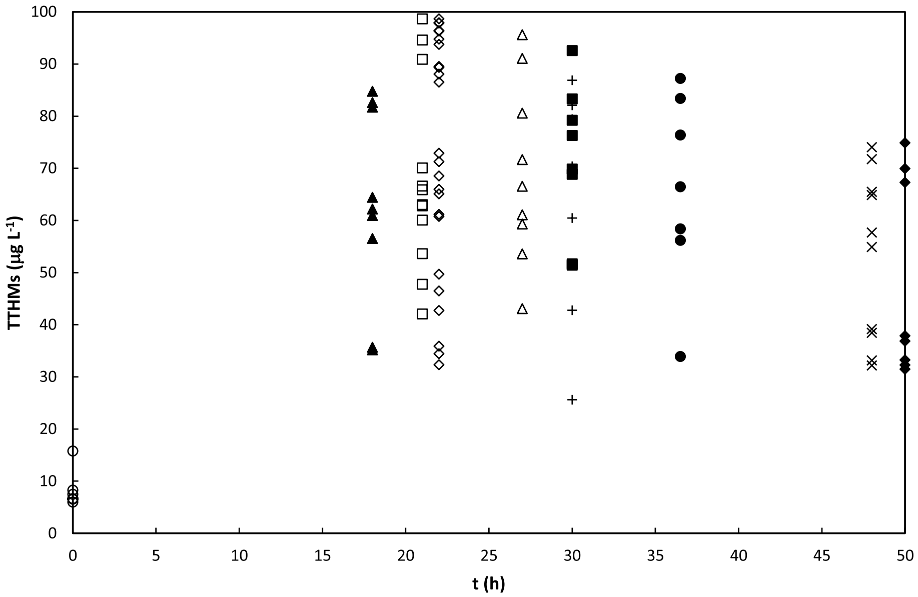
According to previous research, THMs do not present an instant generation and depending on the reaction conditions, its total formation can be completed between one hour or some days (Rawajfeh and Fayyad 2013). Thus, the short residence time along the DWTP (approximately 30 min) is the main reason for the low concentration of THMs measured in the treatment process. Nevertheless, the increase throughout the water supply system is expected to be greater due to a higher residence time in pipes and intermediate water tanks. According to this assumption, the residence time is a key variable for THMs formation, so this parameter was estimated throughout the distribution network.

Figure 5 shows the historical record of trihalomethanes concentration within year 2020 with respect to the estimated residence time. Due to the higher size of Town 1, the results are shown in two different locations. Data of the average concentration of THMs, standard deviation and distance to the DWTP are included in Table S2.

The results of Fig. 5 show a great dispersion of data that corresponds to the different seasons of the year, being TTHMs always the highest in the summer season due to the higher rate of THMs formation and to the higher average concentration of organic matter in the inlet of the DWTP. Moreover, it can be clearly observed that the record of THMs increases with residence time until a maximum concentration is reached for an estimated residence time of approximately 24 h. For this residence time, approximately 5% of the samples measured presented a value of THMs slightly lower but close to the legal limit of 100 μg L^{-1} (those measured in the worst scenario of summer season). For higher values of residence time, the concentration of THMs within the drinking water distribution network decreased. Specifically, for residence times higher than 48 h, all samples measured presented a concentration of total THMs lower than 75 μg L^{-1}, even in summer season.

Thus, these results confirm that THMs concentration increases within a certain time period and decreases afterward, giving the maximum concentration of these species for delivering points with intermediate residence times. This evolution can only be explained if there exists a competition between formation and destruction pathways for THMs. Bibliography about THMs development in water distribution

Fig. 5 Total trihalomethanes concentration (TTHMs) distribution of samples taken throughout year 2022 with respect to the estimated residence time. o DWTP; ▲ Town 1 (Location 1); ▄ Town 1 (Location 2); ◇ Town 2; ● Town 3; + Town 4; □ Town 6; △ Town 7; × Town 8; ◇ Town 9



systems is reduced and contradictory. Some studies ensure that THMs concentration grows always throughout the water distribution pipes (Abokifa et al. 2016), while some others found a reduction of this disinfection by-products at the end of the water network (Elshorbagy et al. 2000).

For this reason, it is important to propose further tests to shed light on the formation and destruction pathways of THMs in drinking water distribution networks. With this aim, the kinetics of THMs formation was accurately studied by performing tests of THMs generation under controlled conditions, the results of which are presented in the next section.

Kinetics experiments

Water was stored for 72 h at different temperatures to see the behavior of disinfection by-products in real water samples. The results of total THMs, free chlorine and speciation of THMs are shown in Fig. 6.

As shown in Fig. 6a, THMs concentration increases during the first 34 h but then starts to decrease till the last sample at 72 h for the three temperatures studied. This behavior corresponds to the evolution of THMs throughout the distribution network that has been previously commented, suggesting the coexistence of two (or more) overlapped processes: one of generation and at least one mechanism of destruction. Both kinetics (generation and destruction) are faster when temperature increases, as observed in Fig. 6a. The highest ($t = 24$–34 h) and the lowest ($t = 72$ h) THMs concentrations are reached with 30 °C, while, when temperature is 20 °C, both rise and decrease are considerably slower.

Regarding THMs speciation, brominated ones follow the pattern explained before (increase for the first 24–34 h and then decrease), while chlorinated ones differ from this and continue growing during the entire 72-h experiment (Fig. 6b). It seems that brominated species react and consume completely ending THMs formation within the first

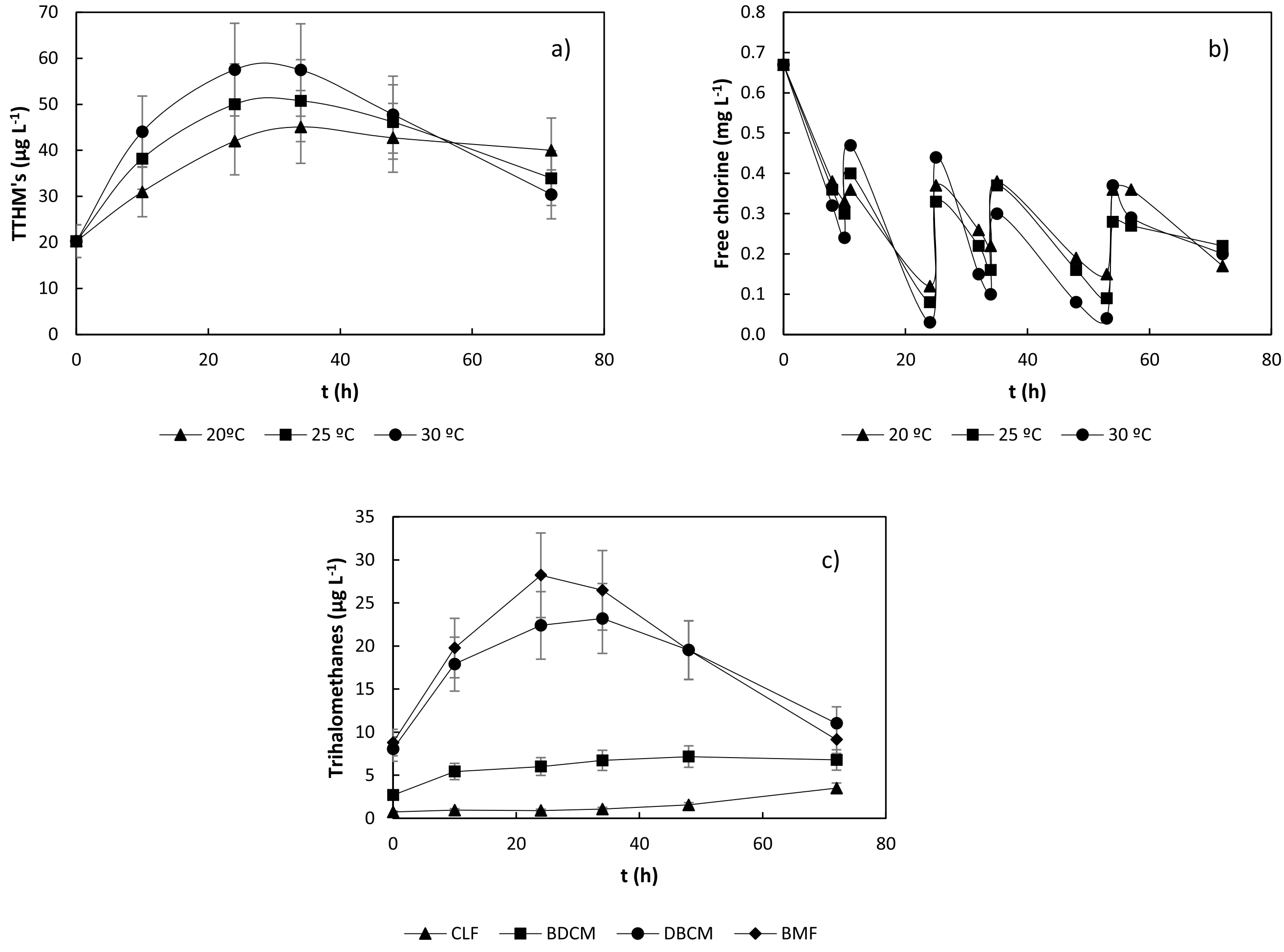


Fig. 6 **a** Total trihalomethanes evolution. **b** Free chlorine evolution. **c** Chloroform (CLF), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (BMF) evolution (30 °C). Samples taken for 0, 10, 24, 34, 48 and 72 h at 20, 25 and 30 °C. Water is stored in 2-L beakers at heaters

34 h, while if chlorine is added, chlorinated THMs concentration continuously increases.

According to the literature, air stripping could be an alternative way of THMs elimination, as some studies confirm THMs removal applying different types of aeration (Brooke and Collins 2011; Cecchetti et al. 2014; Mirzaei and Gorczyca 2020) based on THMs air stripping. Taking this into account, a simplified mass balance can be formulated, considering both the chemical generation and air stripping as the main mechanisms of THMs formation and elimination, respectively. First of all, the generation of THMs can be considered as a first-order chemical reaction with respect to the concentration of organic matter and total oxidants, according to Eq. (7):

$$V \cdot K \cdot [\mathrm{TOC}] \cdot [\mathrm{Ox}] = V \cdot K^{*} \cdot [\mathrm{Ox}] \tag{7}$$

where V is the total volume (L^{-1}), [TOC] and [Ox] are the TOC and oxidants (chlorinated and brominated active species), respectively, concentration ($\mathrm{mg\ L}^{-1}$) and K is the kinetic constant for THMs generation (h^{-1}). TOC concentration is several magnitude orders higher than the maximum concentration expected for THMs, so its concentration can be assumed constant and be included into a pseudo-first-order kinetics constant (K^{*}) (h^{-1}).

On the other hand, the elimination term can be formulated as an absorption expression (Eq. 8):

$$K_m \cdot A \cdot [\mathrm{THMs}] \tag{8}$$

where K_m is an air stripping constant ($\mathrm{L\ h}^{-1}\ \mathrm{m}^{-2}$) and interfacial area is represented with A (m^2) and THMs concentration with [THMs] ($\mathrm{mg\ L}^{-1}$).

Therefore, the model can be raised including the accumulation, generation and eliminations terms, as it is expressed in Eq. (9):

$$V \cdot \frac{\mathrm{d}[\mathrm{THMs}]}{\mathrm{d}t} = V \cdot K^{*} \cdot [Ox] - K_m \cdot A \cdot [\mathrm{THMs}] \tag{9}$$

If all terms of Eq. (9) are divided by the total volume of the system, Eq. 10 can be obtained, which gives the accumulation of THMs as a function of both chemical generation and air stripping rates:

$$\frac{\mathrm{d}[\mathrm{THMs}]}{\mathrm{d}t} = K^{*} \cdot [\mathrm{Ox}] - A/V \cdot K_m \cdot [\mathrm{THMs}] \tag{10}$$

According to Eq. (10), the air stripping rate depends mainly on the relation between interfacial area and volume (A/V), which is equal to the inverse of the height ($1/H$) if a constant area tank is considered. The higher this relation, the greater the rate of THMs air stripping. To prove this assumption, one additional kinetics test with tap water obtained just after the disinfection water treatment was carried out comparing two tanks (a test tube and a beaker) with very different A/V ratios (33.18 and 153.94 $\mathrm{cm}^2\ \mathrm{L}^{-1}$), but the same volume (1 L). The results are presented in Fig. 7.

The results match with the model previously presented, being THMs elimination higher when A/V relation increases, confirming the assumption of the key role of air stripping as a potential mechanism for THMs removal in the storage tanks. Thus, these results are in agreement with works that present aeration as a technology for THMs removal (Mirzaei and Gorczyca 2020). The main objective of aeration is to increase the interfacial area between water and air to increase A/V ratio, thus enhancing air stripping. Another important conclusion that can be obtained from these results is that the removal of THMs is expected to be much higher in water tanks than in pipes, where the contact area between air and water is expected to be null ($A/V=0$). Therefore, it is necessary to look for additional mechanisms to explain the THMs decrease observed along the pipelines.

Apart from air stripping, there is another chemical process found in bibliography which could also contributes to THMs elimination: hydrolysis (Zhang et al. 2015). THMs can hydrolyze in two different pathways: neutral and alkaline. In the neutral hydrolysis pathway, THMs react with a water molecule and form dihalomethanol. This molecule reacts quickly forming carbon monoxide and formic acid (Reactions 11–13), being the Reaction 11 the limiting step (Zhang et al. 2015).

$$\mathrm{CHX_3} + \mathrm{H_2O} \rightarrow \mathrm{CHX_2OH} + \mathrm{HX} \tag{11}$$

$$\mathrm{CHX_2OH} \rightarrow \mathrm{HCOX} + \mathrm{HX} \tag{12}$$

$$(x+y)\mathrm{HCOX} + y\mathrm{H_2O} \rightarrow x\mathrm{CO} + y\mathrm{HCOOH} + (x+y)\mathrm{HX} \tag{13}$$

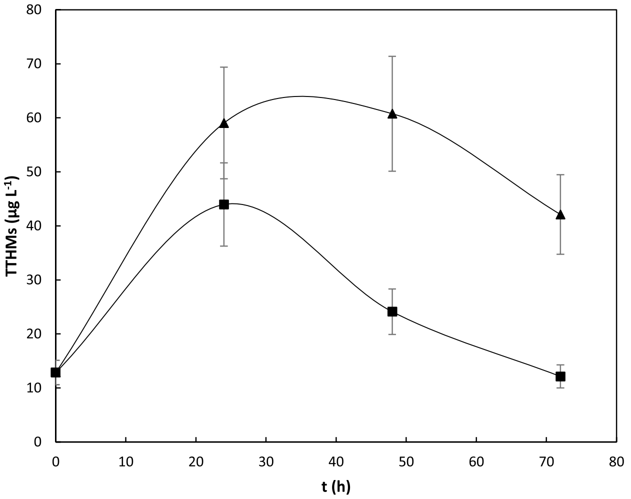


Fig. 7 Total trihalomethanes concentration for a beaker and a test tube with different A/V ratios (33.18 for test tube and 153.94 $\mathrm{cm}^2\ \mathrm{L}^{-1}$ for beaker). ▲ Test tube; ■ Beaker. Temperature 30 °C, volume 1 L

In the alkaline hydrolysis pathway, THMs react with hydroxide ion and forms a carbon trihalide anion and a carbon dihalide. This carbon dihalide quickly turns into carbon monoxide and formic acid (Reactions 14–16). The limiting step is reaction (15).

$$CHX_3 + OH^- \leftrightarrow CX_3^- + H_2O \tag{14}$$

$$CX_3^- \rightarrow CX_2 + X^- \tag{15}$$

$$(x+y)CX_2 + (2x+3y)OH^- \rightarrow \quad xCO + yHCOO^- + 2(x+y)X^- + (x+y)H_2O \tag{16}$$

Elshorbagy et al. (2000) found out that brominated THMs concentration decreased at the end of the water network in a portion of the Abu Dhabi water distribution system due to hydrolysis when subjected to dynamic conditions. Bromoform hydrolysis happens twice as fast as that for chloroform, due to the higher size of the bromine atoms compared to chlorine ones. This caused a higher polarization of carbon and bromine bonds, making it easier to divide (Shams El Din et al. 1998). These two studies match completely with the GSA water network behavior: There is a lower THMs concentration at the end of the water distribution system (Town 8 and Town 9), and brominated THMs are essentially the ones reduced (Table S2).

Based on these results, an additional experiment was carried out to check whether this chemical process is playing a relevant role in the system under study. To do this, water from laboratory tap was stored in different plastic containers entirely full and closed. This way, water was not in contact with air and interfacial area was 0, so air stripping process is expected to be null. Temperatures selected for the experiment were 30 and 80 °C. Although this latter temperature is much higher than that found in real conditions, it helped to speed up the process and confirm the role of hydrolysis, as this chemical process is supposed to be faster when temperature is higher (Zhang et al. 2015). The results are exposed in Fig. 8.

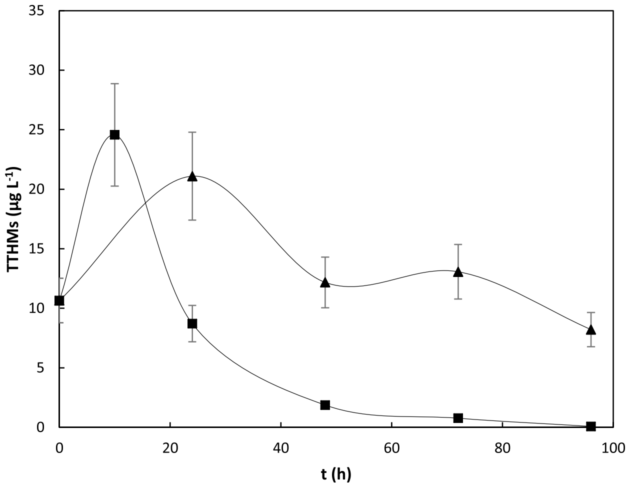


Fig. 8 Total trihalomethanes concentration for hydrolysis experiment. ▲ 30 °C; ■ 80 °C

As can be seen, initially THMs concentration grows because of the remaining disinfection by-products precursors (mainly organic matter and remaining free chlorine). When free chlorine reacts completely, generation kinetics stops and afterward hydrolysis reaction may continue and THMs concentration decreased significantly for 30 °C and totally for 80 °C. According to bibliography, this is the expected behavior for such a different temperature range (Zhang et al. 2015). Thereby, hydrolysis might be another pathway for THMs elimination throughout the water supply system apart from air stripping.

Finally, it is important to take also into account the role biofilm along the water distribution pipes in the THMs destruction mechanisms. Methylotrophic bacteria such as *Methylobacterium*, which is usually found in biofilm of water supply systems and was isolated in previous studies (Gallego et al. 2005), can be taking action in the removal of THMs. It was shown that this type of bacteria decreased almost the half of the initial concentration of THMs when residence time was 24 h. This may occur because the *Methylobacterium* used THMs as a source of energy and carbon for their own growth (Tsagkari and Sloan 2019). Thus, this may represent another influencing factor for the behavior of the concentration of THMs observed in this study. More in-depth studies would be needed to detect this type of bacteria and to confirm this additional removal pathway for THMs.

Conclusions

Key aspects for disinfection by-products accumulation within a real drinking water production system and distribution network have been studied through a collaboration between and academic institution (University of Castilla-La Mancha) and the water sector (Gasset Service Association). According to the results presented in this work, it can be concluded the key role that the transport and storage of drinking water played in the formation of THMs, due to the combination of generation reactions, air stripping, hydrolysis and biofilm (*v. g. Methylobacterium*). These results may serve as the starting point to look for optimal removal processes to reduce the occurrence of DBPs under real working conditions. Apart from this main conclusion, the following partial conclusions can also be drawn:

- Bromide reacts immediately with chlorine generating hypobromous acid and hypobromite, direct precursors of THMs. There is no stage within the DWTP capable of eliminating bromate. TOC is reduced along the purification process mainly on the clarification stages. THMs concentration throughout the DWTP is almost negligible due to its reduced residence time.
- Air stripping is the main mechanism for THMs elimination in water tanks. The relation between interfacial area and water volume (A/V) is crucial for this physicochemical process. The higher the ratio, the greater the removal.
- Hydrolysis may also contribute to THMs destruction. This chemical process is responsible for THMs elimination along the distribution pipes (no contact with air). Temperature and residence time promote this reaction.
- *Methylobacterium* might be acting as suppressors of THM, an additional mechanism for THMs removal.

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Author contributions JL and AdlM were involved in conceptualization and funding acquisition. ÁR and MM contributed to methodology. LP, AS-C, NS and ÁR performed formal analysis. ÁR was involved in writing—original draft preparation. JL was involved in writing—review and editing. All authors read and approved the final manuscript.

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Declarations

Conflict of interest The authors declare that they have no known conflicting financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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