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Removal of disinfection by-product precursors by ion exchange resins

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Abstract

The removal of dissolved organic carbon (DOC) is a key factor in the control of disinfection by-product (DBP) formation in drinking water. Ion exchange process deals with the removal of naturally negatively charged organic matter. A fluidized bed column test has been chosen to test in parallel the efficiency of 4 different anionic exchange resins (Purolite PPA860S, Dowex TAN-1, Amberlite IRA-958 and IRA-410) in terms of DOC fraction removal and related DBP formation reduction. IRA-410 was shown to be the best performing resin in terms of DOC and DBP formation potential reduction followed by PPA860S. These resins removed respectively 41 and 37% of DOC, with humic substances as the main target of the two resins (68 and 72% reduction, respectively, based on size exclusion chromatography with an organic carbon detector). The UV absorbance was reduced in a higher proportion than the DOC demonstrating a preference of the resins for the relatively hydrophobic compounds. The reduction in trihalomethane and haloacetic acid formation was higher than the DOC removal for IRA-410 and PPA860S (53 and 59%, respectively); whereas IRA-958 on the other hand showed a lower reduction in DBP formation potential than its DOC removal. All the resins showed a much higher reduction of iodinated trihalomethanes formation potential (66 to 96% reduction compared to raw water) due to the removals of iodide in addition of organic precursors. However, in a context of increasing halide concentrations, the different resins showed a reduction of their efficiency to control the formation of DBPs.

Keywords: chlorination, bromide, iodide, DBP, NOM

1. Introduction

34 The most commonly applied methods for natural organic matter (NOM) removal from water are
35 coagulation,¹ adsorption² and membrane filtration³. Ion exchange processes (IEX) – where negatively
36 charged NOM fractions are removed by reversible exchange of a counter ion, usually chloride, from
37 the anionic resin surface⁴ – were introduced more recently, with magnetic ion exchange resin (MIEX)
38 early in the 2000s as first industrial application in drinking water.⁵ Since then, different types of resins
39 are regularly developed and tested. Different processes such as suspended ion exchange (SIX)⁶ and
40 fluidized ion exchange (FIX)⁷ have been explored as well. Ion exchange is of particular interest as a pre-
41 treatment before coagulation as it has been shown to significantly reduce the coagulant dose required
42 (by 50 to more than 80%),⁸⁻¹⁰ as well as increase the floc size and strength.¹¹ IEX is also more efficient
43 than coagulation for the removal of charged organic compounds.¹² Using IEX in combination with
44 coagulation, can thus remove both a higher amount of dissolved organic carbon (DOC), and a broader
45 spectrum of DOC as hydrophilic and low molecular weight fractions (LMW) fractions are more difficult
46 to remove using conventional coagulation treatment.^{13,14} The higher DOC removal is often
47 accompanied with an enhanced reduction in disinfection by-product (DBP) formation potential.^{8,15}
48 Furthermore, anionic resins can also remove bromide from certain water sources with low alkalinity¹⁵,
49 thereby potentially reducing the formation of brominated DBPs during disinfection. The removal
50 efficiency of NOM by IEX resins was mainly studied through measuring colour and NOM characteristics
51 such as DOC, TOC, UV absorbance at 254 nm^{12,16,17} and more recently NOM fraction removal.¹⁰ While
52 these studies offer useful guidance in understanding the removal of NOM fractions, less has been done
53 on DBP formation potential, with studies focusing on THMFP and HAAFP generally on one single resin
54 type.¹⁸⁻²¹

55 In this study, the removal of DBP precursors from raw surface water used for drinking water production
56 was investigated on four different ion exchange resins in a fluidized bed column test. The 4 different
57 resins have been compared in term of NOM fraction removal efficiency. These results have been
58 related to the trihalomethane and haloacetic acid formation, including iodinated disinfection by-
59 products. The interest of the IEX process in different scenarios of increasing halide concentrations has
60 been studied in order to evaluate such processes on raw water impacted by high levels of halides and
61 to gain more knowledge on DBP precursors.

62 **2. Materiel and Methods**

63

64 **2.1. Water resource and pilot unit**

65 The raw water is drawn from the river IJzer (Yser) (approximately 80%) downstream of the town of
66 Ieper and from surrounding lowlands (approximately 20%), and stored in a 3 million m³ reservoir.²²
67 The water is characterized by a high NOM content, with an average DOC content of 12 mgC L⁻¹,

68 combined with a high alkalinity and hardness. The Belgian part of the hydrographic basin of the IJzer
69 river covers an area holding 110,000 inhabitants, and a largely agrarian activity, *i.e.* intensive farming
70 and intensive cattle breeding.²³ Due to the combination of high DOC concentration and relatively high
71 alkalinity, the water requires large amounts of coagulant and sulfuric acid during coagulation.²⁴

72 The four resins tested were Purolite PPA860S, Dowex TAN-1, Amberlite IRA-958 and Amberlite IRA-
73 410. The three first mentioned resins are strong base anion type I resins with a quaternary ammonium
74 group, and the last one is a strong base type II resin where a methyl group is replaced with an alcohol
75 group. Their main properties are presented in Table S1. A column experiment was performed in order
76 to better translate the results to a full scale plant. Four parallel transparent PVC columns, with an
77 internal diameter of 86.4 mm were used for performing breakthrough experiments. The resins were
78 pre-treated extensively to avoid possible leaching of residual monomers and to avoid irreversible
79 adsorption of NOM occurring on virgin resins. This procedure consisted of a jar pre-treatment and a
80 dummy loading run in the columns. For the jar pre-treatment, the following regeneration procedure
81 was conducted three times consecutively: regeneration using 3 bed volumes (BV) of a 10% NaCl brine
82 followed by decantation, and a triple rinsing with 3 BV of tap water followed by decantation. After the
83 jar pretreatment procedure, the resins were transferred inside the columns, and a dummy loading run
84 was performed using 500 BV of filtered raw water at an empty bed contact time (EBCT) of 1.73 min,
85 followed by a regeneration with 1 BV of 10% NaCl at an EBCT of 30 minutes and a rinse with 1 BV of
86 tap water at an EBCT of 30 minutes. The latter regeneration procedure has been developed from the
87 long practice on a IEX industrial scale pilot.²⁴ After this extensive pretreatment procedure, the resins
88 were considered to be suitable to perform a representative IEX cycle. The breakthrough experiments
89 were run in parallel for the 4 resins in a fluidized bed modus (*i.e.* bottom – up, Fig. S1) using raw water
90 from the reservoir which had been prefiltered over a 25 µm bag filter (Filtration CVBA, Drogen,
91 Belgium), at an EBCT of 1.73 min.

92 **2.2. Sample collection and analysis prior to chlorination**

93 Samples were taken at 0 BV and every recurring 50 BV, until 500 BV of raw water were treated. To
94 simulate the average treated water quality which would be obtained after 500 BV, a mixed effluent
95 sample was created by mixing equal volumes (208 mL) of each of the 11 taken samples for each resin,
96 for the DBP experiments and LC-OCD measurement. The samples were characterized by size exclusion
97 chromatography (SEC) coupled to organic carbon detection (LC-OCD) at the certified laboratory “Het
98 Waterlaboratorium (HWL)” (Haarlem, Noord-Holland) according to the LC-OCD procedure described
99 in literature.²⁵ The raw water and mixed effluent samples for all four resins were filtered through 0.45
100 µm polyethersulfone (PES) membrane filters within a few hours after sampling. All samples were
101 stored at 4 °C until the chlorination experiments or analysis. Iodide, iodate and bromide were

102 measured using a liquid chromatograph coupled to an inductively coupled plasma mass spectrometer
103 (HPLC-ICP-MS – Agilent 7900). The protocol has been detailed in a previous study.²⁶ The quantification
104 limit was 0.2 $\mu\text{g L}^{-1}$ for all three species. Total iodine and bromine in the water samples were
105 determined by ICP-MS (Varian 820 MS). The quantification limit level was 0.5 $\mu\text{g L}^{-1}$ for both iodine and
106 bromine.

107 **2.3. Chlorination tests**

108 Two different trihalomethane formation potentials have been performed (THM7d and THM24h). The
109 THM7d tests were carried out using a 7-day chlorination procedure according to the Standard Methods
110 5710²⁷ with minor modifications. The samples were placed in either 25 or 50 mL glass reagent bottles
111 with PTFE lined screw caps, buffered with a phosphate solution at $\text{pH } 7.0 \pm 0.2$ and chlorinated using
112 a stock solution of 5 g L^{-1} sodium hypochlorite at different doses in order to ensure samples with free
113 chlorine residuals between 3 and 5 mg L^{-1} at the end of the chlorination test. Samples were incubated
114 in a thermostatically controlled cabinet at $25 \pm 2 \text{ }^\circ\text{C}$ for 7 days, after which the free chlorine residual of
115 each sample was measured using the N, N-diethyl-p-phenylenediamine (DPD) colorimetric method.²⁸
116 In the samples containing a free chlorine residual between 3 and 5 mg L^{-1} , the chlorine residual was
117 quenched using sodium thiosulfate and the samples were stored at 4 $^\circ\text{C}$ in the dark until the THMs
118 were analysed. The 7-day test is the classical procedure to account for the total possible formation of
119 DBPs, however, the high chlorine dose of this test is not suitable for the assessment of iodinated DBPs.
120 To avoid this bias, chlorination experiments have also been performed with a lower chlorine dose, *i.e.*
121 0.3 $\text{mg Cl}_2 \text{ L}^{-1}$ residual after a contact time of 24 h and at a temperature of 20 $^\circ\text{C}$ to assess the evolution
122 of THMs and HAAs after IEX treatment. DBP formation potential tests have been performed on the IEX
123 treated waters either without modifications or with bromide and iodide concentrations equalised in
124 order to compare the efficiency of the different resins in the same halide concentration conditions. In
125 addition, the concentration of halide has been varied in the IEX treated waters. The concentrations of
126 bromide was varied from 2.5 to 27.5 μM (228 to 2200 $\mu\text{g L}^{-1}$) while the iodide concentration was kept
127 constant (0.5 μM *i.e.* 63 $\mu\text{g L}^{-1}$). This led to molar bromide/iodide ratios ranging from 5.7 to 55,
128 comparable to a previous study²⁹ (Table S2). In a second set of experiments, the concentration of
129 iodide was varied from 0.06 to 2 μM (7 to 254 $\mu\text{g L}^{-1}$) with a constant bromide concentration (228 μg
130 L^{-1} *i.e.* the highest residual bromide concentration among the IEX treated waters).

131 **2.4. Disinfection by-product analysis**

132 Our previous study developed high sensitivity headspace-trap methods for the analysis of the 10 THMs
133 and 7 HAAs.²⁶ The same methods were used in this study on a TraceTM 1300 GC ISQ-LT single
134 quadrupole mass spectrometer (Thermo Scientific®) coupled to a TurboMatrix Headspace 40 Trap

135 (Perkin Elmer®) and are briefly described. For THMs analysis, 10 mL of the water samples were
136 transferred into 22 mL glass vials containing 4 g of sodium sulfate (2.8 M), and were spiked with 1,2-
137 dibromopropane as internal standard (6.4 $\mu\text{g L}^{-1}$). The vials were immediately sealed and stirred in a
138 vortex mixer until complete salt dissolution. Haloacetic acids (HAA5 + iodoacetic and
139 bromochloroacetic acids) were analysed by a one-step procedure. HAAs in aqueous medium form ion-
140 pairs with tetrabutylammonium hydrogensulfate and react with dimethylsulfate to produce methyl
141 haloacetates which are directly volatilized in the headspace. 9.84 mL of the water samples (without pH
142 adjustment) were spiked with bromopropionic acid (10 $\mu\text{g L}^{-1}$) as internal standard and placed in a 22
143 mL glass vial containing 4 g of sodium sulfate. 100 μL of a 0.5 M ion pairing agent (tetrabutylammonium
144 hydrogensulfate, final amount of 2.3 μM) and 60 μL of derivatization reagent (dimethylsulfate) were
145 then added. The vials were immediately sealed and stirred before being placed into an autosampler.
146 The analysis was performed after 2 to 4 hours of reaction time, this time should not exceed 5 hours to
147 avoid the hydrolysis of the methylesters formed.

148 **3. Results and discussion**

149

150 **3.1. Effect of ion exchange treatment on NOM and inorganic compounds**

151

152 **3.1.1. Raw water composition**

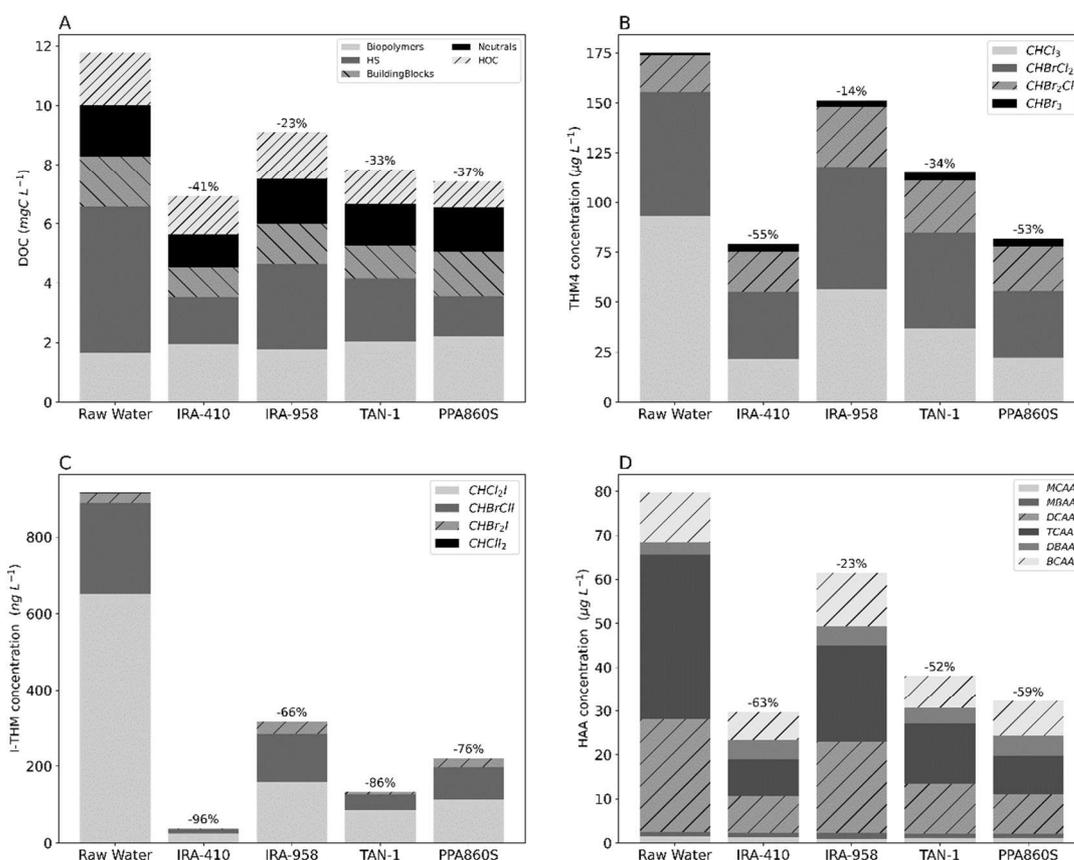
153 The DOC of the raw water was relatively high, around 12 mgC L^{-1} (Fig. 1A), but at a typical level for this
154 site. The SUVA was moderate, around 2 indicating the presence of hydrophilic and/or low molecular
155 weight compounds. LC-OCD fractionation indicated that humic substances (HS) dominated (40%),
156 followed by biopolymers, building blocks (BB) and low molecular weight neutrals (LMWN), these 3
157 fractions each representing approximately 14% of the DOC (Fig. 1A). No low molecular weight acids
158 (LMWA) were found in the feed water by LC-OCD. Additionally, around 15% of the DOC is not eluted
159 through the column presumably due to hydrophobic interactions; this represents the so-called
160 hydrophobic organic carbon fraction (HOC). The mineralization of the water is relatively high, mainly
161 with bicarbonate (247 mg L^{-1}) but also with quite a large amount of chloride (147 mg L^{-1}) and sulfate
162 (104 mg L^{-1}); the cations are dominated by sodium (105 mg L^{-1}) and calcium (72 mg L^{-1}) (Table S3).

163

164 **3.1.2. IEX treated waters**

165 The treatment of raw water by ion exchange removed from 23 up to 41% of the dissolved organic
166 carbon content based on DOC measurement depending on the type of resins (Fig. 1a). The best
167 removal is obtained with the type II strong base resin IRA-410, a styrene divinyl benzene type with a
168 dimethyl ethanol ammonium functional group. This resin has the best total exchange capacity (≥ 1.25

169 eq L⁻¹) according to the manufacturer information (Table S1). This parameter however does not explain
 170 the difference of removals obtained for the 3 other resins, which are all type I resins with a quaternary
 171 ammonium group (from 0.7 to ≥ 0.8 eq L⁻¹). The DOC removal by such resins is usually in the 40-70%
 172 range. In some cases, lower removal rates due to competition with sulfates were observed (Table S4).
 173 In this water, sulfate is effectively competing for the ion exchange (see details below), in addition, the
 174 low SUVA NOM could also be a poor target of exchange sites.



1

176 *Figure 1: Assessment of IEX process efficiency for the 4 different resins compared to raw water for dissolved*
 177 *organic carbon removal and disinfection by-product formation potential (24h – low chlorine residual). A) NOM*
 178 *fraction removal assessed by LC-OCD B) THM4, C) I-THMs and D) HAAs. Numbers above bars correspond to the*
 179 *reduction percentage compared to the concentration of each parameter in raw water.*

180

181 Considering the removal of the different fractions of NOM, the humic substances fraction is the main
 182 one removed by the different IEX resins, both in terms of DOC (from 41 to 72%) and UV254 absorbing
 183 fraction (58-91%), followed by the building block fraction (12-41% for DOC and 35-79% for UV254) and
 184 LMWN fraction for DOC removal (13-36% while the UV254 LMWN showed no removal.) (Fig. 1A, Table

185 S5). After IEX treatment, the concentration of the biopolymer fraction was found to slightly increase
186 by 6-32% in terms of DOC, which may have been caused by the release of polymeric IEX material³⁰ but
187 also in some extent by a different deconvolution due to the lowering of the following HS peak. Overall,
188 the SUVA was lowered by the IEX treatment system by 32-62%, which is higher than the DOC removal,
189 indicating preferential removal of higher-SUVA components. The final SUVA values (0.75-1.34) indicate
190 that the remaining NOM is mainly hydrophilic. These results are in agreement with previous studies
191 (Table S4) that show effective removal of high charge density organic fractions such as HS and less
192 effective removal of BB, LMWN, and no removal of biopolymers due to size exclusion, although one
193 study did find PPA860S to efficiently remove most major NOM fractions, including biopolymers.³¹
194 The most effective resins for the removal of HS was Purolite PPA860S (72% removal) and Amberlite
195 IRA-410 (68%). The later exhibits the most effective removal of BB and LMWN fractions (41% and 36%
196 removal respectively), which then explain its overall best performance (Table S5). The molecular
197 weight of HS in waters treated by 3 resins (IRA 958, TAN-1 and PPA860S) decreased by 15-22% with
198 the lowest MW for PPA860S (centre on 400 g mol⁻¹), indicating a preference for the removal of the
199 highest molecular weights HS. In fact, the macroporous acrylic structure of PPA 860S is generally better
200 for the removal of large anions.^{4,12} On the opposite, the molecular weight of HS after treatment by the
201 IRA-410 did not change. Removal of HS and BB fractions by the anionic resins can mainly be explained
202 by ionic interactions while the removal of the LMWN could possibly be explained by physical
203 adsorption onto the resin material.³⁰ The removal of this later fraction is higher for IRA-410 and TAN-
204 1 resins (36 and 18% respectively) compared to the others (13%). This should be related to the resin
205 types as styrenic structure based resins (structures of TAN-1 and IRA-410) exhibiting more hydrophobic
206 interaction than the acrylic resins (structures of IRA 958 and PPA860S, Table S1).

207 The cation removal for all the resins was low or inexistent as these resins are designed for the exchange
208 of anions. Considering iron, while its concentration is quite low in the raw water (15 µg L⁻¹), the
209 concentrations after treatment were systematically below that level (by 13-33%); its retention possibly
210 happens by complexation with humic substances.^{32,33}

211 A significant increase in Cl⁻ concentrations after ion exchange treatment is obviously observed for all
212 resins (Table S3). However, a large part of this release is attributable to the ion exchange with sulfate
213 (from 44 up to 89% of the initial 104 mg L⁻¹ of sulfate; Table S3). Indeed, sulfate ions are smaller than
214 NOM molecules, hence the ion exchange process is kinetically faster for this ion.³² A nearly 50 %
215 reduction in DOC removal when increasing the sulfate level to a concentration of 100 mg L⁻¹ for Purolite
216 A860³⁴ (PPA860S corresponds to a sieved fraction of A860). Then, a major part of the practical
217 exchange capacity of the resins goes to the removal of sulfate (0.96-1.94 meq L⁻¹, which represents 64-
218 77% of the actual ion exchange), and another small part to bicarbonate (0.08-0.36 meq L⁻¹). The
219 potential release of chloride from incomplete washing of the resin is taken into account considering

220 an equivalent increase of sodium concentrations (0.28-3.47 meq L⁻¹). Finally, only 10 to 19% (0.25-0.32
221 meq L⁻¹) of the total amount of chloride exchanged could be attributed to NOM removal for 3 of the 4
222 resins. For IRA-958, the calculated amount of chloride exchanged for NOM was negative (-0.05 meq L⁻¹)
223 and close to zero, likely due to the uncertainties on the analytical measurements of the ion
224 concentrations. Finally, the concentration of chloride in the treated waters (from 264 to 305 mg L⁻¹)
225 exceeds the European quality guideline of 250 mg L⁻¹ for three of the four resins in the conditions used
226 here. However, in industrial processes, extensive rinses would have to be performed to avoid
227 unnecessary chloride release from salts trapped in micropores that only slowly diffuse when the resin
228 swells in a lower ionic strength water compared to the saline regeneration solutions.

229 In contrast to what has been observed on MIEX resins,¹⁵ bromide was not removed in our experiments
230 and even increased by up to 17%, perhaps due to some bromide contamination during resin
231 regeneration (bromide being a common contaminant of commercially available NaCl). The bromide
232 anions may also have been outcompeted for binding sites by the other anions.¹⁵ This is confirmed by
233 the proportional increase between chloride and bromide concentrations observed for 3 of the 4 resins
234 (the concentration is constant after IRA-410 treatment ; Fig. S2). However, iodide was significantly
235 exchanged onto the resin (18-85%) for IRA-410, TAN-1 and PPA860S (Table S3), which has not been
236 previously reported in the literature for these 3 resins. IRA-958 was not able to significantly remove
237 iodide (3% reduction).

238

239 **3.2. Removal of DBP precursors**

240

241 **3.2.1. THM7d, THM24h and HAA24h speciation**

242 The formation potential of the THM4 after 7 days (THM7d) is around 550 µg L⁻¹ in the raw water (Fig.
243 S3), which is in the same range as noticed for previous experiments on the same site.²⁶ CHCl₃ is the
244 main THM formed in all waters after the 7-day formation potential test. The reduction in THM7d
245 compared to the raw water is in the range 30-60%. The order of THMFP reduction efficiency for the
246 resins was: IRA-958 < TAN-1 ≈ PPA860S < IRA-410 (Fig. S3). Figure 1 shows the decrease in DBP
247 formation potential after 24 hours (residual chlorine 0.3 mgCl₂ L⁻¹) through the treatment of water with
248 the four IEX resins. The THM24h varies from around 80 to 150 µg L⁻¹ in the different IEX treated waters
249 compared to 175 µg L⁻¹ in the raw water. CHBrCl₂ is the major compound, due to the lower chlorine
250 dose used leading to a higher bromide to chlorine ratio. Compared to the 7-day test, not only are the
251 formation potentials 2.5-3.5 times lower after the 24-h test, but the reduction in THMFP compared to
252 the raw water is also lower, by around 25% (mass or molar balance) (Fig. 1B). This observation should
253 be then related to the preferential removal by IEX resins of DBP precursors which have a slow reactivity

254 towards chlorination and THM formation. This could be related to the preferential removal of high
255 molecular weight HS. The sum of 7 HAAs was 2 to 3 times lower than for THMs (*i.e.* 35 to 85 $\mu\text{g L}^{-1}$; Fig.
256 1D). Compared to the THMs the reduction in HAAFP is higher, in the range 23-63% based on the 24-
257 hour HAA formation potential tests (Fig. 1D). DCAA, TCAA and BCAA are the main HAAs formed,
258 representing 78 to 93% of the measured HAAs. The mono-HAAs are at much lower levels, as is usually
259 the case in the literature.³⁵

260 The order of removal efficiency of THM24h and HAA24h precursors by the different resins was the
261 same as for the DOC and THM7d with PPA860S and IRA-410 the best performing resins. The decrease
262 in THM4 and HAA FPs followed the trends of DOC and SUVA reductions, a strong correlation ($R^2 > 0.99$)
263 was observed between THM7d of the raw water and the 4 different treated waters and the DOC as
264 well as UV254 and then SUVA (Fig. S4). These trends show a higher reduction of the THMFP compared
265 to the DOC, thus the different IEX resins are more efficient at removing THM precursors than overall
266 DOC. The THMFP/DOC ratio varies from 47 $\mu\text{g mgC}^{-1}$ for the raw water to 32 to 42 $\mu\text{g mgC}^{-1}$ for the
267 treated waters. Considering UV absorption, its reduction is lower than THMFP (Fig. S4), demonstrating
268 that a fraction of the precursors do not absorb UV, and come from more hydrophilic fractions.
269 According to the curve, if the UV absorbance was equal to zero, approximately 140 $\mu\text{g L}^{-1}$ of THMs
270 would still theoretically be formed. On the contrary, 3.4 mgC L^{-1} (about 30 %) of the DOC does not
271 contribute to the THM formation (Fig. S5). Combining these results, a direct proportionality between
272 THMFP and SUVA is observed (slope of 1 between THM7d/THM7d-raw vs. SUVA/SUVAraw) which
273 underlines the relevance of this parameter in the IEX process. The formation potential of THMs and
274 HAAs after the 24-h test also correlated with the DOC, UV and SUVA (R^2 from 0.85 to 0.93, Fig. S5), but
275 the correlations were not as strong as for THM7d (Fig. S4).

276

277 **3.2.2. I-THM24h**

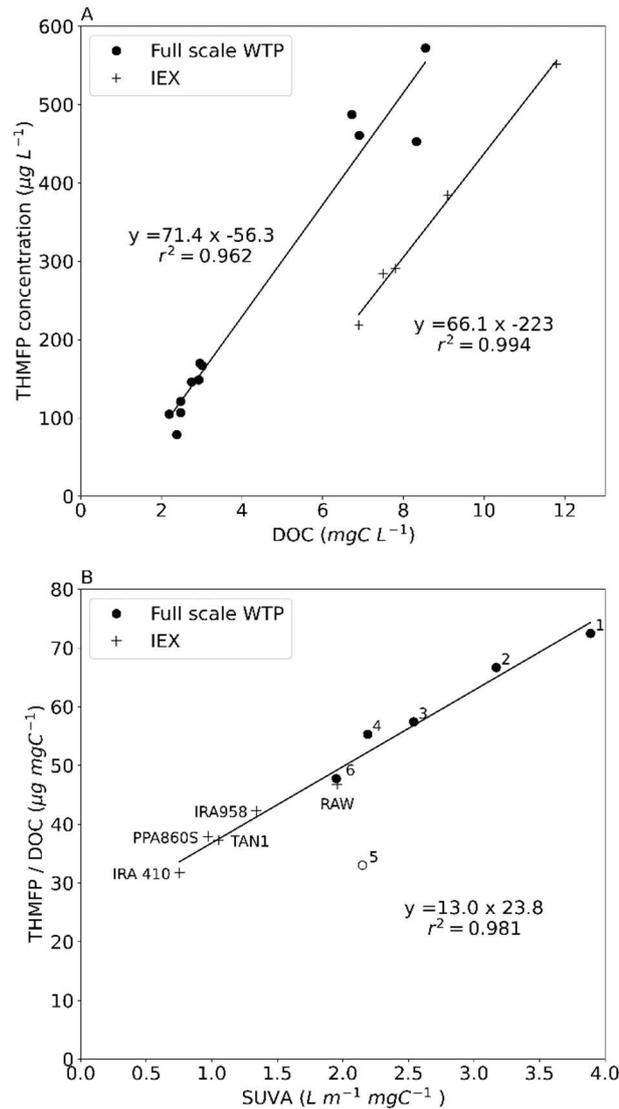
278 Iodinated DBPs are usually more cytotoxic and genotoxic than the brominated and chlorinated
279 analogues.³⁶ Their low odour threshold could also bring issues of medicinal taste and odours to the
280 produced waters.³⁷ From this raw water, the overall I-THM formation is relatively low ($< 1 \mu\text{g L}^{-1}$)
281 certainly due to the low level of iodide in the raw water ($7.2 \mu\text{g L}^{-1}$) but also to its oxidation to iodate
282 (see section 3.3.2). The major I-THMs formed are CHCl_2I followed by CHBrClI and CHBr_2I (Fig. 2B). These
283 compounds correspond to the mono-iodinated compounds which are predominant for low iodide
284 levels.³⁸ In comparison with THM4, the reduction in I-THMFP compared to raw water is 2-10 times
285 higher, in the range 76-96% and much higher than the DOC removal. In fact, the concentration of iodide
286 is reduced after IEX treatment, with different efficiency depending on the resin type. IRA-410 which is

287 the best performing resin for the reduction of I-THMFP reduces the concentration of iodide by more
288 than 80% down to $1.1 \mu\text{g L}^{-1}$. Indeed, the I-THM concentration can be correlated to the iodide
289 concentration ($R^2 = 0.96$; Fig. S6) for all 4 treated waters. However, the formation of I-THMs in the raw
290 water sample is not correlated to the treated waters with much higher I-THMs formed than the
291 correlation with the 4 treated water would have predicted. The content of ammonia in the water (as
292 chloramines favours I-DBP formation compared to chlorine³⁹) does not explain this behaviour either
293 as the raw water shows the same concentration as the waters treated by the IRA-410 and IRA-958
294 resins (around 0.17 mg L^{-1}) and a lower concentration than the waters treated by PPA860S and TAN-1
295 resins (around 0.27 mg L^{-1}). Then, the removal of NOM DBP precursors is a key factor in the control of
296 I-DBP formation. In fact, the IRA-958 resin treated water which shows a low iodide decrease compared
297 to the raw water (<3%) still exhibits a high decrease of I-THMs (76%). This could be due to the removal
298 of specific NOM precursors but also maybe more likely to the increase of iodate formation by favouring
299 the reaction of chlorine (and/or bromine) with iodine reactive species (*i.e.* mainly HOI) compared to
300 the reaction of chlorine (and/or bromine) with NOM.⁴⁰ Thus, all the resins by lowering iodide and/or
301 by removing specific precursors show a beneficial effect, lowering the concentration of I-DBPs.

302

303 **3.2.3. Comparison to the classical treatment line**

304 Sampling campaigns have been performed on the full-scale treatment plant made of nitrification,
305 coagulation-flocculation decantation, intermediate chlorination, sand filtration, activated carbon
306 filtration and final chlorination steps.²⁶ In the classical treatment line, the highest DOC removal occurs
307 during the coagulation step which mainly removes the highest molecular weight fraction, *i.e.*
308 biopolymers and humic substances. The treatment line removes around 70% of DOC for both sampling
309 campaign, with 57 to 65% occurring during the coagulation step. The THMFP is reduced by 80%
310 showing a regular decrease of the ratio THMFP/DOC due to a quite good removal of DBP precursors.²⁶
311 The IEX treatment shows a limited efficiency for the DOC removal compared to the classical treatment.
312 Similarly, the THMFP/DOC ratio is reduced, linked to the decrease of SUVA after IEX treatment (Fig. 2).



313

314 *Figure 2: a) THMFP (7d) in function of DOC and b) THMFP/DOC ratio vs. SUVA values in the full scale treatment*
 315 *plant and IEX treated waters. 1. Raw water 2. nitrification 3. Coagulation-decantation 4.*
 316 *Intermediate chlorination and sand filtration 5. GAC 6. final chlorination. Data from GAC (5) are excluded from*
 317 *the regression equation. Two campaigns from the full scale treatment plant are presented in figure a) while*
 318 *SUVA values were only measured in one of the 2 campaigns in figure b).*

319 When looking to the THMFP in function of DOC or SUVA values (Fig. 2) of treated waters, two different
 320 regression lines are obtained with similar slopes with each of them achieving good coefficients of
 321 determination (R^2 from 0.9 to 0.99, Fig. 2). The existing shift between these two correlations is to be
 322 related to the presence of the biopolymer fraction in the raw and IEX treated waters for which the
 323 experiments were performed in autumn compared to the others performed in spring before the algal
 324 bloom. Then, the SUVA value of the whole water is reduced (2.0) while the SUVA value of the humic
 325 substance fraction is 3.5. In fact, this fraction represents 18 to 28% of the DOC for the IEX treated
 326 waters. This also explain why the THMFP/DOC ratios are rather low for the IEX treated waters (32 to
 327 $42 \mu\text{g mgC}^{-1}$) compared to the treated water from the full scale treatment line (about $45 \mu\text{g mgC}^{-1}$),

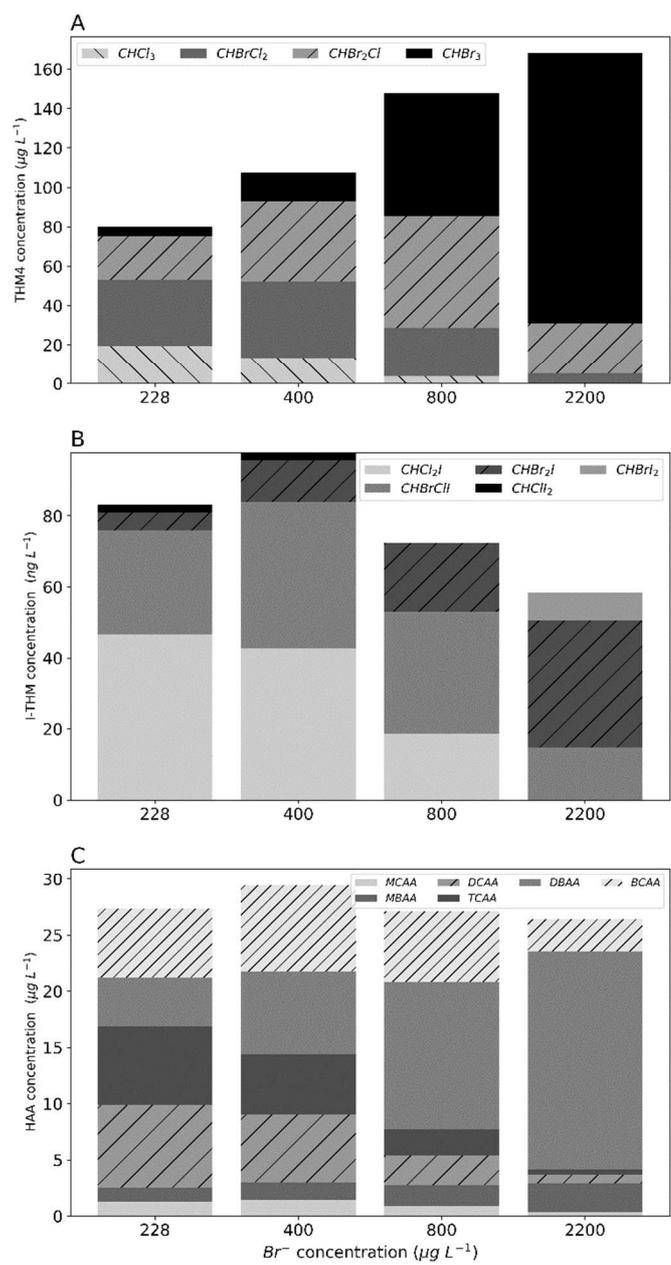
328 while the THMFP is higher (218 to 384 $\mu\text{g L}^{-1}$) for the IEX treated waters compared to the full scale plant
329 for the 7d test (106 $\mu\text{g L}^{-1}$).²⁶ Data of fluorescence acquired either from Fluorescence Excitation
330 Emission Matrices analysed by PARAFAC or the humic like signal (excitation at 244 nm and emission at
331 420 nm) or protein like signal (excitation at 230 nm and emission at 345 nm) of the SEC chromatogram
332 do not improve the characterization of DBP precursors (data not shown).
333 The IEX treatment alone is therefore not appropriate for the treatment of such waters but could still
334 be useful to reduce the amounts of reactants used for clarification. This treatment is however limited
335 in case of sulfate rich waters.

336 **3.3. Assessment of the IEX resins to reduce the formation of DBPs under different halide** 337 **concentration conditions**

338 The IEX resin treatment has been tested in terms of increasing halide concentrations for the control of
339 DBP formation. The concentration of iodide and bromide of the treated waters have been taken into
340 account and equalized to make the comparison of the resin efficiency without considering the variation
341 of halides between the different samples. 4 different scenario with increasing bromide concentrations
342 from 228 up to 2200 $\mu\text{g L}^{-1}$ with a constant iodide concentration of 63 $\mu\text{g L}^{-1}$ (which corresponds to
343 molar Br-/I- ratio from 5.7 up to 55) have been first performed to study the increase of bromide at
344 iodide constant concentration. Additional experiments with extreme iodide concentration (*i.e.* 7 and
345 250 $\mu\text{g L}^{-1}$ in addition to 63 $\mu\text{g L}^{-1}$ performed in the first set of experiments) with a constant
346 concentration of bromide (228 $\mu\text{g L}^{-1}$) have also been performed in order to assess the I-DBP evolution.
347 In the following paragraph, the results of IRA-410, the best performing resin is presented; the results
348 of other resins are available in the SI.

349

350 **3.3.1. Increasing bromide concentration**



351

352 *Figure 3 Evolution of the formation of A) THM4, B) I-THMs and C) HAAs, as function of the increasing bromide*
 353 *concentration for resin IRA-410 treated water (24 hours chlorination test – [I⁻] = 63 µg L⁻¹).*

354 The lowest bromide concentration tested corresponds to the highest level encountered in the IEX
 355 treated waters. For this already quite high concentration (228 µg L⁻¹), the main THM4 were found to
 356 be a mix of CHBrCl₂, CHCl₃ and CHBr₂Cl for the 4 resins (Figs. 3 A and S6-7), with a lower proportion of

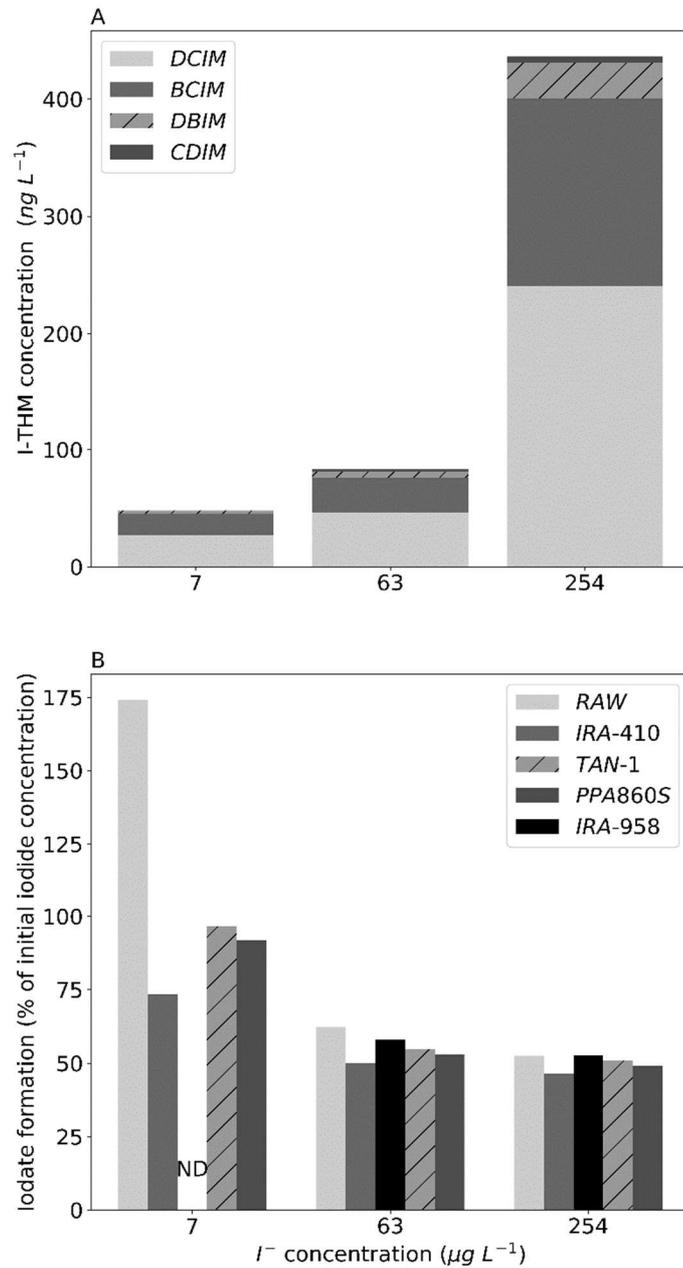
357 CHBr₂Cl for the raw water. Some CHBr₃ was also formed, especially for IRA-410 (Fig. 3A) but was a
358 minor species. When the bromide concentration was increased, naturally, the THM₄ shifted to a higher
359 proportion of brominated species with a concomitant decrease of the chloroform formation. When
360 the bromide concentration was increased to 2200 µg L⁻¹, CHBr₃ was predominant in all 5 samples.
361 However, a different trend is noticed between the raw water and the IEX treated waters. In fact, the
362 quantity of THM₄ (in molar concentration) did not change noticeably for the raw water (average
363 concentration of 1.21 ± 0.01 µM for a concentration of Br⁻ up to 800 µg L⁻¹ and 1.30 µM for the highest
364 bromide concentration). On the opposite, the formation of THM₄ increased for the 4 IEX treated
365 waters with the increase of bromide (from 37 to 44 % for an increasing bromide concentration from
366 228 up to 2200 µg L⁻¹ compared to only 6.5% for the raw water, based on molar concentration).
367 Considering the increasing molecular weight of brominated compounds compared to chlorinated ones,
368 the increase is even higher (from 110 to 120% compared to 68% for raw water). Then, the
369 concentration of THM₄ formed in the IRA-958 treated water with the highest bromide concentration
370 equalized the one achieved in the raw water for the same Br⁻ concentration despite a substantial
371 decrease of the DOC (23%) (Fig. S7). Bromine reacts more with hydrophilic compounds than with
372 hydrophobic compounds,⁴¹ which may be the reason for an overall increase in THM formation from
373 the treated waters where part of hydrophobic compounds were removed. Considering the I-THMs,
374 two different trends are noticed. In fact, for IRA-410, TAN-1 and to a lower extent IRA-958, the
375 concentration of I-THMs first increases with the increase of bromide from 228 to 400 µg L⁻¹ due to the
376 higher formation of brominated substances (mainly CHBrClI), a phenomenon which has already been
377 underlined in the literature.²⁹ With even higher bromide concentrations, the formation of I-THMs then
378 decreases, which is due to the fastest formation of iodate in presence of increasing concentration of
379 bromide.⁴⁰ On the other hand, the I-THM formation uniformly decreases for the raw water and
380 PPA860S treated water with the increase of bromide concentration (Fig. S8). These two waters
381 correspond to the highest I-THM formation with the sums equalling to respectively 1.33 and 0.44 µg L⁻¹
382 for the raw and PPA860S treated waters (having the lowest bromide concentration). The same
383 observation is made considering the molar concentration (Fig. S9). It has to be noticed that the overall
384 I-THM formation is quite low, especially considering the iodide spiking (63 µg L⁻¹). This low I-DBP
385 formation is due to favourable conditions for the iodate formation considering the quite high bromide
386 background concentration (228 µg L⁻¹).

387 The reduction efficiency in I-THM formation in IEX treated water compared to the raw water dropped
388 with the increase of bromide concentration (Fig. S9). For example, for IRA-410, the I-THM formation is
389 lower than in the raw water by a factor of 16 ([Br⁻] = 228 µg L⁻¹), but this factor is reduced to 6.5 for a
390 bromide concentration of 2200 µg L⁻¹. Indeed, the higher competition of DOC for reactive bromine in

391 raw water than in the treated waters at the lower bromide concentrations is less apparent at higher
392 bromide concentrations.

393 The sum of the 7 HAAs remains more or less stable with increasing bromide concentrations as
394 illustrated in the case of resin IRA-410 (Fig. 3C), but the molar concentrations decrease (Fig. S10). This
395 could be due to the trihaloacetic acids (tri-HAAs) speciating towards more brominated tri-HAAs which
396 could not be measured in this study. However, when considering the relative toxicity of the different
397 compounds (dividing the DBP concentration by their respective LC50, Fig. S11) the toxicity related to
398 the THM4 and HAA5 increases with the increase of bromide, as the main toxicity driver is the
399 bromoacetic acid which concentration increases.

400 **3.3.2. Increasing iodide concentration**



401

402 *Figure 4: A. Evolution of the formation of I-THMs as function of the increasing iodide concentration for resin*
 403 *IRA-410 treated water (24h chlorination test). B. % of iodate formation compared to iodide initial concentration*
 404 *for raw and the 4 IEX treated waters for increasing iodide concentration. [Br⁻] = 228 µg L⁻¹; ND: no data.*

405 The effect of increasing iodide concentration (0.06, 0.5 and 2 µM, corresponding to 7, 63 and 254 µg
 406 L⁻¹) has been studied with a bromide concentration kept constant to the minimum background level

407 possible ($2.5 \mu\text{M}$ or $228 \mu\text{g L}^{-1}$). The results of I-THMs formation in the IRA-410 treated water (Fig.4a)
408 show that the increase of I-DBP is not linear with the increasing concentration of iodide. In fact the I-
409 THMs show a moderate increase for a concentration of iodide increasing from 0.06 to $0.5 \mu\text{M}$ (factor
410 of 1.7 similar to the increase of I^- concentration), but a much larger increase with the increase of iodide
411 by a factor of 4 (from 0.5 to $2 \mu\text{M}$), where the I-THM concentration is multiplied by a factor of 5.2 .

412 This behaviour is also noticed for the raw water and IRA-958 treated waters. However, for TAN-1 and
413 the PPA860S, the increase is linear and asymptotic respectively. The 3 main I-THMs formed at low I-
414 concentration (CHCl_2I , CHBrClI and CHBr_2I) are shown to increase in the same proportion for the 3
415 compounds. A small quantity of CHCl_2 appears from $63 \mu\text{g L}^{-1} \text{I}^-$. No CHI_3 was detected which is in
416 agreement with literature where much higher amounts of iodide were needed to form a substantial
417 amount of CHI_3 .⁴² The increase of I-THM formation is much lower than the one predicted by the linear
418 regression obtained in previous section (Fig. S6). This regression was then limited to very low iodide
419 concentration. Considering the iodate formation (Fig. 4b), the raw water exhibits a high formation of
420 iodate at low iodide level, which is even higher than the initial iodide concentration. A part of organic
421 iodine (total iodine equals to $35 \mu\text{g L}^{-1}$) is then transformed into iodate. This phenomena has also been
422 observed on the full scale treatment plant.²⁶ The % of iodate formation compared to the initial iodide
423 content is lower for the IEX treated water (from 74 to 92%). It is interesting to note that the IEX
424 treatment also removes a part of the organic iodine (removal of 40 to 86% of total iodine). The iodate
425 formation yield is reduced with increasing iodide concentration for raw and IEX treated waters (around
426 50% for 63 and $254 \mu\text{g L}^{-1}$). In terms of resin efficiency to remove I-DBP precursors, the IRA-410 resin
427 has a particular behaviour compared to the other resins, with a decreasing capacity to reduce the
428 formation of I-DBPs compared to the DBPs formed in the raw water. For example, the formation of I-
429 THMs is reduced by a factor of almost 20 at low concentration of iodide for the IRA-410 treated water
430 compared to the raw water, this factor dropped to 10 for the highest concentration of iodide tested.
431 On the contrary, the other resins show their capacity of minimizing the I-DBP increasing with the
432 increase of iodide concentration. However, in most of the conditions tested here, IRA-410 treated
433 water provides the lowest I-THMs formation (only TAN-1 with $254 \mu\text{g L}^{-1}$ of iodide show a lower I-THM
434 formation). Low concentrations of iodoacetic acid ($<30 \text{ ng L}^{-1}$), one of the most genotoxic DBP
435 compound identified to-date,⁴³ has only been found in the PPA860S treated waters (spiked at 63 and
436 $254 \mu\text{g L}^{-1}$) and in TAN-1 tread water (spiked at $254 \mu\text{g L}^{-1}$). Considering the yields of iodate formation
437 and the moderate increase of I-THMs, the iodination of a wider type of active moieties of NOM not
438 leading to THM formation could be supposed.

439 Considering the overall DBP formation and the removal of DBP precursors, it is worthwhile to notice
440 that the reduction in DBP formation potential is reduced with increasing concentrations of bromide. It

441 has been shown that bromine is generally a better agent for electrophilic substitution and addition
442 than chlorine.^{29,44} The removal of NOM favouring the bromination, could be worrying in terms of
443 toxicity of DBP formed as brominated DBPs generally exhibit higher toxicity than the chlorinated
444 analogues.⁴⁵ The advantage of resins in the removal of specific DBP precursor is then reduced in
445 presence of high concentration of halides. The effect of increasing concentrations of iodide alone,
446 which may hardly be found in natural waters without a concomitant increase of bromide however
447 shows here that the precursors of I-DBP and/or reactivity of HOI are different from brominated and
448 chlorinated analogues. This would deserve more research to identify the different properties of DBP
449 precursors responsible for DBP speciation.

450 **4. Conclusions**

451 Four ion exchange resins was tested for the removal of NOM and the concomitant assessment of
452 reduction of disinfection by-product formation. It was confirmed that all resins preferentially removes
453 the humic substances fraction. In addition, the SUVA value was lowered by the IEX treatment to a
454 higher extend than the DOC removal demonstrating the preference of resins for the highly
455 hydrophobic compounds exchange. In this source water, a large part of the removal efficiency of the
456 resins is dramatically reduced by the high content of sulfate, which would be a key negative factor for
457 the further upscaling of this process on such raw water. In terms of disinfection by-product formation,
458 the reduction of DBP formation potential compared to the one achieved in raw water is related to the
459 DOC removal efficiency of the resins. The IRA-410 resin showed the best performance followed by the
460 PPA860S. However, from the comparison of the different resins, it has been demonstrated that the
461 efficiency in DBP reduction is better linked to the SUVA removal than to DOC removal. The experiments
462 also showed that the resins preferentially remove the DBP precursors which have a slow reactivity
463 towards chlorination.

464 All resins show a beneficial effect in lowering the concentration of I-DBPs by lowering iodide and/or by
465 the removing of specific precursors. Finally, the advantage of DBP reduction by the IEX treatment is
466 reduced in presence of an increasing concentration of halides. The reduction of efficiency is highly
467 dependent on the resin type and then this aspect would have to be taken into account in addition to
468 the DOC removal efficiency in case of source water impacted by high halide levels or sources showing
469 a risk of increasing halide concentrations in the future due to anthropogenic pressure.

470 **Conflicts of interest**

471 There are no conflicts to declare.

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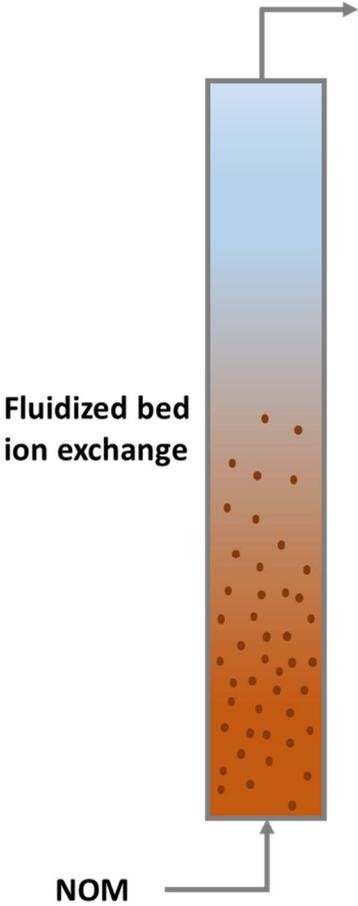
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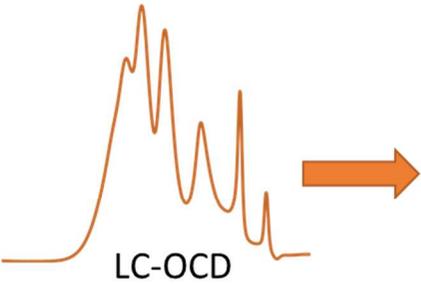
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Graphical Abstract:



| Parameters | IRA410 | IRA958 | TAN-1 | PPA860S |
|------------|--------|--------|-------|---------|
| DOC | ++ | + | + | ++ |
| THM4 | ++ | - | + | ++ |
| HAAs | ++ | + | ++ | ++ |
| I-THMs | +++ | ++ | ++ | ++ |

DBPs under high halide concentrations



| NOM fractions | IRA410 | IRA958 | TAN-1 | PPA860S |
|-------------------------------|--------|--------|-------|---------|
| Humic substances | ++ | + | + | ++ |
| Building blocks | + | - | + | - |
| Low molecular weight neutrals | + | - | - | - |
| Hydrophobic organic carbon | + | - | + | ++ |
| SUVA | ++ | - | + | + |