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## 2 **Iodinated disinfection byproducts: Formation and concerns**

3 Cristina Postigo<sup>1,2</sup>, Bozo Zonja<sup>1</sup>

4 <sup>1</sup> *Water and Soil Quality Research Group, Department of Environmental Chemistry, Institute of*  
5 *Environmental Assessment and Water Research (IDAEA-CSIC), C/ Jordi Girona 18-26, 08034*  
6 *Barcelona, Spain*

7 <sup>2</sup> *Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences,*  
8 *Box 7050, SE-750 07 Uppsala, Sweden*

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### 10 **Abstract**

11 The list of iodinated disinfection byproducts (iodo-DBPs) includes some of the most genotoxic  
12 and cytotoxic DBPs discovered to date. Therefore, human exposure should be minimized by  
13 reducing their presence in drinking water. This manuscript reviews the main iodo-DBP  
14 formation pathways during water disinfection, with focus on the advances reported in the last  
15 two years. We discuss the effect of iodine sources other than iodine salts, e.g., iodinated  
16 contrast media and iodate, on iodo-DBP formation. In addition, we review the anthropogenic  
17 activities (like oil and gas extraction, dairy industry, seawater desalination or advanced  
18 oxidation treatments with persulfate) that may release iodo-DBPs to the aquatic environment  
19 or increase the potential of source waters to generate these compounds when disinfected.

20

21 **Keywords:** chloramination, iodinated contrast media, iodate, iodo-DBPs, iodide sources,  
22 permanganate, drinking water

23

### 24 **1. Introduction**

25 Chemical disinfection of source waters containing iodide may lead to the formation of  
26 iodine containing disinfection by-products (iodo-DBPs). Based on *in vitro* toxicity assay  
27 findings, iodinated and nitrogenous DBPs are considered as the most toxic DBPs in terms of  
28 genotoxicity and cytotoxicity in disinfected water [1, 2]. Despite the facts that toxic evidence  
29 from *in vivo* assays or molecular epidemiology studies for these DBPs are still lacking and they  
30 are not regulated in drinking water, preventive actions call for minimizing their formation in  
31 drinking waters.

32 The existence of iodo-DBPs and in particular that of dichloriodomethane in chlorinated  
33 water was for the first time discovered four decades ago [3]. Since then, and particularly within  
34 the last decade, iodo-DBPs have been reported to form after chemical disinfection of water  
35 with oxidizing agents other than chlorine, e.g., chloramine, chlorine dioxide [4], potassium  
36 permanganate [5], peracetic acid [6], ferrate [7] or iodine. Together with iodo-THMs, different  
37 chemical classes of iodo-DBP, e.g., iodo-acids, iodo-amides, iodo-aldehydes, and iodo-phenols,

38 have been found in disinfected water [8-10]. The list of iodo-DBPs being discovered in  
39 disinfected waters is continuously expanding due to the increasing availability of advanced  
40 sensitive analytical technologies based on high-resolution mass spectrometry [11]. Different  
41 approaches have been proposed in the literature for new iodo-DBP identification [10, 12-16].

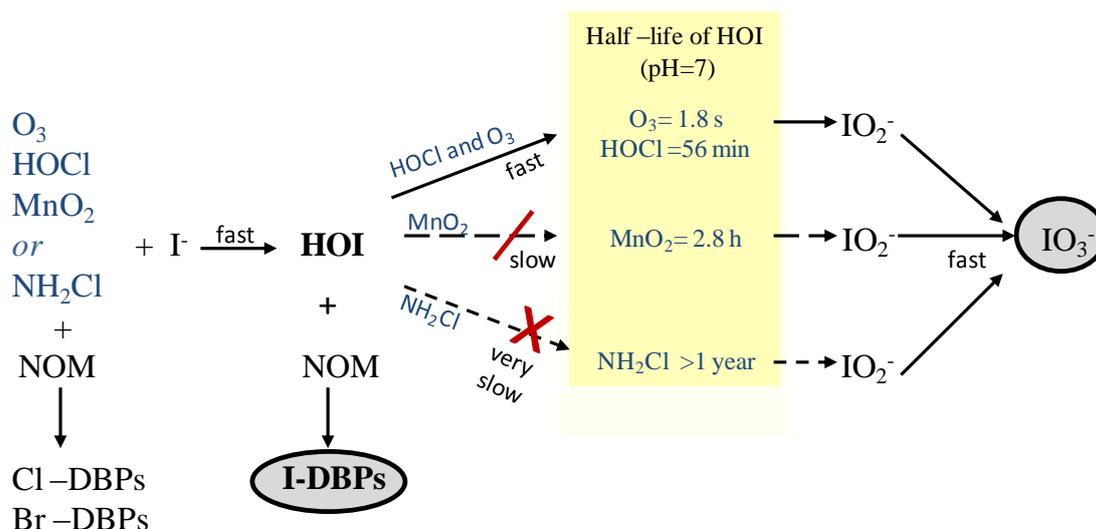
42 Similarly as for any other DBP, the extent of formation of iodo-DBPs during water  
43 disinfection depends on the organic and inorganic precursors (e.g., iodide and bromide)  
44 present in the source water. Additionally, their formation is determined by the type of  
45 disinfectant used and the conditions under which the disinfection process is carried out [17].  
46 Most mechanistic studies conducted to elucidate iodo-DBP formation have used iodo-THMs as  
47 model compounds.

48 This review discusses the main formation pathways of iodo-DBPs during disinfection  
49 reactions and highlights the advances in this field, with focus on the research published in the  
50 last two years. It also tries to raise concern about those anthropogenic activities that may  
51 release iodo-DBPs to the aquatic environment or increase the iodo-DBP formation potential of  
52 drinking water sources.

## 53 **2. Formation mechanisms**

54 Oxidation of the iodide present in water during chemical disinfection processes usually  
55 leads to the formation of hypiodous acid (HOI) which may react with natural organic matter  
56 (NOM) to form iodo-DBPs or further oxidize to iodite and then to iodate (see Figure 1). The  
57 oxidation of HOI to iodate is favored among competing reactions in the presence of chlorine  
58 and ozone. The half-life of HOI is significantly higher under permanganate oxidation, and it is  
59 longest during chloramination (see Figure 1) [18, 19]. Thus the potential for iodo-DBP  
60 formation is also expected to be highest during chloramine-based disinfection of iodide-  
61 containing waters. This has been confirmed by both lab-controlled mechanistic studies and  
62 drinking water plant-scale monitoring studies [20]. However, reduced formation of iodo-DBPs  
63 during chloramination could be achieved if water is previously preoxidized with chlorine,  
64 permanganate at pH <6 or >8 [19], ferrate [7] or ozone [21]. During this preoxidation stage,  
65 iodide gets partially removed from the system by its rapid oxidation to iodate.

66 Several works have focused on investigating the effects of chlorine or chloramine-  
67 based disinfection conditions on iodo-DBP formation. They have covered various i) water pH  
68 values, ii) disinfectant doses and contact times, iii) types of NOM (e.g., effluent wastewater,  
69 standard fulvic and humic substances, and drinking water sources: Llobregat River (Spain),  
70 Aliakmon River (Greece) and Miyun Reservoir (China)), iv) levels of NOM and iodide, or v)  
71 bromide/iodide and iodide/DOC concentration ratios [17, 20, 22-24]. Overall, findings indicate  
72 that iodide incorporation into NOM is enhanced at increasing concentrations of iodide in  
73 water, and reduced at increasing bromide and DOC concentrations. However, such conclusions  
74 were mostly drawn from lab-controlled reactions with simulated water and in some cases,  
75 after addition of high concentrations of iodide into the source water. Thus, they need to be  
76 confirmed in real water at plant scale. Furthermore, most mechanistic studies were focused  
77 only on few DBPs (e.g., iodo-THMs, iodo-acids, iodoacetaldehyde, and iodo-haloacetamides)  
78 that represent a very small part of the total organic iodine formed.



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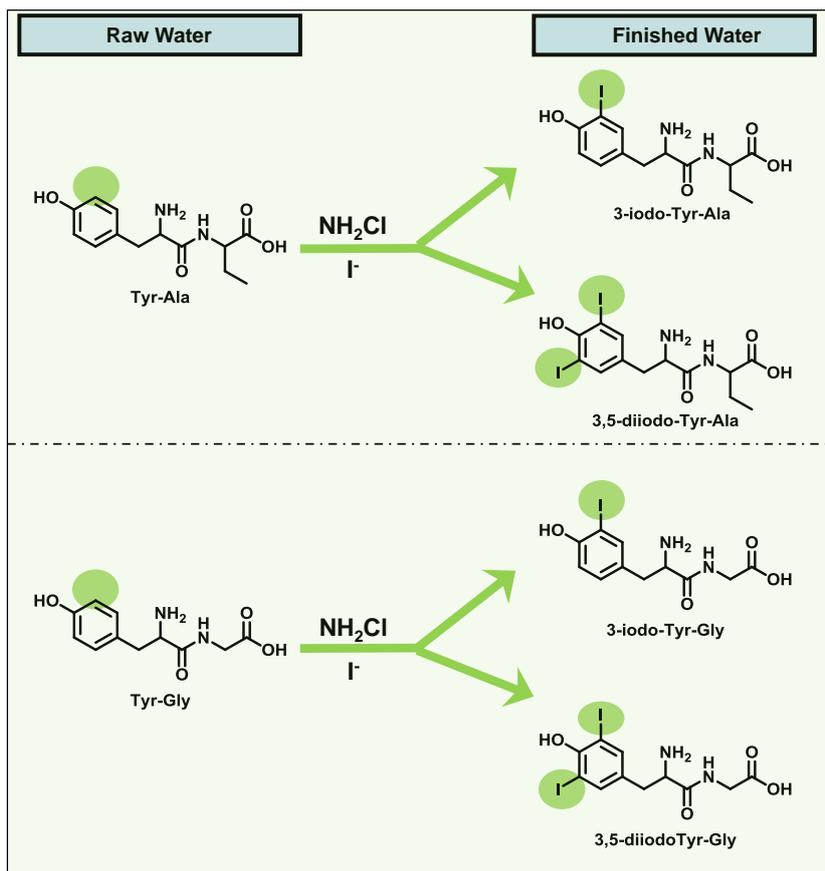
81 **Figure 1.** Reactivity of iodide and HOI in the presence of ozone, free chlorine, permanganate,  
 82 and chloramine.

83 Although little is still known about specific iodo-DBP precursors, experiments with  
 84 simulated drinking water containing Suwannee River fulvic acid (SRFA) and 200  $\mu\text{g/L}$  of iodide  
 85 showed that high aromaticity molecules seem to be highly reactive to chloramine oxidation to  
 86 form iodo-DBPs [16]. However, the formation of specific iodo-DBP classes, i.e., iodo-haloacetic  
 87 acids and iodo-THMs, has been associated to NOM fractions with low aromaticity [17, 20]. This  
 88 was shown in experiments with simulated water containing Suwannee River and Nordic Lake  
 89 NOM and a wide range of iodide levels (50  $\mu\text{g/L}$  to 38  $\text{mg/L}$ ) [17, 20] and by chloramination of  
 90 model compounds known to be present in NOM and to react with free halogens, i.e., several  
 91 amino acids, carboxylic acids and aromatic compounds [17]. The highest iodo-DBP yields (up to  
 92 0.5%) were provided by citric acid, L-aspartic acid, and pyruvic acid [17].

93 Tyrosyl dipeptides were also recently identified as iodo-DBP precursors. Iodine substituted  
 94 tyrosyl dipeptide products, formed after iodine substitution on the 3- or 3,5-positions of the  
 95 tyrosyl-phenol ring were discovered in lab-controlled chloramination reactions of seven tyrosyl  
 96 dipeptides. Four of these iodinated dipeptides (3-iodo- and 3,5-di-iodo-Tyr-Ala and 3-iodo- and  
 97 3,5-di-iodo-Tyr-Gly), and their corresponding precursors (tyrosylalanine and tyrosylglycine),  
 98 were found to be present in real chloraminated tap water (see Figure 2) [25].

99 Iodine incorporation during the reaction of HOI with (hydroxyl)phenolic compounds  
 100 and Nordic Lake and Pony Lake fulvic acid extracts can occur through electrophilic aromatic  
 101 substitution and/or electron transfer. The extent of these processes depends on the number  
 102 and relative position of the hydroxyl moieties on the phenolic compounds [26].

103



104

105 **Figure 2.** Iodine substituted tyrosyl dipeptide compounds found in chloraminated tap water.

106 Mechanisms for iodo-DBP formation during chlorination and chloramination have  
 107 been recently proposed by modeling the formation of total organic iodine (TOI) [27]. These  
 108 models highlighted the importance of not neglecting the decomposition/transformation of  
 109 halogenated DBPs during the disinfection processes. The transformation of iodo-DBPs into  
 110 their chloro- and bromo- analogs accounted for 57-74% of the total iodo-DBPs generated,  
 111 whereas degradation of 52% iodo-DBPs by base-catalyzed hydrolysis deiodination occurred  
 112 during chloramination. In this line, Gong et al. recently reported that 2,4,6-triiodophenol and  
 113 2,6-diiodo-4-nitrophenol, two toxic iodo-phenols commonly found in drinking water may  
 114 originate from the substantial transformation of 4-iodophenol during chloramination and that  
 115 monochloramine was an important nitrogen source for 2,6-diiodo-4-nitrophenol  
 116 formation[28].

117 Diiodoacetic acid, triiodoacetic acid, and iodoform have been reported to degrade  
 118 rapidly under sunlight irradiation (half-lives from 5.3 to 10.2 min). DBP photodegradation  
 119 increased with the number of halogens (tri>di>mono halogenated) and size of the substituted  
 120 halogens (I>Br>Cl). Light screening by NOM (SRFA) reduced the photodegradation rate of iodo-  
 121 DBPs [29]. Iodoform degradation is accelerated during UV/chlorination treatments. High  
 122 chlorine concentrations and low pH values enhanced iodoform degradation, contrary to what  
 123 was observed when SRFA and bicarbonate were present in solution [30].

124

125 **2.1. Reactivity of additional iodine sources in water – effects on iodo-DBP formation**

### 126 **2.1.1. Iodinated X-Ray contrast media**

127 Besides natural iodide salts, iodinated X-ray contrast media (ICM) used for medical  
128 imaging of soft tissues have been discovered as a relevant source of iodine that leads to the  
129 formation of iodo-DBPs during chlorination and chloramination of drinking water sources.  
130 Since the first work carried out on this topic by Duirk et al. [31], several studies have confirmed  
131 this [22, 32-36]. Of all ICM tested (i.e., diatrizoate, iodixanol, iohexol, iomeprol, iopamidol, and  
132 iopromide), iopamidol seems to be the most reactive compound. The highest concentrations  
133 of iodo-THMs and iodo-acids were consistently found in chlorinated iopamidol containing  
134 waters (intake of three water treatment plants in Ohio [31, 36], and one in Shanghai [33]). In  
135 the absence of NOM, only a small percentage of the initial iopamidol concentration (<2% after  
136 24 h) is actually transformed into known low molecular weight iodo-DBPs [32]. The  
137 degradation pathway and kinetics of iopamidol during chlorination and chloramination as well  
138 as the high-molecular weight DBPs formed during these processes have been already  
139 described in the literature [32, 35]. However, such studies were performed in purified water  
140 and the effects of NOM were not investigated.

141 Iopamidol deiodination, and hence, iodo-DBP formation, also can also occur under  
142 Ferrate (Fe(VI)) oxidation [37] and in the presence of zerovalent iron [38]. In the case of Fe<sup>0</sup>,  
143 the reaction was enhanced in acidic conditions and in the presence of specific anions (SO<sub>4</sub><sup>-2</sup>  
144 and Cl-) and monochloramine [38].

145 The release of iodide from ICM after UV irradiation and the effects on iodo-DBP  
146 formation during subsequent chemical oxidation has been studied in several occasions [39-41].  
147 Iodide release from five ICM increased at increasing UV doses and decreased at increasing  
148 Suwannee River NOM concentrations [39]. However, the type of NOM (up to seven types of  
149 NOM tested with specific UV absorbance (SUVA) values ranging 1.6-4.45) did not have a  
150 significant impact on the degradation of iopromide, the formation of iodo-DBPs or the iodine  
151 speciation. For all ICM, higher concentrations of iodo-DBPs were formed during UV/NH<sub>2</sub>Cl than  
152 with UV/HOCl. While iodo-DBP formation was reduced at increasing chlorine doses because  
153 HOI was rapidly converted to iodate, in the case of UV/NH<sub>2</sub>Cl, the chloramine dose did not  
154 have any effect on the iodo-DBP levels formed [39]. Additionally, the release of iodide from  
155 ICM was reported under natural sunlight irradiation, with the subsequent formation of the  
156 deiodinated transformation products (TPs) [42].

### 157 **2.1.2. Iodate**

158 Iodate was always considered an innocuous and stable sink for iodine. However, Tian  
159 et al reported in a recent work that iodate can significantly photoreduce into iodide by UV at  
160 neutral pH [43]. Moreover, the photodegradation rate of iodate could be enhanced in the  
161 presence of NOM (Huangpu River NOM, and SRFA). Thus, the UV pretreatment of iodate-  
162 containing water, especially before chloramination, may enhance iodo-DBP formation.

163 Iodate is also converted into iodide after its reduction by zerovalent iron. This process may  
164 occur in unlined cast iron pipes, widely used in drinking water distribution networks. Higher  
165 zerovalent iron dosages led to increasing formation of iodo-THMs in chloraminated waters

166 without any other iodine source but iodate. The presence of goethite and hematite in the  
167 system enhanced iodo-THM formation [44].

168

### 169 3. Sensitive scenarios

170 Iodo-DBPs are typically analyzed in drinking water. However, their formation may also be  
171 relevant in industries where iodine or iodine-based disinfectants are used for sanitization, such  
172 as the dairy industry. Wastewaters from milk and cheese processing facilities contained up to 6  
173  $\mu\text{g/L}$  of iodo-THMs. The contribution of iodo-THMs to total trihalomethane loads ranged 0-  
174 100%. Diluted concentrations of iodo-THMs were found in surface waters impacted by these  
175 facilities. This finding confirms dairies as a source of these toxic compounds to receiving water  
176 bodies [45].

177 Hydraulic fracturing flow-back fluids and oil and gas wastewater from conventional oil and  
178 gas operations contain high levels of halides, with iodide concentrations reaching up to 28  
179  $\text{mg/L}$  [46]. Thus, their eventual spill or discharge into drinking water sources may result in an  
180 enhanced potential of these waters to form iodo-DBPs during disinfection treatments. Besides  
181 representing a source of iodide into the aquatic environment, the flow-back water may even  
182 contain many iodo-organic compounds, including iodo-acids, whose origin is still not clear  
183 (biotic or abiotic reactions, shale origin or fracking additives) [14, 47]. Oil and gas produced  
184 wastewater also showed the potential to form a wide spectrum of iodo-phenols during  
185 chloramination reactions. Methylphenol and dimethylphenol, of geogenic origin, were  
186 identified as the main precursors of the iodo-phenols formed [15].

187 Desalinated seawater, a water resource increasingly being used worldwide to fulfill  
188 drinking water demands, may contain considerable amounts of bromide and iodide. Residual  
189 iodide levels may be more relevant in reverse osmosis-based desalination plants than in  
190 thermal-based desalination plants. However, and in spite of the fact that chemical disinfection  
191 is usually conducted during the desalination process, DBP formation in desalinated water is not  
192 relevant due to its low NOM content. The risk for iodo-DBP formation arises when desalinated  
193 water is blended with the final product of a conventional drinking water treatment plant since  
194 NOM is introduced in the system for reaction. Likewise, high risk of iodo-DBP formation  
195 potentially exists if the desalinated water gets into contact with the biofilm which is present  
196 along the drinking water distribution system network. Research needs in this field proposed by  
197 Kim et al. [48] have been hardly covered to date.

198 Advanced oxidation processes (AOPs) using persulfate or peroxymonosulfate have shown  
199 applicability in remediation of soil/groundwater pollution. Contrary to hydroxyl radicals, the  
200 sulfate radical ( $\text{SO}_4^{\cdot-}$ ) generated during these processes are preferentially scavenged by halides  
201 than by NOM. As a result halogen radical species and free halogens are formed, and  
202 consequently iodo-DBPs, like iodo-di-haloacetamides [49] or iodoform and iodoacids in a  
203 carbon nanotube activated persulfate oxidation system [50]. Considerable amounts of TOI  
204 were also reported to get formed after peroxymonosulfate oxidation of iodide in Suwannee  
205 River NOM solutions [51]. Recently, Wang et al reported the formation of iodoform and  
206 iodoacetic acids from phenol (the model compound used to mimic reactivity of dissolved NOM  
207 in the study) in a heat activated persulfate system [52]. Iodophenols were also detected as

208 intermediates during the process. However, all iodo-DBPs formed were found to further  
209 oxidate to iodate in excess of sulfate radicals.

210

#### 211 **4. Future research needs**

212 Known iodo-DBPs constitute a small part of TOI in water. Thus, formation mechanisms  
213 of iodo-DBPs should be investigated preferably taking also into account the unknown fraction  
214 of TOI. For this, reliable and novel methodologies to measure TOI are needed. Some works  
215 have been focused recently on this aspect [53, 54]. Furthermore, new analytical approaches  
216 and methodologies are needed to discover relevant iodo-DBPs in the DBP mixture. Current  
217 advances on analytical technology, e.g., development and commercialization of benchtop  
218 easy-to-operate sensitive high-resolution mass spectrometry instruments, may contribute to  
219 overcoming this analytical challenge.

220 Formation mechanisms of iodo-DBPs need to be further investigated at environmental  
221 conditions, and preferably at industrial plant scale so that findings can be easily applied to  
222 improve drinking water quality. Exhaustive characterization of the drinking water source in  
223 each case is needed so that results can be scaled up to different treatment plants. The  
224 formation of iodo-DBPs in reclaimed water should be also assessed when a chlorine-based  
225 disinfection treatment is used for water regeneration. Formation mechanisms of iodo-DBPs in  
226 wastewater are expected to differ from those observed in drinking water due to the different  
227 nature of the NOM present in these matrices.

228 Despite the fact that concentrations of individual iodo-DBPs in drinking water are  
229 usually much lower in mass than those measured for individual regulated trihalomethanes  
230 and haloacetic acids (<1 ppb vs few to tens of ppb), their presence may still represent a  
231 potential risk for human health since they have exhibited a comparatively higher toxicity than  
232 their bromine and chlorine analogues in different *in vitro* studies. Thus minimization of iodo-  
233 DBP exposure and protection of human and ecosystems health calls for adopting adequate  
234 measures to minimize iodine sources and iodo-DBP release into surface waters and to remove  
235 iodo-DBP precursors in drinking water sources before their disinfection.

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#### 244 **References**

- 245 1. Richardson, S.D., et al., *Occurrence, genotoxicity, and carcinogenicity of regulated and*  
246 *emerging disinfection by-products in drinking water: A review and roadmap for*  
247 *research*. Mutation Research/Reviews in Mutation Research, 2007. **636**(1): p. 178-242.  
248 \*\* This manuscript is a comprehensive review of the data available regarding the  
249 occurrence and toxicity of 85 DBPs and the gaps of knowledge in this field of research.

- 250 2. Cortés, C. and R. Marcos, *Genotoxicity of disinfection byproducts and disinfected*  
251 *waters: A review of recent literature*. Mutation Research/Genetic Toxicology and  
252 Environmental Mutagenesis, 2018. **831**: p. 1-12.
- 253 3. Thomas, R. and M. Weisner, in *Thomas, R.F., Weisner M.J., Brass HJ (1980) The fifth*  
254 *trihalomethane: dichloriodomethane. Its stability and occurrence in chlorinated*  
255 *drinking water*. In: Jolley RL, Brungs WA, Cumming RB, Jacobs VA (eds) *Water*  
256 *chlorination: environmental impact and health effects*, vol 3. Ann Arbor Science, Ann  
257 Arbor, MI, pp 161–168.
- 258 4. Ye, T., et al., *Formation of iodinated disinfection by-products during oxidation of iodide-*  
259 *containing waters with chlorine dioxide*. Water Research, 2013. **47**(9): p. 3006-3014.
- 260 5. Ye, T., et al., *Formation of iodinated disinfection by-products during oxidation of iodide-*  
261 *containing water with potassium permanganate*. Journal of Hazardous Materials,  
262 2012. **241-242**: p. 348-354.
- 263 6. Xue, R., et al., *Evaluation of thirteen haloacetic acids and ten trihalomethanes*  
264 *formation by peracetic acid and chlorine drinking water disinfection*. Chemosphere,  
265 2017. **189**: p. 349-356.
- 266 7. Zhang, M.S., et al., *Formation of iodinated trihalomethanes after ferrate pre-oxidation*  
267 *during chlorination and chloramination of iodide-containing water*. Journal of the  
268 Taiwan Institute of Chemical Engineers, 2016. **60**: p. 453-459.
- 269 8. Richardson, S.D. and C. Postigo, *Formation of DBPs: State of the Science*, in *ACS*  
270 *Symposium Series*. 2015. p. 189-214.  
271 \*\*Authors review the formation mechanisms of DBPs during disinfection of water.  
272
- 273 9. Pan, Y., et al., *Formation and occurrence of new polar iodinated disinfection byproducts*  
274 *in drinking water*. Chemosphere, 2016. **144**: p. 2312-2320.
- 275 10. Gong, T. and X. Zhang, *Detection, identification and formation of new iodinated*  
276 *disinfection byproducts in chlorinated saline wastewater effluents*. Water Research,  
277 2015. **68**: p. 77-86.
- 278 11. Richardson, S.D. and C. Postigo, *Liquid Chromatography–Mass Spectrometry of*  
279 *Emerging Disinfection By-products*, in *Comprehensive Analytical Chemistry*. 2018. p.  
280 267-295.
- 281 12. Gallidabino, M.D., et al., *Suspect screening of halogenated carboxylic acids in drinking*  
282 *water using ion exchange chromatography – High resolution (Orbitrap) mass*  
283 *spectrometry (IC-HRMS)*. Talanta, 2018. **178**: p. 57-68.
- 284 13. Postigo, C., et al., *Characterization of iodinated disinfection by-products in chlorinated*  
285 *and chloraminated waters using Orbitrap based gas chromatography-mass*  
286 *spectrometry*. Analytical and Bioanalytical Chemistry, 2016. **408**(13): p. 3401-3411.
- 287 14. Luek, J.L., et al., *Halogenated Organic Compounds Identified in Hydraulic Fracturing*  
288 *Wastewaters Using Ultrahigh Resolution Mass Spectrometry*. Environmental Science  
289 and Technology, 2017. **51**(10): p. 5377-5385.
- 290 15. Liberatore, H.K., et al., *Identification and Comparative Mammalian Cell Cytotoxicity of*  
291 *New Iodo-Phenolic Disinfection Byproducts in Chloraminated Oil and Gas Wastewaters*.  
292 Environmental Science and Technology Letters, 2017. **4**(11): p. 475-480.
- 293 16. Wang, X., et al., *Characterization of unknown iodinated disinfection byproducts during*  
294 *chlorination/chloramination using ultrahigh resolution mass spectrometry*. Science of  
295 the Total Environment, 2016. **554-555**: p. 83-88.
- 296 17. Liu, S., et al., *Formation of iodo-trihalomethanes, iodo-acetic acids, and iodo-*  
297 *acetamides during chloramination of iodide-containing waters: Factors influencing*  
298 *formation and reaction pathways*. Journal of Hazardous Materials, 2017. **321**: p. 28-36.
- 299 18. Bichsel, Y. and U. Von Gunten, *Oxidation of iodide and hypiodous acid in the*  
300 *disinfection of natural waters*. Environmental Science and Technology, 1999. **33**(22): p.  
301 4040-4045.

- 302 \* Authors evaluated the sink for iodine during ozonation, chlorination, and  
 303 chloramination of natural waters by determining the kinetics of several oxidation  
 304 reactions of hypiodous acid, and discusses its relevance for the formation of  
 305 iodoorganic compounds.
- 306 19. Zhao, X., et al., *Kinetic and Mechanistic Aspects of the Reactions of Iodide and*  
 307 *Hypiodous Acid with Permanganate: Oxidation and Disproportionation.*  
 308 *Environmental Science and Technology*, 2016. **50**(8): p. 4358-4365.  
 309 \* Authors studied the oxidation kinetics of iodide and HOI with potassium  
 310 permanganate in the pH range of 5-10
- 311 20. Postigo, C., S.D. Richardson, and D. Barceló, *Formation of iodo-trihalomethanes, iodo-*  
 312 *haloacetic acids, and haloacetaldehydes during chlorination and chloramination of*  
 313 *iodine containing waters in laboratory controlled reactions.* *Journal of environmental*  
 314 *sciences (China)*, 2017. **58**: p. 127-134.
- 315 21. Allard, S., et al., *Ozonation of iodide-containing waters: Selective oxidation of iodide to*  
 316 *iodate with simultaneous minimization of bromate and I-THMs.* *Water Research*, 2013.  
 317 **47**(6): p. 1953-1960.
- 318 22. Pantelaki, I. and D. Voutsas, *Formation of iodinated THMs during chlorination of water*  
 319 *and wastewater in the presence of different iodine sources.* *Science of The Total*  
 320 *Environment*, 2018. **613-614**: p. 389-397.
- 321 23. Liu, Z., et al., *Formation of iodinated trihalomethanes during breakpoint chlorination of*  
 322 *iodide-containing water.* *Journal of Hazardous Materials*, 2018. **353**: p. 505-513.
- 323 24. Zhang, J., et al., *Role of NOM molecular size on iodo-trihalomethane formation during*  
 324 *chlorination and chloramination.* *Water Research*, 2016. **102**: p. 533-541.
- 325 25. Huang, G., et al., *Formation and Occurrence of Iodinated Tyrosyl Dipeptides in*  
 326 *Disinfected Drinking Water.* *Environmental Science and Technology*, 2018. **52**(7): p.  
 327 4218-4226.
- 328 26. Zhao, X., J. Ma, and U. von Gunten, *Reactions of hypiodous acid with model*  
 329 *compounds and the formation of iodoform in absence/presence of permanganate.*  
 330 *Water Research*, 2017. **119**: p. 126-135.
- 331 27. Zhu, X. and X. Zhang, *Modeling the formation of TOCl, TOBr and TOI during*  
 332 *chlor(am)ination of drinking water.* *Water Research*, 2016. **96**: p. 166-176.
- 333 28. Gong, T., et al., *Transformation among Aromatic Iodinated Disinfection Byproducts in*  
 334 *the Presence of Monochloramine: From Monoiodophenol to Triiodophenol and*  
 335 *Diiodonitrophenol.* *Environmental Science and Technology*, 2017. **51**(18): p. 10562-  
 336 10571.
- 337 29. Abusallout, I. and G. Hua, *Photolytic dehalogenation of disinfection byproducts in*  
 338 *water by natural sunlight irradiation.* *Chemosphere*, 2016. **159**: p. 184-192.
- 339 30. Wang, A.Q., et al., *Kinetics and modeling of iodoform degradation during UV/chlorine*  
 340 *advanced oxidation process.* *Chemical Engineering Journal*, 2017. **323**: p. 312-319.
- 341 31. Duirk, S.E., et al., *Formation of toxic iodinated disinfection by-products from*  
 342 *compounds used in medical imaging.* *Environmental Science and Technology*, 2011.  
 343 **45**(16): p. 6845-6854.  
 344 \*This is the first study that evaluated X-Ray contrast media as iodine sources and the  
 345 potential implications for iodo-DBP formation.
- 346 32. Wendel, F.M., et al., *Transformation of iopamidol during chlorination.* *Environmental*  
 347 *Science and Technology*, 2014. **48**(21): p. 12689-12697.

- 348 33. Ye, T., et al., *Comparison of iodinated trihalomethanes formation during aqueous*  
349 *chlor(am)ination of different iodinated X-ray contrast media compounds in the*  
350 *presence of natural organic matter*. *Water Research*, 2014. **66**: p. 390-398.
- 351 34. Jeong, C.H., et al., *The impact of iodinated X-ray contrast agents on formation and*  
352 *toxicity of disinfection by-products in drinking water*. *Journal of Environmental*  
353 *Sciences*, 2017. **58**: p. 173-182.
- 354 35. Tian, F.X., et al., *Chlor(am)ination of iopamidol: Kinetics, pathways and disinfection by-*  
355 *products formation*. *Chemosphere*, 2017. **184**: p. 489-497.
- 356 36. Ackerson, N.O.B., et al., *Formation of DBPs and halogen-specific TOX in the presence of*  
357 *iopamidol and chlorinated oxidants*. *Chemosphere*, 2018. **202**: p. 349-357.
- 358 37. Dong, H., et al., *Oxidation of iopamidol with ferrate (Fe(VI)): Kinetics and formation of*  
359 *toxic iodinated disinfection by-products*. *Water Research*, 2018. **130**: p. 200-207.
- 360 38. Dong, H., et al., *Deiodination of iopamidol by zero valent iron (ZVI) enhances formation*  
361 *of iodinated disinfection by-products during chloramination*. *Water Research*, 2018.  
362 **129**: p. 319-326.
- 363 39. Allard, S., et al., *Photodecomposition of iodinated contrast media and subsequent*  
364 *formation of toxic iodinated moieties during final disinfection with chlorinated*  
365 *oxidants*. *Water Research*, 2016. **103**: p. 453-461.
- 366 40. Wang, Z., et al., *Degradation of iohexol by UV/chlorine process and formation of*  
367 *iodinated trihalomethanes during post-chlorination*. *Chemical Engineering Journal*,  
368 2016. **283**: p. 1090-1096.
- 369 41. Tian, F.X., et al., *Photodegradation kinetics of iopamidol by UV irradiation and*  
370 *enhanced formation of iodinated disinfection by-products in sequential oxidation*  
371 *processes*. *Water Research*, 2014. **58**: p. 198-208.
- 372 42. Zonja, B., et al., *LC-HRMS Suspect Screening for Detection-Based Prioritization of*  
373 *Iodinated Contrast Media Photodegradates in Surface Waters*. *Environmental Science*  
374 *& Technology*, 2015. **49**(6): p. 3464-3472.
- 375 43. Tian, F.X., et al., *Phototransformation of iodate by UV irradiation: Kinetics and*  
376 *iodinated trihalomethane formation during subsequent chlor(am)ination*. *Journal of*  
377 *Hazardous Materials*, 2017. **326**: p. 138-144.
- 378 44. Xia, Y., et al., *Iodinated trihalomethane formation during chloramination of iodate-*  
379 *containing waters in the presence of zero valent iron*. *Water Research*, 2017. **124**: p.  
380 219-226.
- 381 45. Hladik, M.L., et al., *Dairy-Impacted Wastewater Is a Source of Iodinated Disinfection*  
382 *Byproducts in the Environment*. *Environmental Science and Technology Letters*, 2016.  
383 **3**(5): p. 190-193.
- 384 \*Authors investigated dairy industry as a potential source of iodo-DBPs into the  
385 environment
- 386 46. Harkness, J.S., et al., *Iodide, bromide, and ammonium in hydraulic fracturing and oil*  
387 *and gas wastewaters: Environmental implications*. *Environmental Science and*  
388 *Technology*, 2015. **49**(3): p. 1955-1963.
- 389 47. Hladik, M.L., M.J. Focazio, and M. Engle, *Discharges of produced waters from oil and*  
390 *gas extraction via wastewater treatment plants are sources of disinfection by-products*  
391 *to receiving streams*. *Science of the Total Environment*, 2014. **466-467**: p. 1085-1083.
- 392 48. Kim, D., G.L. Amy, and T. Karanfil, *Disinfection by-product formation during seawater*  
393 *desalination: A review*. *Water Research*, 2015. **81**: p. 343-355.
- 394 49. Chu, W., et al., *Water temperature significantly impacts the formation of iodinated*  
395 *haloacetamides during persulfate oxidation*. *Water Research*, 2016. **98**: p. 47-55.
- 396 50. Guan, C., et al., *Transformation of Iodide by Carbon Nanotube Activated*  
397 *Peroxydisulfate and Formation of Iodoorganic Compounds in the Presence of Natural*  
398 *Organic Matter*. *Environmental Science & Technology*, 2017. **51**(1): p. 479-487.

- 399 51. Li, J., et al., *Kinetics of Oxidation of Iodide (I<sup>-</sup>) and Hypoiodous Acid (HOI) by*  
400 *Peroxymonosulfate (PMS) and Formation of Iodinated Products in the PMS/I<sup>-</sup>/NOM*  
401 *System*. Environmental Science & Technology Letters, 2017. **4**(2): p. 76-82.
- 402 52. Wang, L., et al., *Transformation of iodide and formation of iodinated by-products in*  
403 *heat activated persulfate oxidation process*. Chemosphere, 2017. **181**: p. 400-408.
- 404 53. Kinani, A., et al., *Determination of adsorbable organic halogens in surface water*  
405 *samples by combustion–microcoulometry versus combustion–ion chromatography*  
406 *titration*. Journal of Chromatography A, 2018. **1539**: p. 41-52.
- 407 54. Sayess, R. and D.A. Reckhow, *An improved method for total organic iodine in drinking*  
408 *water*. Water Research, 2017. **108**: p. 250-259.

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410