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

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13 **Abstract:**

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

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

34 **Keywords:**

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

36

37

38 **1. Introduction**

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

56 The concentration and properties of aqueous NOM have a significant influence on the formation of
57 DBPs during disinfection. The different reactive fractions of NOM can be present in a wide range of
58 concentration and preponderance within the same geographical area as for example the hydrophobic
59 fraction representing from 30 to 84% of the raw water NOM in 30 resources across Scotland (Golea et
60 al. 2017). In addition, the level of bromide and iodide in water plays an important role in DBP
61 formation, inducing the formation of a mix of chlorinated, brominated and iodinated DBPs (Bichsel
62 2000; Jones et al. 2011; Hua et Reckhow 2012; Roccaro et al. 2014; Zhang et al. 2015; Allard et

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

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

80

81 **2. Material and Methods**

82 **2.1. Water resource, drinking water treatment plant and sample collection**

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

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

96

97 Samples were collected from the reservoir (raw water) and after each treatment step in the spring and
98 summer of 2018. Three different campaigns were performed, two campaigns (A and B) for the
99 determination of the THM formation potential (THMFP) and the characterization of precursors, and
100 one (campaign C) for the determination of THMs and HAAs (Table S1). Amber glass bottles of 2.5 L
101 were used for the collection of samples to perform chlorination tests and for determination of initial
102 DBP concentrations. A quenching agent (sodium thiosulfate for THMs (4.65 mg L^{-1}) and ascorbic acid
103 (5 mg L^{-1}) for HAAs) was added in excess to the sand filtrate, GAC filtrate and final water, as these three
104 water samples contain or potentially contain some residual free chlorine. Samples were filtered
105 through $0.45 \text{ }\mu\text{m}$ polyethersulfone (PES) membrane filters within a few hours after sampling. In
106 addition, 30 mL samples were taken for dissolved organic carbon (DOC) and size exclusion
107 chromatography (HPSEC) analysis. These were taken at the same sampling locations using a glass
108 syringe, immediately filtered using $0.45 \text{ }\mu\text{m}$ PES syringe filters (after discarding the first 5 mL of filtrate),
109 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
110 chlorination experiments or analysis.

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

113 (Agilent® 1260 Infinity II) equipped with a size exclusion column (Agilent® Bio SEC-5 column, 100 Å;
114 300 mm x 7.8 mm, 5 µm particle size), with an exclusion limit range of 100 to approximately 100,000
115 Da. A phosphate buffer eluent was used: 1 g L⁻¹; pH 6.8 and ionic strength of 0.039 M (Zhou et al.
116 2000; Song et al. 2010). Other parameters used during exclusion chromatography are an injection
117 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.
118 The HPSEC is coupled to a diode array detector equipped with a 60 mm high sensitivity cell. The eluting
119 dissolved organic matter fractions were detected using UV absorbance at 254 nm. Samples with
120 organic carbon concentrations exceeding 5 mgC L⁻¹ were diluted before analysis to avoid fouling of the
121 column and signal saturation.

122 2.2 Development of high sensitivity methods

123 A headspace-trap method has been developed for the analysis of the 10 THMs. The analytical
124 instrument used was a Trace™ 1300 GC coupled with an ISQ-LT single quadrupole mass spectrometer
125 (Thermo Scientific®) operating in SIM mode. A ZB-5MS (Phenomenex®) column (30 m × 0.25 mm ID, 1
126 µm film thickness) was used for gas chromatographic separations. The headspace trap injector (Perkin
127 Elmer® TurboMatrix Headspace 40 Trap) was directly connected to the GC-MS bypassing the inlet split
128 of the GC injector. For THMs analysis, 10 mL of the water samples were transferred into 22 mL glass
129 vials containing 4 g of sodium sulfate (2.8 M), and were spiked with 1,2-dibromopropane as internal
130 standard (6.4 µg L⁻¹). The vials were immediately sealed and stirred in a vortex mixer until complete
131 salt dissolution. This method ensured low quantification limits for the 10 THMs included in this study,
132 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).

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

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

145 **Table 1**

146 **Iodide, iodate and bromide** were measured (on quenched samples) using a liquid chromatograph
147 coupled to an inductively coupled plasma mass spectrometer (HPLC-ICP-MS). Separation was done by
148 a Dionex IonPac AS16 (2 x 250 mm) analytical column with an AG16 (2 x 50 mm) guard column using
149 NaOH 20 mM gradient eluent (Table S5). ICP-MS (Agilent 7900) conditions were set at an RF Power of
150 1550W, no gas mode (collision cell), with an aerosol dilution (0.1 L min^{-1}), and bromine and iodine were
151 determined through their ^{79}Br and ^{127}I isotopes, respectively. The quantification limit was $0.2 \mu\text{g L}^{-1}$ for
152 all 4 species. Total iodine and bromine in the water samples were determined by ICP-MS (Varian 820
153 MS) in 0.5% tetramethylammonium hydroxide matrixes with ^{129}Xe as internal standard (Balaram et al.
154 2012). Analyses were performed using He at 100 mL min^{-1} at the collision reaction interface (skimmer
155 cone) to handle potential polyatomic interferences. The quantification limit level was $0.5 \mu\text{g L}^{-1}$ for
156 both iodine and bromine.

157 **2.2. Chlorination tests**

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

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

173

174 **3. Results and discussion**

175 **3.1. THMFP vs. NOM fractions**

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

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

187 the 27 to 167 $\mu\text{g THM}/\text{mgC}$ range (Table S6). As such, the DOC in this surface water has an intermediate
188 reactivity towards the formation of DBPs compared to the full range of NOM characterized in
189 literature. The THMFP/DOC ratio (Figure S2) decreases progressively along the treatment line (around
190 35% for both campaigns), thus the THMFP is more reduced than the DOC during treatment. The same
191 behavior has been observed in several studies (Table S6). For example, Golea et al. (2017) show a 50%
192 decrease of the THMFP/DOC ratio during water treatment. This reflects a more preferential removal
193 of the highly reactive organic THM precursors by the water treatment process – such as reactive
194 hydrophobic fractions by coagulation-decantation – or the progressive transformation of NOM
195 towards less reactive moieties as the DOC is not significantly removed during nitrification nor in the
196 filtration steps.

197 **Figure 1**

198 Considering the speciation of the THM4 formed in the THMFP tests (Figure S1), CHCl_3 is the main THM
199 formed at all treatment steps. Of the four regulated THMs, the three brominated species were present
200 in relatively low concentrations, accounting for 12-51% (mass weighted) of the THM4 despite a
201 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
202 brominated THM species present, being formed at all treatment steps. In the standardized protocol of
203 the formation potential tests, chlorine is introduced in a large excess explaining the predominance of
204 chloroform and the extremely low I-THMs levels ($<0.1 \mu\text{g L}^{-1}$). In the chlorinated final water from the
205 drinking water treatment plant (residual = $0.3 \pm 0.1 \text{ mgCl}_2 \text{ L}^{-1}$) the main species found were CHBrCl_2
206 and CHBr_2Cl . This difference in detected THM species is due to the higher rate constants observed for
207 reactive bromine species compared to reactive chlorine species (Criquet et al. 2015), thus the NOM
208 precursor sites are preferentially brominated at low chlorine doses. The THM4 in the final water ranged
209 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
210 Union.

211 In Figure 1, a similar trend is shown between the reductions of the Δ THMFP with DOC (a) and the humic
 212 substance fraction measured using SEC-UV (b). This fraction, corresponding to compounds of relatively
 213 high molecular weight, is the main fraction removed by the coagulation step (reduction of around 90%
 214 of its UV absorbance in the SEC chromatogram; Figure 1d). These results are in good agreement with
 215 previous studies which have found good correlation with this particular fraction (Vasyukova et al.
 216 2013; Li et al. 2014; Golea et al. 2017). Assuming that the UV absorbance properties of humic
 217 substances (HS) are not significantly changed during coagulation, a lower reduction of THMFP (70%)
 218 compared to humic substances (90%) is observed, underlining the role of other organic fractions in
 219 addition to HS as THM precursors. In addition, the DBPFP was further reduced while the humic
 220 substances were not removed by the following treatment steps (Figure 1b). A proportional decrease
 221 of the THMFP vs. the building-block fraction was then observed during the two sampling campaigns
 222 (Figure 1c). Good correlations were obtained for the steps after coagulation/decantation ($r^2 = 0.79$,
 223 Figure 1c) when the remaining humic substances were no longer removed.

224 3.2. Bromine incorporation

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

$$230 \quad BIF (THMs) = \frac{[CHBrCl_2] + 2 [CHBr_2Cl] + 3 [CHBr_3]}{[CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]} \quad \text{Eq. 1}$$

231 The incorporation of bromine into THMs after the THMFP tests increases along the treatment line
 232 (Figure 2). The BIF after the THMFP test is low for the raw water and after the nitrification step (around
 233 0.15), then increases after coagulation to approximately 0.4, and increases further after GAC filtration
 234 (from 0.5 to 0.65 for campaigns A and B, respectively). It has to be noted that the bromide
 235 concentration decreases after sand filtration due to the intermediate chlorination step, but increases

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

238

239 **Figure 2**

240 The BIF for Δ THMFP was found to increase linearly in function of the Br⁻/DOC (Figure 3). Effectively, a
241 higher Br⁻/DOC ratio (usually the result of DOC removal during treatment) favors reaction of chlorine
242 with Br⁻ instead of DOC, resulting in the formation of reactive bromine species (which in turn react
243 with NOM to form brominated THMs, resulting in a higher BIF). The maximum BIF value (0.63) is
244 reached after GAC filtration, where the Br⁻/DOC ratio is highest. Even though this value represents a
245 quite moderate bromine incorporation into THMs, one should keep in mind that the formation
246 potential protocol favors reactive chlorine species over bromine species. The samples from both A and
247 B campaigns show a single correlation between the BIF and Br⁻/DOC ratio (Figure 2), however when
248 correcting the Br⁻/DOC ratio for the amount of Cl₂ consumed, different correlations for campaigns A
249 and B are found (Figure S6). In addition, adjusting the Br⁻/DOC ratio with consumed chlorine increases
250 the linearity of the established correlations with BIF, as indicated by regression coefficients of 0.99 and
251 0.91 for campaigns A and B respectively (Figure S6 – with correction for Cl₂ consumed), and regression
252 coefficients of 0.80 and 0.83 for campaigns A and B respectively (Figure 3, regression lines not shown
253 – without correction for Cl₂ consumed). The different slopes could be due to the higher bromide
254 concentration in the raw water for the campaign B (170 µg L⁻¹) compared to campaign A (140 µg L⁻¹) in
255 conjunction with lower DOC values (6.7 and 8.5 mgC L⁻¹ respectively for campaigns B and A). Then, the
256 competition between NOM and Br⁻ is in favor of a higher formation of bromine active species in
257 campaign B.

258 The BIFs of the treated water having a chlorine residual around 0.3 mgCl₂ L⁻¹ (sampled from the water
259 treatment works without further treatment except chlorine residual quenching), ranged from 1.1 to
260 1.4 for campaigns A and B respectively, which is much higher than the ones observed for the THMFP.
261 This matches BIF values found by Hong et al. (2013), ranging between 0.86 and 1.42 for bromide values

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

267

268 **3.3. Iodine speciation and I-DBP formation**

269 The level of iodide ion found in the raw water during this survey highly varied, with concentrations
270 between < 0.2 and $18.2 \mu\text{g L}^{-1}$. These concentrations are however in line with the range of
271 concentrations usually found in surface waters (Snyder et Fehn 2004; Salminen et al. 2005). During
272 campaign A (Figure 3), iodide was not detected and iodate was below the quantification limit ($< 0.2 \mu\text{g}$
273 L^{-1}) in the raw water, however, some I-THMs and mainly iodate were found after intermediate
274 chlorination (see below). Then, a part of iodine could certainly be present in the raw water as
275 incorporated in the organic matrix. Analysis of total iodine by ICP-MS during campaign B confirmed
276 this fact, with only 17% of the total iodine present as iodide in the raw water (total iodine = 33.3
277 $\mu\text{g L}^{-1}$; $[\text{I}^-] = 5.6 \mu\text{g L}^{-1}$ and $[\text{IO}_3^-] < 0.2 \mu\text{g L}^{-1}$) which is in the same range as that found by Gilfedder et
278 al. (2009) (15% of iodine as inorganic iodine in a lake). The absence of supplementary peaks on the
279 HPLC-ICP-MS chromatogram suggests that the iodine is bound to non-ionic organic species. Regular
280 monitoring since 2017 shows the presence of iopromide and iomeprol up to $0.3 \mu\text{g L}^{-1}$ in the raw
281 water. However, these target substances could represent only a small part of the iodinated
282 anthropogenic substances present in this water; no extensive study has been performed on iodine
283 speciation and importance of the organic fraction. In addition, other sources of organic iodine may
284 originate from the surrounding agricultural activities, and may include iodinated cattle feed
285 supplements (Moreno-Reyes et al. 2011), as well as iodophor medication, iodine-containing
286 sterilizers of milking equipment, teat dips and udder washes, or pesticides and fungicides containing

287 iodine (Scientific Committee on Food; Health and Consumer Protection Directorate-General
288 2002). One should also consider that some authors suggest that the major fraction of iodine in a
289 number of natural fresh waters is bound to high molecular weight humic substances (Gilfedder et al.
290 2009). This complexation could then interfere with the analysis of iodide. Iodate was near absent
291 ($< 0.2 \mu\text{g L}^{-1}$) in raw water and all treatment steps before intermediate chlorination.

292 **Figure 3**

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

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

319 **3.4. Impact of GAC filtration on DBPs: THMs, I-THMs and HAAs**

320 The presence of an intermediate chlorination step in this water treatment plant allows to assess the
321 efficiency of the full-scale activated carbon filtration to remove DBPs. While two previous studies
322 found that some I-THMs were removed by GAC filtration (Cancho et al. 2000; Cuthbertson et al.
323 2019), scarce information on the removal efficiency of I-DBPs in a full scale drinking water treatment
324 plant is available. THM₄ were formed (from 15 up to 28 µg L⁻¹) and are present in the treatment steps
325 after intermediate chlorination. Some iodinated THMs were formed as well, adding up to a total of
326 270-312 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
327 analyzed (Figure 5).

328 **Figure 4**

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

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

352 **Figure 5**

353 HAAs show high removal efficiency by activated carbon filtration, from 87% (trichloroacetic acid) up to
354 97% (bromo- and dibromoacetic acids). The overall removal, based on total mass of the 7 HAAs
355 analyzed in this study is around 95% (Table S7, the same removal efficiency is obtained considering the
356 HAA5). Tung et al. (2006) showed that adsorption plays a minor role in HAA removal and GAC filters
357 have a lower adsorption capacity for mono- and dihaloacetic acids than for the regulated THMs. On the
358 other hand, Kim et Kang (2008) showed that the removal of HAA5 by adsorption was high at the early
359 stage of GAC operation and better than for THM4, with breakthrough occurring later. The GAC
360 filtration here consists of 6 filters with 4 to 5 filters working in parallel during the campaigns. The
361 average time since reactivation varied from 305 to 350 days for the 3 campaigns corresponding to bed

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

370 **3.5. Relative toxicity assessment**

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

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

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

395 Considering THMs, the general trend of cytotoxicity is similar to the species-specific concentration
396 (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
397 despite exhibiting the highest concentration only the relative toxicity of $CHBrCl_2$, having the highest
398 LC_{50} , is reduced compared with the other species. Considering I-THMs, their low concentrations and
399 the absence of iodoform (most cytotoxic I-THM, $LC_{50} = 4.47 \times 10^{-5}$ M), induce a low contribution of only
400 0.48-0.58% to the overall THM cytotoxicity in final waters. The GAC filtration showing high removal of
401 I-THMs contributes significantly to reduce the impact of these species to the relative cytotoxicity, as
402 their contribution has been seen to account for up to 4.5% (campaign B) of the overall cytotoxicity of
403 the THMs formed from the intermediate chlorination.

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

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

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

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

434

435

436 3. Conclusion

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

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

452 In this water treatment plant, the activated carbon filtration is effective to remove the HAAs and I-
453 THMs (> 80%) formed during intermediate chlorination but to a lesser extent for THM4 (< 40%). A
454 preferential removal in the order I-DBPs>Br-DBPs>Cl-DBPs is observed with no clear trend related to
455 the compound hydrophobicity suggesting other factors such as biodegradation or halogen bonding are
456 also governing DBP removal on GAC. The amount of DBPs formed per quantity of DOC decreases
457 through the treatment line showing the preferential removal of the highly reactive precursors. This is
458 especially the case for HAAs that are not formed in a high extent during the final chlorination step.
459 From a theoretical assessment, the relative cytotoxicity of HAAs is more important than the one of
460 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

471 **Figure captions**

472 **Figure 1:** Evolution of the ΔTHMFP ($[\text{THM}]_{\text{FP}} - [\text{THM}]_0$) in waters sampled after the different
473 treatment steps in function of (A) the DOC content (B) the fraction of humic substances and (C) the
474 fraction of building blocks for treatment steps after coagulation. (D) Size exclusion chromatograms
475 with UV detection (254 nm) for campaign A (campaigns B and C in Figure S3). 1- raw water, 2- after
476 nitrification, 3- after coagulation-decantation, 4- after intermediate chlorination and sand filtration,
477 5- after GAC filtration, 6- after final chlorination. (a.u.: arbitrary unit)

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

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

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

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

492

493

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