Formation and removal of disinfection by-products in a full scale drinking water treatment plant

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Abstract:

In this case study, high sensitivity simple methods for the analysis of trihalomethanes (THM₄), iodinated-trihalomethanes (I-THMs), haloacetic acids (HAAs), bromide, iodide and iodate have been developed. A one-step procedure for the analysis of haloacetic acids by head-space GC-MS provides good reproducibility and low limits of quantification ($\leq 50 \text{ ng L}^{-1}$). These methods were applied to characterize the formation of DBPs in a full scale drinking water treatment plant. In this treatment plant, the incorporation of bromine into THMs increases throughout the water treatment line, due to the formation of bromine reactive species favored by the decrease of competition between DOC and bromide towards chlorine. A linear correlation has been observed between the bromine incorporation factor and the Br^-/DOC mass ratio. The conversion of iodine to iodate by chlorination occurs in this water due to the relatively high bromide concentration. Moreover, a higher formation of iodate compared to iodide levels in the raw water is observed indicating a degradation of organic iodinated compounds. The formation of I-THMs was constant in terms of quantity and speciation between campaigns despite fluctuating concentrations of DOC and total iodine in the raw water. A preferential

removal of DBPs formed by the intermediate chlorination in the order I-DBPs>Br-DBPs>Cl-DBPs occurs during the subsequent activated carbon filtration. The removal rates range from 25 to 36% for the regulated THM₄, from 82 to 93% for the Σ I-THMs and 95% for haloacetic acids. The assessment of the relative toxicity shows that despite a much lower concentration of HAAs (less than 10% of the total mass of measured DBPs) compared to THMs, these compounds are responsible for 75% of the relative cytotoxicity of the treated water. Bromoacetic acid on its own accounts for more than 60% of the overall toxicity of the 17 compounds included in this study.

Keywords:

DBPs, chlorination, activated carbon, trihalomethanes, haloacetic acids, natural organic matter.

1. Introduction

Chlorine is the main chemical disinfectant used in drinking water treatment, especially as a final step to maintain a residual concentration in the distribution network, avoiding bacterial regrowth. Pre-chlorination or intermediate chlorination is also used to oxidize iron or manganese or to avoid biofouling of filters. However, chlorine also reacts with natural organic matter (NOM) and halides to form a variety of disinfection by-products (DBPs) (Sedlak and von Gunten 2011). The removal of NOM is effective to control the DBP formation, however, literature shows that the efficiency of physical-chemical processes for NOM removal is highly variable and that the same treatment process can lead to different treatment efficiencies when applied to different water types (Bond et al. 2011). Coagulation can effectively remove the humic substances with a high hydrophobic character but will be much less effective for the hydrophilic fractions; then activated carbon could be useful for the removal of these remaining fractions (Bond et al. 2011). Activated carbon (GAC) is considered as an advanced treatment for NOM removal through adsorption and/or biodegradation (Yang et al. 2010; Chili et al. 2012; Fu et al. 2017) for the control of DBP formation. However, only few studies deal with the interest of GAC for the removal of DBPs preformed from pre-chlorination or intermediate chlorination (Tung et al. 2006; Kim and Kang 2008; Cuthbertson et al. 2019). Prechlorination has been shown as a detrimental process in terms of DBP formation. However, Cuthbertson et al. (2019) recently showed the reduction of the relative toxicity of the prechlorinated water by GAC.

The concentration and properties of aqueous NOM have a significant influence on the formation of DBPs during disinfection. The different reactive fractions of NOM can be present in a wide range of concentration and preponderance within the same geographical area as for example the hydrophobic fraction representing from 30 to 84% of the raw water NOM in 30 resources across Scotland (Golea et al. 2017). In addition, the level of bromide and iodide in water plays an important role in DBP formation, inducing the formation of a mix of chlorinated, brominated and iodinated DBPs (Bichsel 2000; Jones et al. 2011; Hua et al. 2012; Roccaro et al. 2014; Zhang et al. 2015; Allard et

al. 2015). Bromide also plays a role in the speciation of iodine species by the enhancement of iodate formation, a safe end-product for iodide, hence reducing the risk of formation of I-DBPs during chlorination (Criquet et al. 2012). Considering the toxicity, iodinated DBPs (I-DBPs) are usually more cytotoxic and genotoxic than the brominated analogues which already are considered as more toxic than the chlorinated ones (Richardson et al. 2007). First identified in drinking waters in 1976 (Shackelford et Keith 1976), iodinated THMs (I-THMs) were the first I-DBPs studied due to early concerns about medicinal taste and odors in drinking water (Hansson et al. 1987) with the lowest odor threshold at 0.03 $\mu\text{g L}^{-1}$ for iodoform (Cancho et al. 2001). I-THMs are the most important class of I-DBPs in terms of occurrence, sometimes even exceeding the THM4 (Richardson et al. 2008; Allard et al. 2015; Tugulea et al. 2015, 2018).

In this study, we investigated the removal of DBP precursors in a full scale water treatment plant in relation to bromine and iodine incorporation and DBP formation. A high sensitivity new method for the analysis of THMs and HAAs is described. An assessment of individual DBP removal by GAC has been carried out at higher levels of halides than what could be found in literature. This study is the first to report the effectiveness of I-THM removal by GAC in a full scale plant and to relate it to physical-chemical properties of DBPs. Finally, a comparison of theoretical relative toxicity from regulated and unregulated DBPs analyzed in this study is presented.

2. Material and Methods

2.1. Water resource, drinking water treatment plant and sample collection

The water samples used in this study were sourced from a drinking water treatment plant, located in the West of Flanders in Belgium and designed for a production of 40,000 $\text{m}^3 \text{ day}^{-1}$. The raw water is drawn from the river IJzer (approximately 80%) and from surrounding lowlands (approximately 20%) (De Watergroep 2015), and stored in a 3 million m^3 reservoir. The water is characterized by a high NOM content, with an average DOC content of 12 mgC L^{-1} , combined with a high alkalinity and

hardness. The Belgian part of the hydrographic basin of the IJzer river covers an area holding 110,000 inhabitants, and a largely agrarian activity, *i.e.* intensive farming and intensive cattle breeding (Baert et al. 1996). The water is treated by a conventional treatment train consisting of biological ammonia oxidation, enhanced coagulation with ferric chloride, decantation, rapid sand filtration, granular activated carbon (GAC) filtration and disinfection with sodium hypochlorite. A pH adjustment is performed before and after coagulation by adding sulfuric acid and sodium hydroxide respectively. An intermediate chlorination is performed before sand filtration in order to enhance manganese oxidation, which is then removed during sand filtration.

Samples were collected from the reservoir (raw water) and after each treatment step in the spring and summer of 2018. Three different campaigns were performed, two campaigns (A and B) for the determination of the THM formation potential (THMFP) and the characterization of precursors, and one (campaign C) for the determination of THMs and HAAs (Table S1). Amber glass bottles of 2.5 L were used for the collection of samples to perform chlorination tests and for determination of initial DBP concentrations. A quenching agent (sodium thiosulfate for THMs (4.65 mg L^{-1}) and ascorbic acid (5 mg L^{-1}) for HAAs) was added in excess to the sand filtrate, GAC filtrate and final water, as these three water samples contain or potentially contain some residual free chlorine. Samples were filtered through $0.45 \text{ }\mu\text{m}$ polyethersulfone (PES) membrane filters within a few hours after sampling. In addition, 30 mL samples were taken for dissolved organic carbon (DOC) and size exclusion chromatography (HPSEC) analysis. These were taken at the same sampling locations using a glass syringe, immediately filtered using $0.45 \text{ }\mu\text{m}$ PES syringe filters (after discarding the first 5 mL of filtrate), and spiked with 150 μL of sodium azide (6.5 g L^{-1}). Finally, all samples were stored at $4 \text{ }^{\circ}\text{C}$ until the chlorination experiments or analysis.

The concentration of dissolved organic carbon was determined using a TOC analyzer (Shimadzu® VCSH). NOM size fractionation was performed using high performance liquid chromatography

(Agilent® 1260 Infinity II) equipped with a size exclusion column (Agilent® Bio SEC-5 column, 100 Å; 300 mm x 7.8 mm, 5 µm particle size), with an exclusion limit range of 100 to approximately 100,000 Da. A phosphate buffer eluent was used: 1 g L⁻¹; pH 6.8 and ionic strength of 0.039 M (Zhou et al. 2000; Song et al. 2010). Other parameters used during exclusion chromatography are an injection volume of 100 µL, a flow rate of 1.0 mL min⁻¹, a pressure of around 80 bar and a temperature of 23 °C. The HPSEC is coupled to a diode array detector equipped with a 60 mm high sensitivity cell. The eluting dissolved organic matter fractions were detected using UV absorbance at 254 nm. Samples with organic carbon concentrations exceeding 5 mgC L⁻¹ were diluted before analysis to avoid fouling of the column and signal saturation.

2.2 Development of high sensitivity methods

A headspace-trap method has been developed for the analysis of the 10 THMs. The analytical instrument used was a Trace™ 1300 GC coupled with an ISQ-LT single quadrupole mass spectrometer (Thermo Scientific®) operating in SIM mode. A ZB-5MS (Phenomenex®) column (30 m × 0.25 mm ID, 1 µm film thickness) was used for gas chromatographic separations. The headspace trap injector (Perkin Elmer® TurboMatrix Headspace 40 Trap) was directly connected to the GC-MS bypassing the inlet split of the GC injector. For THMs analysis, 10 mL of the water samples were transferred into 22 mL glass vials containing 4 g of sodium sulfate (2.8 M), and were spiked with 1,2-dibromopropane as internal standard (6.4 µg L⁻¹). The vials were immediately sealed and stirred in a vortex mixer until complete salt dissolution. This method ensured low quantification limits for the 10 THMs included in this study, ranging from 0.4 ng L⁻¹ (CHBr₂I) to 2 ng L⁻¹ (CHI₃) for I-THMs and 3 ng L⁻¹ for THM4 (Table 1).

Haloacetic acids (HAA5 + iodoacetic and bromochloroacetic acids) were analyzed by a one-step procedure. HAAs in aqueous medium forms an ion-pair with tetrabutylammonium hydrogensulfate and react with dimethylsulfate to produce methyl haloacetates which are directly volatilized in the head-space. 9.84 mL of the water samples were spiked with bromopropionic acid (10 µg L⁻¹) as internal standard, acidified to pH 2.6 using sulfuric acid, and placed in a 22 mL glass vial containing 4 g (2.8 M)

of sodium sulfate. 100 μL of a 0.5 M ion pairing agent (tetrabutylammonium hydrogensulfate, final aqueous concentration of 2.3 μM) and 60 μL of derivatization reagent (dimethylsulfate) were then added. The vials were immediately sealed and stirred before being placed into an autosampler. The analysis was performed after 2 to 4 hours of reaction time, this time should not exceed 5 hours to avoid the hydrolysis of methylester. The limit of quantification ranged from 2 ng L^{-1} (iodoacetic acid) to 50 ng L^{-1} (chloroacetic acid) (Table 1). The Headspace-trap-GC-MS operating parameters are specified in the Supporting Information (Tables S2-S4).

Table 1

Iodide, iodate and bromide were measured (on quenched samples) using a liquid chromatograph coupled to an inductively coupled plasma mass spectrometer (HPLC-ICP-MS). Separation was done by a Dionex IonPac AS16 (2 x 250 mm) analytical column with an AG16 (2 x 50 mm) guard column using NaOH 20 mM gradient eluent (Table S5). ICP-MS (Agilent 7900) conditions were set at an RF Power of 1550W, no gas mode (collision cell), with an aerosol dilution (0.1 L min^{-1}), and bromine and iodine were determined through their ^{79}Br and ^{127}I isotopes, respectively. The quantification limit was 0.2 $\mu\text{g L}^{-1}$ for all 4 species. Total iodine and bromine in the water samples were determined by ICP-MS (Varian 820 MS) in 0.5% tetramethylammonium hydroxide matrixes with ^{129}Xe as internal standard (Balaram et al. 2012). Analyses were performed using He at 100 mL min^{-1} at the collision reaction interface (skimmer cone) to handle potential polyatomic interferences. The quantification limit level was 0.5 $\mu\text{g L}^{-1}$ for both iodine and bromine.

2.2. Chlorination tests

The THMFP tests were carried out using a 7-day chlorination procedure according to the Standard Methods 5710 for the formation of trihalomethanes and other by-products (Standard method, 2017) with minor modifications. The samples were placed in either 25 or 50 mL glass reagent bottles with PTFE lined screw caps, buffered with a phosphate solution at $\text{pH } 7.0 \pm 0.2$ and chlorinated using a stock solution of 5000 mg L^{-1} sodium hypochlorite at different doses in order to ensure samples with free

chlorine residuals between 3 and 5 mg L⁻¹ at the end of the chlorination test. Samples were incubated in a thermostatically controlled cabinet at 25 ± 2 °C for 7 days, after which the free chlorine residual of each sample was measured using the *N, N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method (Rodier et al. 2016). In the samples containing a free chlorine residual between 3 and 5 mg L⁻¹, the chlorine residual was quenched using sodium thiosulfate and the samples were stored at 4 °C in the dark until the THMs were analyzed. Note that for the sample after nitrification (campaign A), no bottle having a free chlorine residual between 3 and 5 mg L⁻¹ was obtained, therefore the bottle with the closest chlorine residual (*i.e.* 1.9 mgCl₂ L⁻¹) was selected. Results are presented as ΔTHMFP corresponding to the difference between THM concentrations after chlorination tests and THMs already formed in the treatment line (Standard method, 2017).

3. Results and discussion

3.1. THMFP vs. NOM fractions

The DOC concentration decreases from 8.5 to around 2.5 mgC L⁻¹ for campaign A and from 6.7 to 2.2 mgC L⁻¹ for campaign B along the treatment line, corresponding to a removal of around 70% of DOC for both campaigns. The biggest removal occurs during the coagulation step – from 57 to 65% – which are high removal efficiencies when comparing to the literature (14-66% (Liang et Singer 2003; Boyer et Singer 2005; Vasyukova et al. 2013)). The DOC decrease in subsequent steps is quite low with less than 12% of the initial DOC content removed during activated carbon filtration (Figure 1a).

The removal of THM precursors is slightly higher than the DOC removal with a decrease of the THMFP of around 80% for the entire treatment (Figure S1). The THMFP/DOC ratio is around 70 µg THM/mgC in the raw waters for both campaigns A and B, despite the different DOC concentrations of 8.5 and 6.7 mgC L⁻¹, for campaigns A and B, respectively (Figure S2). This result is in agreement with the literature showing good correlation between THMFP and DOC in raw waters with THMFP/DOC ratios usually in

the 27 to 167 $\mu\text{g THM}/\text{mgC}$ range (Table S6). As such, the DOC in this surface water has an intermediate reactivity towards the formation of DBPs compared to the full range of NOM characterized in literature. The THMFP/DOC ratio (Figure S2) decreases progressively along the treatment line (around 35% for both campaigns), thus the THMFP is more reduced than the DOC during treatment. The same behavior has been observed in several studies (Table S6). For example, Golea et al. (2017) show a 50% decrease of the THMFP/DOC ratio during water treatment. This reflects a more preferential removal of the highly reactive organic THM precursors by the water treatment process – such as reactive hydrophobic fractions by coagulation-decantation – or the progressive transformation of NOM towards less reactive moieties as the DOC is not significantly removed during nitrification nor in the filtration steps.

Figure 1

Considering the speciation of the THM4 formed in the THMFP tests (Figure S1), CHCl_3 is the main THM formed at all treatment steps. Of the four regulated THMs, the three brominated species were present in relatively low concentrations, accounting for 12-51% (mass weighted) of the THM4 despite a consequent level of bromide in raw water $[\text{Br}^-] = 140\text{-}170 \mu\text{g L}^{-1}$. CHBrCl_2 was found to be the main brominated THM species present, being formed at all treatment steps. In the standardized protocol of the formation potential tests, chlorine is introduced in a large excess explaining the predominance of chloroform and the extremely low I-THMs levels ($<0.1 \mu\text{g L}^{-1}$). In the chlorinated final water from the drinking water treatment plant (residual = $0.3 \pm 0.1 \text{ mgCl}_2 \text{ L}^{-1}$) the main species found were CHBrCl_2 and CHBr_2Cl . This difference in detected THM species is due to the higher rate constants observed for reactive bromine species compared to reactive chlorine species (Criquet et al. 2015), thus the NOM precursor sites are preferentially brominated at low chlorine doses. The THM4 in the final water ranged from 26 up to $34 \mu\text{g L}^{-1}$, well below the THM regulation level of $100 \mu\text{g L}^{-1}$ imposed by the European Union.

In Figure 1, a similar trend is shown between the reductions of the Δ THMFP with DOC (a) and the humic substance fraction measured using SEC-UV (b). This fraction, corresponding to compounds of relatively high molecular weight, is the main fraction removed by the coagulation step (reduction of around 90% of its UV absorbance in the SEC chromatogram; Figure 1d). These results are in good agreement with previous studies which have found good correlation with this particular fraction (Vasyukova et al. 2013; Li et al. 2014; Golea et al. 2017). Assuming that the UV absorbance properties of humic substances (HS) are not significantly changed during coagulation, a lower reduction of THMFP (70%) compared to humic substances (90%) is observed, underlining the role of other organic fractions in addition to HS as THM precursors. In addition, the DBPFP was further reduced while the humic substances were not removed by the following treatment steps (Figure 1b). A proportional decrease of the THMFP vs. the building-block fraction was then observed during the two sampling campaigns (Figure 1c). Good correlations were obtained for the steps after coagulation/decantation ($r^2 = 0.79$, Figure 1c) when the remaining humic substances were no longer removed.

3.2. Bromine incorporation

The formation of bromine-containing DBPs is of particular interest as they are generally more toxic than chlorine-containing compounds (Plewa et al. 2004). The bromine incorporation factor (BIF), first developed by Gould et al. (1983), describes the molar contribution of all brominated species (Eq.1, with THMs in molar concentrations), and can range from 0 to 3, with values closer to 3 representing a more brominated THM sample.

$$BIF (THMs) = \frac{[CHBrCl_2] + 2 [CHBr_2Cl] + 3 [CHBr_3]}{[CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]} \quad \text{Eq. 1}$$

The incorporation of bromine into THMs after the THMFP tests increases along the treatment line (Figure 2). The BIF after the THMFP test is low for the raw water and after the nitrification step (around 0.15), then increases after coagulation to approximately 0.4, and increases further after GAC filtration (from 0.5 to 0.65 for campaigns A and B, respectively). It has to be noted that the bromide concentration decreases after sand filtration due to the intermediate chlorination step, but increases

once more after GAC filtration indicating bromide release while DOC is slightly removed (Figure 3). This could be due to microbial degradation of some brominated compounds adsorbed on GAC.

Figure 2

The BIF for Δ THMFP was found to increase linearly in function of the Br^-/DOC (Figure 3). Effectively, a higher Br^-/DOC ratio (usually the result of DOC removal during treatment) favors reaction of chlorine with Br^- instead of DOC, resulting in the formation of reactive bromine species (which in turn react with NOM to form brominated THMs, resulting in a higher BIF). The maximum BIF value (0.63) is reached after GAC filtration, where the Br^-/DOC ratio is highest. Even though this value represents a quite moderate bromine incorporation into THMs, one should keep in mind that the formation potential protocol favors reactive chlorine species over bromine species. The samples from both A and B campaigns show a single correlation between the BIF and Br^-/DOC ratio (Figure 2), however when correcting the Br^-/DOC ratio for the amount of Cl_2 consumed, different correlations for campaigns A and B are found (Figure S6). In addition, adjusting the Br^-/DOC ratio with consumed chlorine increases the linearity of the established correlations with BIF, as indicated by regression coefficients of 0.99 and 0.91 for campaigns A and B respectively (Figure S6 – with correction for Cl_2 consumed), and regression coefficients of 0.80 and 0.83 for campaigns A and B respectively (Figure 3, regression lines not shown – without correction for Cl_2 consumed). The different slopes could be due to the higher bromide concentration in the raw water for the campaign B ($170 \mu\text{g L}^{-1}$) compared to campaign A ($140 \mu\text{g L}^{-1}$) in conjunction with lower DOC values (6.7 and 8.5 mgC L^{-1} respectively for campaigns B and A). Then, the competition between NOM and Br^- is in favor of a higher formation of bromine active species in campaign B.

The BIFs of the treated water having a chlorine residual around $0.3 \text{ mgCl}_2 \text{ L}^{-1}$ (sampled from the water treatment works without further treatment except chlorine residual quenching), ranged from 1.1 to 1.4 for campaigns A and B respectively, which is much higher than the ones observed for the THMFP. This matches BIF values found by Hong et al. (2013), ranging between 0.86 and 1.42 for bromide values

between 109 and 209 $\mu\text{g L}^{-1}$. The removal of bromide ions from the raw water to the final chlorination ranges from 37 to 56%, which is due to incorporation of bromide into the organic matrix through the chlorination steps. During final chlorination, 20 to 40% of the bromide content is incorporated into NOM (Figure S5). This result is in agreement with the literature showing from 10 to 40% of halogen incorporated into NOM (Criquet et al. 2015; Zhao et al. 2017).

3.3. Iodine speciation and I-DBP formation

The level of iodide ion found in the raw water during this survey highly varied, with concentrations between < 0.2 and $18.2 \mu\text{g L}^{-1}$. These concentrations are however in line with the range of concentrations usually found in surface waters (Snyder et Fehn 2004; Salminen et al. 2005). During campaign A (Figure 3), iodide was not detected and iodate was below the quantification limit ($< 0.2 \mu\text{g L}^{-1}$) in the raw water, however, some I-THMs and mainly iodate were found after intermediate chlorination (see below). Then, a part of iodine could certainly be present in the raw water as incorporated in the organic matrix. Analysis of total iodine by ICP-MS during campaign B confirmed this fact, with only 17% of the total iodine present as iodide in the raw water (total iodine = $33.3 \mu\text{g L}^{-1}$; $[\text{I}^-] = 5.6 \mu\text{g L}^{-1}$ and $[\text{IO}_3^-] < 0.2 \mu\text{g L}^{-1}$) which is in the same range as that found by Gilfedder et al. (2009) (15% of iodine as inorganic iodine in a lake). The absence of supplementary peaks on the HPLC-ICP-MS chromatogram suggests that the iodine is bound to non-ionic organic species. Regular monitoring since 2017 shows the presence of iopromide and iomeprol up to $0.3 \mu\text{g L}^{-1}$ in the raw water. However, these target substances could represent only a small part of the iodinated anthropogenic substances present in this water; no extensive study has been performed on iodine speciation and importance of the organic fraction. In addition, other sources of organic iodine may originate from the surrounding agricultural activities, and may include iodinated cattle feed supplements (Moreno-Reyes et al. 2011), as well as iodophor medication, iodine-containing sterilizers of milking equipment, teat dips and udder washes, or pesticides and fungicides containing

iodine (Scientific Committee on Food; Health and Consumer Protection Directorate-General 2002). One should also consider that some authors suggest that the major fraction of iodine in a number of natural fresh waters is bound to high molecular weight humic substances (Gilfedder et al. 2009). This complexation could then interfere with the analysis of iodide. Iodate was near absent ($< 0.2 \mu\text{g L}^{-1}$) in raw water and all treatment steps before intermediate chlorination.

Figure 3

The speciation of iodine and I-THMs formation has been assessed directly on the (filtered) water samples from the treatment plant without further experiments involving chemical modification (such as a DBPFP test). In fact, the DBPFP test is not suitable for I-DBPs, as the large chlorine dose would favor the formation of iodate and I-THMs would hardly be detected. The organic iodine (TOI) has been assessed by the difference between the total iodine concentration obtained by ICP-MS and the inorganic species, *i.e.* I^- and iodate contents determined by HPLC-ICP-MS. According to Figure 4, a part of organic iodine is removed after nitrification while the concentration of iodide stays unchanged. This behavior is not fully explained, especially because the DOC remains unchanged at this step. It is possible that organic iodine is incorporated into the biomass. A second decrease of organic iodine without significant change of iodide is observed during coagulation suggesting that a part of the organic iodine is bound to the high molecular weight NOM, which constitutes the major fraction removed during this process (Figure 1d). After the intermediate chlorination step, most of the iodine is converted into iodate. In fact, the quantity of iodate formed is higher than the initial iodide present in the water before chlorination, indicating that a part of the organic iodine also contributes to the formation of iodate. This behavior has been observed for the 3 campaigns (Figure 3). This high degree of transformation is certainly due to the relatively high concentration of bromide, which plays a role of a catalyst in iodide oxidation to iodate during chlorination (Criquet et al. 2012). Interestingly, the iodate concentrations varies from 5 to $13 \mu\text{g L}^{-1}$ in the treated water between sampling campaigns, however despite this variation a surprisingly stable I-THMs formation and speciation is observed

(Figure 3). The same reproducibility between the campaigns is observed for the intermediate chlorination step. The sum of I-THMs formed ranges from 73 to 80 ng L⁻¹ in the distributed water which corresponds to less than 0.6% (on a mass basis) of the total THMs formed. The major I-THMs formed are the CHBrClI and CHCl₂I followed by CHBr₂I, while no iodoform has been observed. These compounds correspond to the mono-iodinated compounds which are predominant for low iodide levels (Zhang et al. 2015). Iodoacetic acid reached a concentration of around 20 ng L⁻¹ after the intermediate chlorination step but was below detection level (< 2 ng L⁻¹) in the final water (Figure 4b).

3.4. Impact of GAC filtration on DBPs: THMs, I-THMs and HAAs

The presence of an intermediate chlorination step in this water treatment plant allows to assess the efficiency of the full-scale activated carbon filtration to remove DBPs. While two previous studies found that some I-THMs were removed by GAC filtration (Cancho et al. 2000; Cuthbertson et al. 2019), scarce information on the removal efficiency of I-DBPs in a full scale drinking water treatment plant is available. THM4 were formed (from 15 up to 28 µg L⁻¹) and are present in the treatment steps after intermediate chlorination. Some iodinated THMs were formed as well, adding up to a total of 270-312 ng L⁻¹ of I-THMs, as well as HAAs reaching 8.4 µg L⁻¹ (campaign C) for the sum of the 7 HAAs analyzed (Figure 5).

Figure 4

The concentrations after activated carbon filtration showed a decrease in all analyzed DBPs. The removal based on the total mass ranged from 25 to 36% for the THM4 (3 campaigns); from 82 to 93% for the Σ I-THMs (3 campaigns) and 95% for HAAs (campaign C). Considering the THM4, CHBr₃ shows the highest removal (58% on average) followed by CHBr₂Cl (43%), CHBrCl₂ (18%) and CHCl₃ (15%). This indicates that the removal of the highly brominated THMs is significantly higher than the chlorinated ones. This is also corroborated by Speth and Miltner (1990), who investigated the activated carbon adsorption behavior of different halogenated compounds including THM4, and reported increasing Freundlich adsorption constants with increasing bromine content. The removal efficiency increases

with increasing molecular weight and increasing hydrophobicity (Figure 5). In addition, I-THMs show much higher removal, ranging between 77 and 99% on average for each compound. The same trend of increased removal with increasing molecular weight is observed (CHCl₂ showing the best removal – note that iodoform and CHBrI₂ were not detected, Figure 5). A positive relationship has been found between these two parameters ($R^2 = 0.83$, Figure 5), however I-THMs seems to have their own proportional increase with the molecular weight. Considering the hydrophobicity of the compounds, THM4 and I-THMs are in a similar range of K_{ow} (Table S7), and then this parameter could only explain the variation within iodinated or non-iodinated compound families (Figure 6), therefore other factors such as biodegradation (Cuthbertson et al. 2019) or halogen bonding (Poltzer et al., 2007; Anderson et al. 2018) could have impacted the THM removal on GAC. The latter process involves interactions with basic sites present on the activated carbon surface (Tessmer et al. 1997), and its bond strength increases in the order of Cl < Br < I (two references above). In comparison to other commercially available activated carbon types, the GAC type used in this drinking water treatment plant (Filtrisorb F400, Calgon Carbon – Chemviron and Norit GAC1240) indeed contains a substantial amount of basic sites on its surface.

Figure 5

HAA5 show high removal efficiency by activated carbon filtration, from 87% (trichloroacetic acid) up to 97% (bromo- and dibromoacetic acids). The overall removal, based on total mass of the 7 HAAs analyzed in this study is around 95% (Table S7, the same removal efficiency is obtained considering the HAA5). Tung et al. (2006) showed that adsorption plays a minor role in HAA removal and GAC filters have a lower adsorption capacity for mono- and dihaloacetic acids than for the regulated THMs. On the other hand, Kim et Kang (2008) showed that the removal of HAA5 by adsorption was high at the early stage of GAC operation and better than for THM4, with breakthrough occurring later. The GAC filtration here consists of 6 filters with 4 to 5 filters working in parallel during the campaigns. The average time since reactivation varied from 305 to 350 days for the 3 campaigns corresponding to bed

volumes from 19000 to 21150. The contact time also varied between campaigns from 16 to 32 minutes. Considering the different varying parameters it is difficult to assess the main factor modifying the DBP removal. However, CHCl_3 and CHCl_2Br showing the lowest adsorption on the one hand and CHBr_2I , CHClI_2 and CHBrClI showing the highest removal on the other hand, show the same variation with the different parameter (data not shown). More contrasted parameters would be necessary to assess the key parameters of adsorption, halogen bonding and/or biodegradation and to explain the higher variability of THM4 removal. The latter process can in fact play an important role especially considering the different removal efficiency of compounds showing the same hydrophobicity.

3.5. Relative toxicity assessment

A final chlorination step is performed after activated carbon filtration. The chlorine dose is controlled to achieve a target value of $0.3 \text{ mgCl}_2 \text{ L}^{-1}$ in the treated water leaving the plant. The median concentration of THM4 in the treated water is $25 \text{ } \mu\text{g L}^{-1}$ ($n = 135$, from routine monitoring analysis results from January 2016 until May 2019). In this study, the THM4 reached a concentration ranging from 25 to $34 \text{ } \mu\text{g L}^{-1}$ for the 3 campaigns which is far below the EU and US guidelines (respectively 100 (CELEX-EUR 1998) and $80 \text{ } \mu\text{g L}^{-1}$ (EPA 2016)). The highest concentration was found during campaign A, which coincides with the highest DOC concentration. The quantity of THM4 present in the water after final chlorination is always higher than the quantity present after the intermediate chlorination. The increase is however limited, *i.e.* from 4 to $11 \text{ } \mu\text{g L}^{-1}$. The concentration of THM4 corrected of the chlorine dose lower in the final step is indeed lower than during the intermediate chlorination. In addition, the quantity of I-THMs and HAAs formed during final chlorination is much lower compared to the quantity formed during intermediate chlorination. The occurrence of both I-THMs and HAAs is a factor 3 to 4 lower after postchlorination compared to intermediate chlorination. The low formation of I-THMs can be explained by the conversion of iodide into iodate, while the organic HAA-precursors has to be supposed to be the limiting parameter of HAA formation. Cuthbertson et al. (2019) on the

contrary showed a chlorine controlled HAA formation, i.e. a continuous increase of HAA formation with the increasing chlorine dose.

In order to prioritize the different DBPs, regardless of the non-toxicity of the produced water and the compliance with the national and supranational quality guidelines, an assessment of relative toxicity has been performed using the mammalian cell cytotoxicity data as reported in Table S8. In this approach, the concentration of each DBP is divided by its respective $LC_{50} \times 10^6$ (lethal concentration for 50% of a population) (Wagner and Plewa 2017), as the contribution of a DBP to toxicity is a function of both concentration and toxic potency. The relative cytotoxicity of THMs and HAAs has been summed to compare the toxicity of these two families.

Considering THMs, the general trend of cytotoxicity is similar to the species-specific concentration (Figures 5a and 5c). The LC_{50} s of the regulated THM4 are between 4.0×10^{-3} and 1.2×10^{-2} M, and despite exhibiting the highest concentration only the relative toxicity of $CHBrCl_2$, having the highest LC_{50} , is reduced compared with the other species. Considering I-THMs, their low concentrations and the absence of iodoform (most cytotoxic I-THM, $LC_{50} = 4.47 \times 10^{-5}$ M), induce a low contribution of only 0.48-0.58% to the overall THM cytotoxicity in final waters. The GAC filtration showing high removal of I-THMs contributes significantly to reduce the impact of these species to the relative cytotoxicity, as their contribution has been seen to account for up to 4.5% (campaign B) of the overall cytotoxicity of the THMs formed from the intermediate chlorination.

Compared to THMs, HAAs show much lower LC_{50} values, indicating their higher relative toxicity. This is especially the case for bromoacetic acid (9.6×10^{-6} M) and iodoacetic acid (2.95×10^{-6} M). The main HAAs present (dichloroacetic acid, dibromoacetic acid, trichloroacetic acid and bromochloroacetic acid) do not contribute much to the total relative cytotoxicity of HAAs (Figure 4d). On the contrary, bromoacetic acid contributes the most with 80% of the relative cytotoxicity of HAAs in the final water. Considering the intermediate chlorination, iodoacetic acid (showing the lowest LC_{50} value) contributes to 16% of the relative cytotoxicity despite a concentration of at least a factor 10 lower than the other

HAAs (23 ng L⁻¹). However, the iodoacetic acid is removed well from the water by the GAC filtration and is no further formed in the final chlorination. The GAC filtration reduces the total relative toxicity by a factor higher than 10.

As stated in paragraph 3.5, the HAAs formed during intermediate chlorination are well removed in the subsequent GAC filtration (95%), while the DOC reduction only accounts for around 10% of the initial DOC. Then it could be questioned if the HAAs would have been much higher in the final water without intermediate chlorination, as their NOM precursors may not be specifically removed by the GAC (Cuthbertson et al. 2019). Remarkably, HAAs represent less than 10% of the total mass of measured DBPs (*i.e.* THMs + HAAs) but account for more than 75% of the relative cytotoxicity of the treated water. Bromoacetic acid by itself accounts for more than 60% of the overall toxicity of the 17 compounds included in this study. In the present case, the intermediate chlorination seems to be beneficial for the quality of the treated water, as long as the GAC capacity to retain HAA is maintained. A closer look to the HAA adsorption in function of practical parameters of GAC is then essential to be performed to limit HAAs in the treated waters.

It is clear that currently unregulated DBPs (*i.e.* HAAs or I-DBPs) can have a higher contribution to the relative toxicity of chlorinated waters than currently regulated DBPs (*i.e.* THM4). However THM4 serve as an indicator parameter for DBPs in general in the European drinking water directive. Drinking water companies should apply a risk based approach to minimize formation of DBPs by removing precursors in the treatment and by limiting the amount of disinfectant used, however without compromising the disinfection efficiency (EPRS 2019). Nonetheless, the WHO (2017) recently commended to include 9 chlorinated and brominated HAAs in the drinking water legislation, as these substances are formed to a higher extent under acidic conditions. Together with THM4, these 9 HAAs should then serve as indicator parameter for all DBPs formed and all water types.

3. Conclusion

THMFP tests performed on samples taken from a drinking water treatment plant in addition to the characterization of organic matter give some valuable information on the DBP formation and the removal of NOM fractions during the different steps of water treatment. First, the majority of DOC, especially high molecular weight fractions, are removed during coagulation, which was accompanied by the highest decrease of THMFP. However, a further decrease of the THMFP is seen with the subsequent removal of the building block fraction despite the relatively low removal of the overall DOC. The possible incorporation of bromine into THMs is seen to increase throughout the water treatment plant, since the reduction of DOC concentration results in a lower competition for chlorine to react with bromide, forming bromine reactive species.

Despite large modifications of water quality in terms of DOC and iodine concentrations, the formation of I-THMs was constant in terms of quantity and speciation between campaigns. A high conversion of iodine into iodate by chlorination is observed in this water certainly due to the relatively high bromide level which catalyzes iodate formation. A degradation of organic iodinated compounds is observed in this water treatment plant with a larger formation of iodate compared to iodide levels in the raw water.

In this water treatment plant, the activated carbon filtration is effective to remove the HAAs and I-THMs (> 80%) formed during intermediate chlorination but to a lesser extent for THM4 (< 40%). A preferential removal in the order I-DBPs>Br-DBPs>Cl-DBPs is observed with no clear trend related to the compound hydrophobicity suggesting other factors such as biodegradation or halogen bonding are also governing DBP removal on GAC. The amount of DBPs formed per quantity of DOC decreases through the treatment line showing the preferential removal of the highly reactive precursors. This is especially the case for HAAs that are not formed in a high extent during the final chlorination step. From a theoretical assessment, the relative cytotoxicity of HAAs is more important than the one of THMs, even considering their much lower concentrations. Bromoacetic acid accounts for 60% of the

461 relative cytotoxicity of THMs and HAAs formed in the distributed water. These results would support
462 the importance of inclusion of HAAs in the future European regulation considering their higher toxicity,
463 their different behavior and formation compared to THMs presently used as a surrogate for all DBPs.

464

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469

470

Figure captions

Figure 1: Evolution of the ΔTHMFP ($[\text{THM}]_{\text{FP}} - [\text{THM}]_0$) in waters sampled after the different treatment steps in function of (A) the DOC content (B) the fraction of humic substances and (C) the fraction of building blocks for treatment steps after coagulation. (D) Size exclusion chromatograms with UV detection (254 nm) for campaign A (campaigns B and C in Figure S3). 1- raw water, 2- after nitrification, 3- after coagulation-decantation, 4- after intermediate chlorination and sand filtration, 5- after GAC filtration, 6- after final chlorination. (a.u.: arbitrary unit)

Figure 2: Correlation between the bromine incorporation factor (BIF) from ΔTHMFP vs. Br-/DOC in the treatment line including sampling campaigns A and B.

Figure 3: A) Iodine speciation after each treatment step of the water treatment plant (campaign B) and B) I-THMs formation after final chlorination for the 3 campaigns. Iodide and iodate were analyzed by IC-ICP-MS. Total Organic Iodine was assessed by the difference between total iodine measured by ICP-MS and inorganic iodine species (iodide and iodate).

Figure 4: Concentrations of (a) THM4, sum of I-THMs and (b) HAAs in the water treatment plant (campaign C) after intermediate chlorination-sand filtration, activated carbon filtration (GAC) and final chlorination steps. Relative cytotoxicity of (c) THMs and (d) HAAs in the treated water for the same treatment steps. The relative cytotoxicity has been calculated using the LC50 related to each compounds (see paragraph 3.5).

Figure 5: Percentage of trihalomethane removal through the granular activated carbon filtration expressed in function of molecular weight and hydrophobicity (values and references in Table S8) Error bars represent the deviation of data from 3 campaigns.

4. References

- S. Allard, J. Tan, C. A. Joll and U. von Gunten. '**Mechanistic Study on the Formation of Cl-/Br-/I-Trihalomethanes during Chlorination/Chloramination Combined with a Theoretical Cytotoxicity Evaluation**'. *Environmental Science & Technology*, 49 (18) (2015), pp. 11105-11114. <https://doi.org/10.1021/acs.est.5b02624>.
- N.L. Anderson, F.W. Aquino, A.E. Raeber, X. Chen and B.W. Wong '**Halogen bonding interactions: revised benchmarks and a new assessment of exchange vs dispersion**' *Journal of Chemical Theory and Computation*, 14 (1) (2018), pp. 180-190. <https://doi.org/10.1021/acs.jctc.7b01078>.
- R. Baert, R. Loontjens and M. Devos. '**Potassium and Nitrate Pollution of Surface Water in the Catchment Area of the "Blankaert" Water Production Centre in Flanders (Belgium)**'. In *Proceedings _ 4th International Conference On Environmental Compliance And Enforcement*, Chiang Mai, Thailand, (1996), pp. 2:635-642.
- V. Balaram, M. Satyanarayanan, D.V. Avdeev, N. Berdnikov, P. Roy, S.S. Sawant, K. Subramanyam, et al. '**Use of Xenon as Internal Standard for the Accurate Determination of Trace Elements in Water Samples by ICP-MS**'. *Atomic Spectroscopy*, 33 (2012), pp. 41-47.
- Y. Bichsel. '**Behavior of Iodine Species in Oxidative Processes During Drinking Water Treatment**'. Doctoral thesis Diss. ETH, No. 13429.
- T. Bond, E.H. Goslan, S.A. Parsons and B. Jefferson (2011) '**Treatment of disinfection by-product precursors**'. *Environmental Technology*, 32:1, 1-25, DOI:10.1080/09593330.2010.495138
- T. H. Boyer and P. C. Singer. '**Bench-Scale Testing of a Magnetic Ion Exchange Resin for Removal of Disinfection by-Product Precursors**'. *Water Research*, 39 (7) (2005), pp. 1265-1276. <https://doi.org/10.1016/j.watres.2005.01.002>.

517 B. Cancho, C. Fabrellas, A. Diaz and F. Ventura. '**Determination of the Odor Threshold Concentrations**
518 **Of Iodinated Trihalomethanes in Drinking Water**'. Journal of Agricultural and Food Chemistry,
519 49 (4) (2001), pp. 1881-1884. <https://doi.org/10.1021/jf001252m>.

520 B. Cancho, F. Ventura, M. T. Galceran, A. Diaz and S. Ricart. '**Determination, Synthesis and Survey of**
521 **Iodinated Trihalomethanes in Water Treatment Processes**'. Water Research, 34 (13) (2000),
522 pp. 3380-3390. [https://doi.org/10.1016/S0043-1354\(00\)00079-8](https://doi.org/10.1016/S0043-1354(00)00079-8)

523 CELEX-EUR. 1998. « **Council Directive 98/83/EC of 3 November 1998 on the quality of water intended**
524 **for human consumption** ». *Official Journal of the European Communities*, L 330 41: 32-54.

525 C. A. Chili, P. Westerhoff, and A. Ghosh. '**GAC Removal of Organic Nitrogen and Other DBP Precursors**'.
526 Journal AWWA, 104 (7) (2012), pp. E406-415. <https://doi.org/10.5942/jawwa.2012.104.0090>.

527 J. Criquet, S. Allard, E. Salhi, C. A. Joll, A. Heitz and U. von Gunten. '**Iodate and Iodo-Trihalomethane**
528 **Formation during Chlorination of Iodide-Containing Waters: Role of Bromide**'. Environmental
529 Science & Technology, 46 (13) (2012), pp. 7350-7357. <https://doi.org/10.1021/es301301g>.

530 J. Criquet, E. M. Rodriguez, S. Allard, S. Wellauer, E. Salhi, C. A. Joll and U. von Gunten. '**Reaction of**
531 **Bromine and Chlorine with Phenolic Compounds and Natural Organic Matter Extracts –**
532 **Electrophilic Aromatic Substitution and Oxidation**'. Water Research, 85 (2015), pp. 476-486.
533 <https://doi.org/10.1016/j.watres.2015.08.051>.

534 A. Cuthbertson, S. Kimura, H. Liberatore, R. S. Summers, D. Knappe, Benjamin D. Stanford, J. C. Maness,
535 R. Mulhern, M. Selbes and S. Richardson. '**Does GAC with Chlorination Produce Safer Drinking**
536 **Water? From DBPs and TOX to Calculated Toxicity**'. Environmental Science & Technology, 53
537 (2019), pp. 5987-5999. <https://doi.org/10.1021/acs.est.9b00023>.

538 De Watergroep Annual activity report De Watergroep: '**Activiteitenverslag 2015**' (2015). Accessible on
539 line: <https://www.dewatergroep.be/nl-be/over-de-watergroep/wat-doen-we/jaarverslagen>.

540 EPRS European Parliamentary Research Service (2019) '**Revision of the Drinking Water Directive**' 15-
541 04-2019. Accessible on line:

542 [http://www.europarl.europa.eu/thinktank/en/document.html?reference=EPRS_BRI\(2018\)625](http://www.europarl.europa.eu/thinktank/en/document.html?reference=EPRS_BRI(2018)625)
543 179.

544 EPA. **'Six-Year Review 3 Technical Support Document for Disinfectants/Disinfection Byproducts**
545 **Rules'**. (2016), 468 p.

546 B. S. Gilfedder, M. Petri and H. Biester. **'Iodine Speciation and Cycling in Fresh Waters: A Case Study**
547 **from a Humic Rich Headwater Lake (Mummelsee)'**. Journal of Limnology, 68 (2) (2009), pp.
548 396-408. <https://doi.org/10.4081/jlimnol.2009.396>.

549 D. M. Golea, A. Upton, P. Jarvis, G. Moore, S. Sutherland, S. A. Parsons and S. J. Judd. **'THM and HAA**
550 **formation from NOM in raw and treated surface waters'**. Water Research, 112 (2017), pp.
551 226-235. <https://doi.org/10.1016/j.watres.2017.01.051>.

552 R. C. Hansson, M. J. Henderson, P. Jack and R. D. Taylor. **'Iodoform Taste Complaints in**
553 **Chloramination'**. Water Research, 21 (10) (1987), pp. 1265-1271.
554 [https://doi.org/10.1016/0043-1354\(87\)90179-5](https://doi.org/10.1016/0043-1354(87)90179-5).

555 H. Hong, Y. Xiong, M. Ruan, F. Liao, H. Lin and Y. Liang. **'Factors affecting THMs, HAAs and HNMs**
556 **formation of Jin Lan Reservoir water exposed to chlorine and monochloramine'**. Science of
557 The Total Environment, 444 (2013), pp. 196-204.
558 <https://doi.org/10.1016/j.scitotenv.2012.11.086>.

559 G. Hua and D. A. Reckhow. **'Evaluation of Bromine Substitution Factors of DBPs during Chlorination**
560 **and Chloramination'**. Water Research, 46 (13) (2012), pp. 4208-4216.
561 <https://doi.org/10.1016/j.watres.2012.05.031>.

562 D. B. Jones, A. Saglam, A. Triger, H. Song and T. Karanfil. **'I-THM Formation and Speciation: Preformed**
563 **Monochloramine versus Prechlorination Followed by Ammonia Addition'**. Environmental
564 Science & Technology, 45 (24) (2011), pp. 10429-10437. <https://doi.org/10.1021/es202745t>.

565 J. Kim and B. Kang. **'DBPs Removal in GAC Filter-Adsorber'**. Water Research, 42 (1-2) (2008), pp. 145-
566 152. <https://doi.org/10.1016/j.watres.2007.07.040>.

567 J. Fu, W-N. Lee, C. Coleman, K. Nowack, J. Carter, and C-H. Huang. '**Removal of Disinfection Byproduct**
568 **(DBP) Precursors in Water by Two-Stage Biofiltration Treatment**'. Water Research, 123
569 (2017), pp. 224-235. <https://doi.org/10.1016/j.watres.2017.06.073>.

570 A. Li, X. Zhao, R. Mao, H. Liu and J. Qu. '**Characterization of Dissolved Organic Matter from Surface**
571 **Waters with Low to High Dissolved Organic Carbon and the Related Disinfection Byproduct**
572 **Formation Potential**'. Journal of Hazardous Materials, 271 (2014), pp. 228-235.
573 <https://doi.org/10.1016/j.jhazmat.2014.02.009>.

574 L. Liang and P. C. Singer. '**Factors Influencing the Formation and Relative Distribution of Haloacetic**
575 **Acids and Trihalomethanes in Drinking Water**'. Environmental Science & Technology, 37 (13)
576 (2003), pp. 2920-2928. <https://doi.org/10.1021/es026230q>.

577 R. Moreno-Reyes, H. Van Oyen and S. Vandevijvere. '**Optimization of Iodine Intake in Belgium**'.
578 Annales d'Endocrinologie, 72 (2) (2011), pp. 158-161.
579 <https://doi.org/10.1016/j.ando.2011.03.021>.

580 M. J. Plewa, E. D. Wagner, S. D. Richardson, A. D. Thruston, Y-T. Woo and A. B. McKague. '**Chemical**
581 **and Biological Characterization of Newly Discovered Iodoacid Drinking Water Disinfection**
582 **Byproducts**'. Environmental Science & Technology, 38 (18) (2004), pp. 4713-4722.
583 <https://doi.org/10.1021/es049971v>.

584 P. Politzer, P. Lane, M.C. Concha, Y. Ma and J.S. Murray. '**An overview of halogen bonding**'. Journal of
585 Molecular Modeling, 13 (2) (2007), pp. 305-311. <https://doi.org/10.1007/s00894-006-0154-7>.

586 S. D. Richardson, M. J. Plewa, E. D. Wagner, R. Schoeny and D. M. DeMarini. '**Occurrence, genotoxicity,**
587 **and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A**
588 **review and roadmap for research**'. Mutation Research, 636 (1-3) (2007), pp. 178-242.
589 <https://doi.org/10.1016/j.mrrev.2007.09.001>.

590 S. D. Richardson, F. Fasano, J. J. Ellington, F. G. Crumley, K. M. Buettner, J. J. Evans, B. C. Blount, L. K.
591 Silva, T. J. Waite, G. W. Luther, A. B. McKague, R. J. Miltner, E. D. Wagner and M. J. Plewa.
592 '**Occurrence and Mammalian Cell Toxicity of Iodinated Disinfection Byproducts in Drinking**

593 **Water**'. Environmental Science & Technology, 42 (22) (2008), pp. 8330-8338.
 594 <https://doi.org/10.1021/es801169k>.

595 P. Roccaro, G. V. Korshin, D. Cook, C. W.K. Chow and M. Drikas. '**Effects of pH on the Speciation**
 596 **Coefficients in Models of Bromide Influence on the Formation of Trihalomethanes and**
 597 **Haloacetic Acids**'. Water Research, 62 (2014), pp. 117-126.
 598 <https://doi.org/10.1016/j.watres.2014.05.024>.

599 J. Rodier, B. Legube and N. Merlet. '**L'analyse de l'eau**'. Technique et ingénierie, Dunod (10e édition)
 600 (2016), 1600 p.

601 R. Salminen, M. J. Batista, M. Bidovec and T. Tarvainen. '**Geochemical Atlas of Europe. Part 1 -**
 602 **Background Information, Methodology and Maps**'. Geological Survey of Finland, Otamedia
 603 Oy, Espoo, (2005). <http://weppi.gtk.fi/publ/foregsatlas/text/l.pdf>.

604 Scientific Committee on Food; Health and Consumer Protection Directorate-General. '**Opinion of the**
 605 **Scientific Committee on Food on the Tolerable Upper Intake Level of iodine**'.
 606 SCF/CS/NUT/UPPLEV/26 Final. Brussels: European Commission (2002), 25 p.

607 D. S. Sedlak and U. von Gunten. '**The Chlorine Dilemma**'. Science, 331 (6013) (2011), pp. 42-43.
 608 <https://doi.org/10.1126/science.1196397>.

609 W. M. Shackelford and L. H. Keith. '**Frequency of Organic Compounds Identified in Water**'. Athens,
 610 Georgia: US Environmental Protection Agency, (1976). EPA-600/4-76-062.

611 G. Snyder and U. Fehn. '**Global Distribution of ¹²⁹I in Rivers and Lakes: Implications for Iodine Cycling**
 612 **in Surface Reservoirs**'. Nuclear Instruments and Methods in Physics Research Section B: Beam
 613 Interactions with Materials and Atoms, Proceedings of the Ninth International Conference on
 614 Accelerator Mass Spectrometry, 223-224 (2004), pp. 579-586.
 615 <https://doi.org/10.1016/j.nimb.2004.04.107>.

616 J. Song, W. Huang, P. Peng, B. Xiao and Y. Ma. '**Humic Acid Molecular Weight Estimation by High-**
 617 **Performance Size-Exclusion Chromatography with Ultraviolet Absorbance Detection and**

618 **Refractive Index Detection**'. Soil Science Society of America Journal, 74 (6) (2013), pp. 2013-
619 2020. <https://doi.org/10.2136/sssaj2010.0011>.

620 T.F. Speth and R.J. Miltner. '**Technical note: Adsorption capacity of GAC for synthetic organics**'.
621 Journal AWWA, 82 (2) (1990), pp. 72-75. <https://doi.org/10.1002/j.1551-8833.1990.tb06922.x>.

622 Standard Methods For the Examination of Water and Wastewater (5710) '**Formation of**
623 **trihalomethanes and other disinfection by-products**'. (2017), DOI: 10.2105/SMWW.2882.112.

624 C.H. Tessmer, D. Radisav, V. Lois and J. Uranowski. '**Impact of Oxygen-Containing Surface Functional**
625 **Groups on Activated Carbon Adsorption of Phenols**'. Environmental Science & Technology, 31
626 (7) (1997), pp. 1872-1878. <https://doi.org/10.1021/es960474r>.

627 A-C. Tugulea, R. Aranda-Rodriguez, D. Bérubé, M. Giddings, F. Lemieux, J. Hnatiw, L. Dabeka, and F.
628 Breton. '**The Influence of Precursors and Treatment Process on the Formation of Iodo-THMs**
629 **in Canadian Drinking Water**'. Water Research, 130 (2018), pp. 215-223.
630 <https://doi.org/10.1016/j.watres.2017.11.055>.

631 A-C. Tugulea, R. Aranda-Rodriguez, M. Giddings, F. Lemieux and J. Hnatiw. '**Iodo-THM Formation**
632 **During Chlorination of Source Waters With Naturally Occurring Ammonium and High Sodium**
633 **Content**'. In *Disinfection By-Products in Drinking Water*, Special Publication No. 352, (2015),
634 pp. 46-58. The Royal Society of Chemistry. K. C. Thompson, S. Gillespie, E. Goslan.
635 <https://doi.org/10.1039/9781782622710-00046>.

636 H.-H. Tung, R. F. Unz, and Y. F. Xie. '**HAA Removal by GAC Adsorption**'. American Water Works
637 Association, 98 (6) (2006), pp. 107-112. <https://doi.org/10.1002/j.1551-8833.2006.tb07687.x>.

638 E. Vasyukova, R. Proft, J. Jousten, I. Slavik, and W. Uhl. '**Removal of Natural Organic Matter and**
639 **Trihalomethane Formation Potential in a Full-Scale Drinking Water Treatment Plant**'. Water
640 Science and Technology: Water Supply, 13 (4) (2013), pp. 1099-1108.
641 <https://doi.org/10.2166/ws.2013.095>.

- E. D. Wagner and M. J. Plewa. '**CHO Cell Cytotoxicity and Genotoxicity Analyses of Disinfection By-Products: An Updated Review**'. Journal of Environmental Sciences, 58 (2017), pp. 64-76.
<https://doi.org/10.1016/j.jes.2017.04.021>.
- World Health Organization - Regional office for Europe. '**Support to the revision of Annex I Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption (Drinking Water Directive) Recommendations.**' (2017) 240 p.
https://ec.europa.eu/environment/water/water-drink/pdf/WHO_parameter_report.pdf.
- J-S. Yang, D-X. Yuan, and T-P. Weng. '**Pilot Study of Drinking Water Treatment with GAC, O3/BAC and Membrane Processes in Kinmen Island, Taiwan**'. Desalination, 263 (1–3) (2010), pp. 271-278.
<https://doi.org/10.1016/j.desal.2010.06.069>.
- T-Y. Zhang, B. Xu, C-Y. Hu, Y-L. Lin, L. Lin, T. Ye, and F-X. Tian. '**A Comparison of Iodinated Trihalomethane Formation from Chlorine, Chlorine Dioxide and Potassium Permanganate Oxidation Processes**'. Water Research, 68 (2015), pp. 394-403.
<https://doi.org/10.1016/j.watres.2014.09.040>.
- X. Zhao, J. Ma and U. von Gunten. '**Reactions of Hypoiodous Acid with Model Compounds and the Formation of Iodoform in Absence/Presence of Permanganate**'. Water Research, 119 (2017), pp. 126-135. <https://doi.org/10.1016/j.watres.2017.04.033>.
- Q. Zhou, S. E. Cabaniss and P. A. Maurice. '**Considerations in the Use of High-Pressure Size Exclusion Chromatography (HPSEC) for Determining Molecular Weights of Aquatic Humic Substances**'. Water Research, 34 (14) (2000), pp. 3505-3514. [https://doi.org/10.1016/S0043-1354\(00\)00115-9](https://doi.org/10.1016/S0043-1354(00)00115-9).