



# **Iodide sources in the aquatic environment and its fate during oxidative water treatment – A critical review**

Henry Mackeown, Urs von Gunten, Justine Criquet

## **► To cite this version:**

Henry Mackeown, Urs von Gunten, Justine Criquet. Iodide sources in the aquatic environment and its fate during oxidative water treatment – A critical review. *Water Research*, 2022, 217, pp.118417. <10.1016/j.watres.2022.118417>. <hal-03672858>

**HAL Id: hal-03672858**

**<https://hal.science/hal-03672858v1>**

Submitted on 19 May 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# Iodide sources in the aquatic environment and its fate during oxidative water treatment – A critical review

Henry MacKeown<sup>1</sup>, Urs von Gunten<sup>2,3,4</sup> and Justine Criquet<sup>1\*</sup>

<sup>1</sup> Univ. Lille, CNRS, UMR 8516 - LASIRE, Laboratory of Advanced Spectroscopy for Interactions, Reactivity and Environment F-59000 Lille, France.

<sup>2</sup> Eawag, Swiss Federal Institute of Aquatic Science and Technology, Ueberlandstrasse 133, 8600 Dübendorf, Switzerland.

<sup>3</sup> Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, 8092 Zurich, Switzerland.

<sup>4</sup> School of Architecture, Civil and Environmental Engineering (ENAC), École Polytechnique Fédérale de Lausanne (EPFL), 1015, Lausanne, Switzerland.

\* Corresponding author: [justine.criquet@univ-lille.fr](mailto:justine.criquet@univ-lille.fr)

## Abstract

Iodine is a naturally-occurring halogen in natural waters generally present in concentrations between 0.5 and 100  $\mu\text{g L}^{-1}$ . During oxidative drinking water treatment, iodine-containing disinfection by-products (I-DBPs) can be formed. The formation of I-DBPs was mostly associated to taste and odor issues in the produced tap water but has become a potential health problem more recently due to the generally more toxic character of I-DBPs compared to their chlorinated and brominated analogues.

This paper is a systematic and critical review on the reactivity of iodide and on the most common intermediate reactive iodine species HOI. The first step of oxidation of  $\text{I}^-$  to HOI is rapid for most oxidants (apparent second-order rate constant,  $k_{\text{app}} > 10^3 \text{ M}^{-1}\text{s}^{-1}$  at pH 7). The reactivity of hypoiodous acid with inorganic and organic compounds appears to be intermediate between chlorine and bromine. The life times of HOI during oxidative treatment determines the extent of the formation of I-DBPs. Based on this assessment, chloramine, chlorine dioxide and permanganate are of the highest concern when treating iodide-containing waters. The conditions for the formation of iodo-organic compounds are also critically reviewed.

From an evaluation of I-DBPs in more than 650 drinking waters, it can be concluded that one third show low levels of I-THMs ( $< 1 \mu\text{g L}^{-1}$ ), and 18% of exhibit concentrations  $> 10 \mu\text{g L}^{-1}$ . The most frequently

detected I-THM is  $\text{CHCl}_2\text{I}$  followed by  $\text{CHBrClI}$ . More polar I-DBPs, as iodoacetic acid in particular, have been reviewed as well.

Finally, the transformation of iodide to iodate, a safe iodine-derived end-product, has been proposed to mitigate the formation of I-DBPs in drinking water processes. For this purpose a pre-oxidation step with either ozone or ferrate(VI) to completely oxidize iodide to iodate is an efficient process. Activated carbon has also been shown to be efficient in reducing I-DBPs during drinking water oxidation.

**Keywords:** drinking water, oxidation, iodine, disinfection by-products, chlorination, chloramination, I-THM

## 1. Introduction

Chemical disinfectants are widely used in drinking water to serve two main purposes: inactivation of microorganisms during primary treatment and avoiding their regrowth in distribution systems (Sedlak and von Gunten, 2011). Chemical oxidants are also used for iron and manganese removal (Allard et al., 2013a), abatement of taste and color (Bruchet et al., 2004) and micropollutants (von Gunten, 2018, 2003), improving the coagulation and filtration efficiency, and preventing algal growth in sedimentation basins and filters (Spellman, 2013). Commonly applied chemical oxidants in water treatment are chlorine, chloramine, ozone, chlorine dioxide and permanganate (von Gunten, 2018). Disinfectants mainly react with dissolved organic matter (DOM) to produce undesired disinfection by-products (DBPs) (Sedlak and von Gunten, 2011). Since chloroform was first identified (Rook, 1974; Bellar, et al. 1974), more than 700 other DBPs have been detected (Richardson and Ternes, 2018). The majority of identified DBPs in drinking water are halogenated compounds, through a direct incorporation of chlorine into DOM or indirectly by the incorporation of bromine and/or iodine in presence of bromide and/or iodide (Hrudey and Charrois, 2012). To minimize exposure to DBPs, several compounds are currently regulated in numerous countries (four trihalomethanes (THMs), five haloacetic acids (HAAs), chlorite and bromate). THMs and HAAs were chosen for regulation as they are generally found at the highest concentrations (Hrudey and Charrois, 2012). It was assumed that

applying conditions to effectively mitigate formation of regulated THMs and HAAs would also limit the occurrence of many other known or unknown unregulated DBPs (Krasner, 2009; Hrudey and Charrois, 2012). However, an application of alternative disinfectants to chlorine to minimize the formation of the regulated DBPs can favor the formation of potentially more toxic emerging DBPs, including iodinated compounds and nitrogenous compounds such as nitrosamines (Krasner, 2009; Dong et al. 2019). It has been demonstrated for all classes of halogenated DBPs, that iodine-containing species (I-DBPs) are generally the most toxic (Gonsioroski et al., 2020; Wagner and Plewa, 2017), followed by bromine-containing and chlorine-containing analogues (Krasner, 2012).

Iodinated trihalomethanes (I-THMs) were the first studied I-DBPs due to concerns about a strong medicinal taste and odor in drinking water (Hansson et al., 1987) and have received more attention subsequently to improve the understanding of their formation (Bichsel and von Gunten, 2000a; Krasner et al., 2006; Hua and Reckhow, 2007a; Jones et al., 2012; Allard et al., 2015).

After presenting the different iodine sources in the environment, this review paper analyses oxidation pathways of iodide and reactive iodine species by selected oxidants used in drinking water treatment and assesses second-order rate constants of the corresponding reactions. The aqueous iodine chemistry is presented to better understand the fate of iodide and the formation of iodinated disinfection by-products in drinking water. The available second-order rate constants for the reactions of iodine with inorganic and organic compounds are also presented and discussed.

The different factors influencing the formation of I-DBPs are discussed and a modeling is provided to explain the interplay between bromide concentration and pH. An assessment of the occurrence of I-DBPs worldwide and a risk assessment related to I-DBP formation and mitigation strategies complete this review.

## **2. Iodine in atmospheric, aqueous and terrestrial natural systems**

Iodine is a naturally-occurring halogen in many chemical forms and oxidation states, ranging from -1 to +7 (Risher et al., 2004). Iodide (-1) and iodate (+5) are the predominant species in the aqueous

environment (Preedy et al., 2009). Iodine occurs naturally as the stable isotope ( $^{127}\text{I}$ ) and the radioisotope ( $^{129}\text{I}$ ), additionally, eight other synthetic radioisotopes exist (Risher et al., 2004). The global cycling of iodine is presented in detail by Fuge and Johnson (2015) in a review of the role of iodine environmental geochemistry on human health. The following discussion of the iodine cycle will mainly focus on its transport and its role for water resources used for drinking purposes.

*Figure 1*

## **2.1 The marine environment: The largest compartment of available iodine**

Despite only representing about 1% of the total iodine (Preedy et al., 2009), the ocean is the largest compartment of accessible iodine corresponding to an average concentration of between 45 and 60  $\mu\text{g L}^{-1}$  (Risher et al., 2004). By contrast, chlorine and bromine have an average seawater concentration of 19.4  $\text{g L}^{-1}$  and 67  $\text{mg L}^{-1}$  respectively (Millero et al., 2008). In the open ocean, more than 95% of the dissolved iodine is present as inorganic iodine (mainly iodide and iodate) (Preedy et al., 2009; Fuge and Johnson, 2015). Iodate, is the most abundant species, as it is the thermodynamically stable form in oxygenated, alkaline seawater (Fuge, 2013). However surface and shallow shelf waters are enriched in iodide (up to 50%) (Fuge, 2013; Preedy et al., 2009). This is a result of the conversion of stable iodate to metastable iodide, through the action of phytoplankton, some macroalgae, and possibly through some abiotic processes such as photolysis (Figure 1) (Fuge and Johnson, 2015). Once formed, iodide is slowly re-oxidised to iodate (Fuge, 2013), after a first oxidation step of iodide to iodine, mediated by iodide-oxidising bacteria, followed by spontaneous hydrolysis to HOI, which finally disproportionates to iodate (Bichsel and von Gunten, 2000b; Amachi, 2008).

Volatile organo-iodine species such as  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{I}_2$  and  $\text{CH}_2\text{ClI}$  can be formed through biological activity (Amachi, 2008). From the knowledge based on aqueous chemistry of halogenation of organic matter and considering the formation of HOI as the key reactant in cells, it would be expected that iodoform ( $\text{CHI}_3$ ) is the first product formed through the haloform reaction. Subsequently, this may lead to the formation of  $\text{CH}_3\text{I}$  by dehalogenation. However, this mechanism has never been confirmed in living organisms. Organoiodine compounds, mainly iodoform, may also be formed by HOI and  $\text{I}_2$  – produced

by ozone (see section 2.2.4.) – reacting with dissolved organic matter at the sea surface (Bichsel and von Gunten, 2000a; Martino et al., 2009).

## **2.2 Atmospheric iodine chemistry**

All the volatilized compounds photodissociate rapidly in the atmosphere (Figure 1) – with a lifetime of a few seconds for  $I_2$  up to 10 days for  $CH_3I$  – to generate the iodine atom (Keppler et al. 2003; Sherwen et al. 2016). Subsequently, iodine atoms react mainly with ozone in the lower atmosphere to generate iodine monoxide ( $IO^*$ ) (Preedy V. R. et al., 2009). Iodine and iodinated compounds are then an important ozone-depleting family especially in the global marine upper troposphere (Saiz-Lopez et al., 2014). Different atmospheric species were characterized, *e. g.*,  $OIO$ ,  $I_2O_2$ ,  $HOI$ ,  $IONO_2$ ,  $I_2O_2$ ,  $I_2O_3$ ,  $I_2O_4$  and  $I_2O_5$ . Polymerisation of oxides could also lead to the production of iodine oxide particles (IOPs) (Figure 1) (Preedy V. R. et al., 2009). Iodine is transferred to the land surface through wet and dry deposition (Risher et al., 2004). The iodine content of rainwater is usually in the range 0.5 to 2.5  $\mu g L^{-1}$  (Fuge and Johnson, 2015). Rainwater concentrations of iodine are higher near the coast, wherefore, soils in the coastal zone are subjected to a greater input of iodine (Fuge and Johnson, 2015). However further inland, there is apparently no significant correlation between the iodine content in the soil and the distance from the sea because this also depends on total annual rainfall (Johnson, 2003). Over the sea or along the coast, iodate has been found as the dominant species in several studies (Hou et al., 2009; Truesdalea and Jones, 1996), whereas further inland, organo-iodine can become the most dominant fraction, with lower fractions of iodate than iodide (Gilfedder et al., 2007).

## **2.3 Iodine in soil**

In comprehensive worldwide databases of published iodine analysis, iodine concentrations varied from < 0.1 to up to 660  $mg kg^{-1}$ , with a median at 3  $mg kg^{-1}$  (Johnson, 2003; Smyth and Johnson, 2011). The input of iodine to soil occurs predominantly through transfer from the atmosphere (Risher J. et al., 2004). The input of iodine to soil also occurs through weathering of recent marine sediments or through the decay of vegetation or animals. Soil iodine is mainly in an organic form with variable fractions of iodate and iodide (Fuge and Johnson, 2015). After transfer from the atmosphere,

dissolved inorganic iodine is rapidly transformed to organic forms – through abiotic or biotic processes (Seki et al., 2013; Yamaguchi et al., 2010). For example,  $\text{MnO}_2$  has been found to oxidise  $\text{I}^-$  to  $\text{I}_2$  and then to iodate ( $\text{IO}_3^-$ ) or iodinated organic compounds in the presence of humic substances (Gallard et al., 2009). Organic-rich soils have the highest iodine fixation potential, especially peat soils, and humus may constitute the primary reservoir of iodine. Other components such as iron(III)- and/or aluminium(III)-(hydr)oxides and clay minerals also enhance the iodine fixation potential (Johnson, 2003; Fuge and Johnson, 2015), due to anion exchange processes on their positively charged surfaces (Preedy et al., 2009).

## **2.4 Iodine in fresh waters**

Most natural surface waters have total iodine concentrations between 0.5 and 100  $\mu\text{g L}^{-1}$  and often below 20  $\mu\text{g L}^{-1}$  (Table S1). In 807 samples taken in rivers across Europe, iodide concentrations ranged from < 0.01 to 104  $\mu\text{g L}^{-1}$  with a quite low median concentration (0.33  $\mu\text{g L}^{-1}$ ) (Salminen et al., 2005). Central continental and mountainous areas in particular tend to have lower concentrations, typically in the range 0.1 to 18  $\mu\text{g L}^{-1}$  (Salminen et al., 2005).

Compared to surface waters, groundwaters are generally more enriched in iodine with concentrations generally below sea concentrations (*i.e.* < 60  $\mu\text{g L}^{-1}$ ). Iodine in groundwaters mainly originates from breakdown of iodine-containing organic matter, leaching from marine sediments in slow-moving aquifers, and evapo-concentration in arid areas (Fuge and Johnson, 2015). The main species of iodine in groundwater is generally iodide with a small proportion of iodate (Tang et al., 2013), but in some cases organic iodine can also be important (Zhang et al., 2013).

Nevertheless, iodine concentrations higher than in sea water were reported in some drinking waters, with iodine levels in the  $\text{mg L}^{-1}$  range (Tang et al., 2013; Zhang et al., 2013). 72% of 950 water samples in the southwestern Taiyuan Basin, China had iodine concentrations > 150  $\mu\text{g L}^{-1}$  (Tang et al., 2013).

The iodine content of surface waters is also influenced by anthropogenic activities. Wastewaters from hydraulic fracturing are characterized by high chloride, bromide and iodide concentrations ( $\leq 56 \text{ mg L}^{-1}$ ). They may impact drinking water utilities downstream from disposal or accidental spill sites

(Harkness et al., 2015). Additional iodine may originate from agricultural activities by application of pesticides or herbicides containing methyl iodide or via fertilizers with trace levels of iodine (Moran et al., 2002; Salminen et al., 2005). Another source of iodide to surface and groundwaters is the discharge of persistent iodinated pollutants such as iodinated X-ray contrast media (ICM), which are a class of pharmaceuticals used in the medical imaging of soft tissues. Due to poor removal through conventional wastewater treatment – in some cases as low as 10% – ICM concentrations in surface waters can exceed  $1 \mu\text{g L}^{-1}$  (Schulz et al., 2008; Duirk et al., 2011; Xu et al., 2017) (Table S2). In some cases, iodine may be added directly to water to make it drinkable and/or to relieve endemic goitre in certain regions (Maberly et al., 1981; Vigneri et al., 1993; Smith et al., 2010). However, salt iodization for iodine supplementation to iodine-deficient populations remains the most appropriate and widespread measure to relieve endemic goitre (Eastman and Zimmermann, 2000; Bürgi et al., 2001). Iodine-based disinfectants (iodine solutions or iodine resins) have been a popular option for point-of-use drinking water disinfection by campers, the military, and rural consumers in developing countries (Goodyer and Behrens, 2000; Smith et al., 2010). However, use of iodination for full-scale water disinfection has been rare, due to the high cost of elemental iodine (Smith et al., 2010). Therefore, this source will not be a major contribution to iodine in fresh water systems.

### **3. Fate and reactivity of iodide and aqueous iodine during drinking water treatment**

#### **3.1. Specific removal of iodide**

Due to the absence of regulatory limits on bromide and iodide – except in Australia:  $0.5 \text{ mg L}^{-1}$  for iodide (NHMRC and NRMCC, 2011) – little effort has been made to develop drinking water treatment for bromide and/or iodide removal. However, based on the need to mitigate Br/I-DBP formation the potential benefits in lowering bromide and iodide concentrations have been assessed. Some processes, which are commonly used in drinking water treatment – while not used specifically for

halide removal – may also remove bromide and iodide before a disinfection step. It has been shown that membrane processes such as reverse osmosis, nanofiltration, ion exchange membranes, electrodialysis have good to excellent halide removal efficiencies – with reverse osmosis being the most effective (Watson et al., 2012). Studies on bromide and/or iodide removal using adsorption techniques (layered double hydroxides, silver impregnated activated carbons and carbon aerogels, ion-exchange resins, aluminium coagulation) – some of which are used in drinking water treatment – showed varied results, as their efficiency was mainly limited by interference from competing anions and DOM present in water resources (Sánchez-Polo et al., 2006; Watson et al., 2012).

### 3.2. Oxidation of iodide and iodine

During oxidative water treatment,  $I^-$  is first oxidised to reactive iodine species (usually HOI) which can further react with oxidants and/or organic matter (Figure 2). The specific reactivity of iodide and iodine with the main oxidants used in water treatment is described in this section. The reactivity of several other oxidants (Mn(VII),  $MnO_2$ , Fe(VI) as well as peroxides  $HSO_5^-$ ,  $S_2O_8^{2-}$ ,  $H_2O_2$  and their activation processes) has been recently reviewed (Li et al., 2020), wherefore, only kinetic information will be presented here for these oxidants (Table 1). A compilation of all oxidation processes is provided in Table 1 and Figure 2, including those, which are not discussed in detail in this publication.

Overall, the reactivity of oxidants towards iodide increases in the following order:  $MnO_2 < MnO_4^- < ClO_2 < NH_2Cl < HFeVO_4^- < HOCl < O_3 < HOBr$  (Table 1 and Figure 2). The oxidation of  $I^-$  to HOI is rapid for most oxidants ( $k_{app} > 10^3 \text{ M}^{-1}\text{s}^{-1}$  at pH 7), but relatively slow for permanganate and  $MnO_2$ . For chlorination, chloramination, ozonation and permanganate, HOI is the initial oxidation product in oxidative drinking water treatment. In the case of chlorine dioxide, ferrate, sulfate radicals, hydrogen peroxide and UV treatment, iodine atoms are formed which then can undergo various follow-up transformations (Ye et al., 2012; Zhang et al., 2015; Kralchevska et al., 2016).

The further reactivity of iodine with various oxidants is also discussed with second-order rate constants, the main products and half-life times being summarized in Table 1. At neutral pH, the

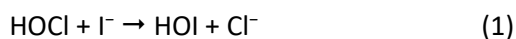
oxidants can be divided into three groups: (i) HOCl, HOBr, NH<sub>2</sub>Cl, O<sub>3</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> for which the second-order rate constants for the reactions with I<sup>-</sup> are higher than those for HOI; (ii) HSO<sub>5</sub><sup>-</sup> and MnO<sub>4</sub><sup>-</sup>, which have similar second-order rate constants for the reactions both with I<sup>-</sup> and HOI and (iii) HFeO<sub>4</sub><sup>-</sup>, which is more reactive towards HOI than towards I<sup>-</sup>. In the later case, electrostatic repulsion has been hypothesized to explain this paradox (Shin et al., 2018). Within the first group, the differences in reactivities are high. The half-life times of reactive iodine species such as HOI during oxidative treatment will determine the extent of the formation of iodinated organic compounds (see Figure 2 and section 5.1).

*Figure 2*

*Table 1*

### 3.2.1. Chlorine

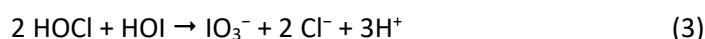
If iodide-containing waters are treated with chlorine, iodide (I<sup>-</sup>) is rapidly oxidised to hypoiodous acid (HOI) or hypiodite (OI<sup>-</sup>) (Eqs. 1 and 2). The rate of this reaction depends on the pH, *i.e.* the speciation of chlorine with HOCl or ClO<sup>-</sup> (pK<sub>a</sub> (HOCl/OCl<sup>-</sup>) = 7.53 (Martell, 1976)) (Nagy et al., 1988; Gerritsen and Margerum, 1990; Bichsel and von Gunten, 1999, 2000b) (Table 1).



These reactions occur via a Cl<sup>+</sup> transfer and a formation of ICl as a transient species. This intermediate product is unstable and hydrolyses to OI<sup>-</sup> (Kumar et al., 1986). During disinfection by chlorine, HOCl is the dominant reactive species for the reaction with iodide ( $k(\text{HOCl} + \text{I}^-) \geq 10^6 k(\text{OCl}^- + \text{I}^-)$ ) (Deborde and von Gunten, 2008). For typical concentrations of chlorine in drinking water treatment, HOCl/OCl<sup>-</sup> transforms I<sup>-</sup> to HOI/OI<sup>-</sup> within < 1 ms (Bichsel and von Gunten, 1999) (Table 1).

A further oxidation of HOI by chlorine occurs through a combination of second- and third-order reactions (Bichsel and von Gunten, 1999). There are two hypothetical pathways for HOI oxidation by HOCl: (i) The I-atom in HOI is attacked by the O-atom of HOCl, leading to iodite (IO<sub>2</sub><sup>-</sup>) formation, which is quickly further oxidised by HOCl to IO<sub>3</sub><sup>-</sup>; (ii) HOI is attacked by the Cl-atom of HOCl leading to the formation of an intermediate with a iodine-chlorine bond (HOI-ClOH) which then either dissociates

back to the initial compounds or further reacts with a second HOCl to form HOI(ClOH)<sub>2</sub> which would quickly hydrolyse to IO<sub>3</sub><sup>-</sup> (Bichsel and von Gunten, 1999). Eqs. (3) and (4) show the stoichiometries of these reactions with the corresponding rate constants in Table 1 (Bichsel and von Gunten, 1999). In these reactions, the formation of the intermediate species is the rate limiting step resulting in the measured second-order rate constants.



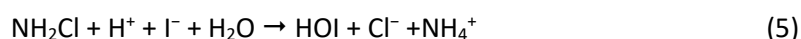
Eq. (4) is the dominant reaction, contributing between 60% (pH 7) and 99.5% (pH 9) to the overall HOI oxidation by chlorine (Bichsel and von Gunten, 1999). This process is relatively slow, with a half-life time of 1 hour under typical drinking water treatment conditions (Table 1).

In the presence of bromide, HOBr and OBr<sup>-</sup> (pK<sub>a</sub> (HOBr/OBr<sup>-</sup>) = 8.8) formed from the reaction between chlorine and bromide (Heeb et al., 2014) are also able to oxidise I<sup>-</sup> to HOI or OI<sup>-</sup> (Table 1) through an analogous reaction pathway. The formation of iodate is accelerated due to the relatively high reactivity of HOBr and OBr<sup>-</sup> with HOI/OI<sup>-</sup> (Table 1), which outcompetes the reactions with chlorine (Criquet et al., 2012).

In addition, cupric oxide (CuO) – one of the major corrosion products of copper pipes – can activate HOCl, thus enhancing its reactivity towards HOI and increasing the rate of formation of iodate compared to the absence of cupric oxide. Iodate can also be further oxidised to periodate (IO<sub>4</sub><sup>-</sup>) by CuO-activated hypohalous acids (Liu et al., 2014).

### 3.2.2. Chloramines

Unlike the reaction between monochloramine and bromide, which mainly leads to the formation of a mixed haloamine NHBrCl (Luh and Mariñas, 2014) the product of the reaction of monochloramine with iodide is assumed to be hypoiodous acid (Eq. (5)). NH<sub>2</sub>Cl transforms I<sup>-</sup> into HOI/OI<sup>-</sup> within < 15 minutes under typical drinking water treatment conditions (Bichsel and von Gunten, 1999) (Table 1).



The second-order rate constant for the reaction of iodide with dichloramine is much lower than with monochloramine (Table 1). This difference is explained by the predominant reaction of NH<sub>3</sub>Cl<sup>+</sup> in

chloramination processes (Heeb M. B. et al., 2017) along with the difference of the  $pK_a$  of mono- (1.5) and dichloramine (-6.0) (Trogolo and Arey, 2017).  $NCl_3$  oxidises  $I^-$  with a higher second-order rate constant than the two other chloramines but no values were determined (Kumar et al., 1986) (Table 1). This leads to the formation of an intermediate  $NCl_3I^-$  which further decomposes by a first-order process to  $NHCl_2$  and  $ICl$  (Nagy et al., 1988).

A further oxidation of  $HOI$  to iodate by monochloramine can be neglected with a low second-order rate constant (Table 1) leading to a long lifetime of  $HOI$  and minor iodate formation in chloramination processes (Bichsel and von Gunten, 1999). Zhu and Zhang (2016) proposed the formation of the mixed haloamine  $NHClI$  ( $k = 2.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ ) to explain the iodine incorporation into DOM in their model, however this species has not been experimentally confirmed.

In bromide-containing waters, bromochloramine ( $NHBrCl$ ) as well as  $HOBr$ ,  $NH_2Br$  and  $NHBr_2$  can be formed during chloramination (Luh and Mariñas, 2014; Trofe et al., 1980). Small amounts of  $HOBr$  may also be formed from hydrolysis of chloramines (by  $HOCl$  that can react with  $Br^-$  to  $HOBr$ ) (Zhai et al., 2014) or bromamines (Luh and Mariñas, 2014). Bromamines are typically more reactive than their chloramine analogues, however the reactivity of  $I^-$  with bromamines in drinking water treatment has not been reported yet (Heeb et al., 2017).

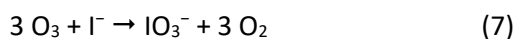
### 3.2.3. Ozone

Ozone ( $O_3$ ) oxidises  $I^-$  very rapidly to  $OI^-$ , which is in equilibrium with  $HOI$  (section 4.1). The reaction occurs by an oxygen atom transfer via an intermediate adduct  $I-OOO^-$  (Liu et al., 2001; von Gunten, 2003).  $O_3$  transforms  $I^-$  to  $HOI/OI^-$  within  $< 1$  ms during drinking water treatment (Eq.6) (Bichsel and von Gunten, 1999) (Table 1). Due to the fast direct ozone reaction, the oxidation by the secondarily formed hydroxyl radicals ( $\cdot OH$ ) can be neglected (Allard et al., 2013b).



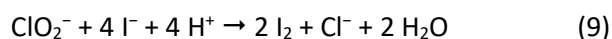
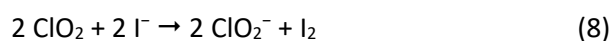
In contrast to aqueous chlorine, both  $HOI$  and  $OI^-$  are quickly further oxidized to iodate by ozone (Bichsel and von Gunten (1999), Table 1). Oxidation by ozone occurs predominantly via  $HOI$  for  $pH \leq 8$ . At  $pH > 8$ , the oxidation of  $OI^-$  by ozone contributes significantly to the overall oxidation process

(Bichsel and von Gunten, 1999). The second-order rate constants of these reactions (Table 1) lead to half-life times for HOI/OI<sup>-</sup> of 0.35 or 0.92 s, respectively for pH 9 and 6 and 1 mgO<sub>3</sub> L<sup>-1</sup>. The overall stoichiometry of the reaction shows a consumption of 3 moles of ozone to oxidise iodide to iodate (Eq. (7)) (Bichsel and von Gunten, 1999).



#### 3.2.4. Chlorine dioxide

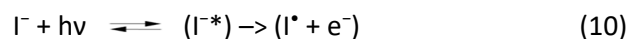
The chlorine dioxide (ClO<sub>2</sub>) reaction with iodide is complex. Until recently, most of the studies were performed either at low pH and/or with a high iodide concentration. ClO<sub>2</sub> has been shown to form I- atoms (I<sup>•</sup>) and finally I<sub>2</sub> via electron-transfer reactions (Eq. (8); k(ClO<sub>2</sub>/I<sup>•</sup>) = 1.87 x 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> (Fabian and Gordon, 1997). A further redox reaction between ClO<sub>2</sub><sup>-</sup> and I<sup>-</sup> is possible (Eq. (9)) (Kern and Kim, 1965), however, in slightly acidic to neutral solutions, the corresponding second-order rate constant is several orders of magnitude lower and this reaction can be neglected under typical drinking water treatment conditions (Fabian and Gordon, 1997) (Table 1).



A significant portion of ClO<sub>2</sub> degrades to free available chlorine upon reaction with DOM (about 20-25% under drinking water treatment conditions) which can oxidize I<sup>-</sup> to HOI and eventually to iodate. Similarly to chlorination, bromide could enhance the formation of iodate through the formation of HOBr during this process (Rougé et al., 2018; Terhalle et al., 2018). It has been reported that the presence of bromide enhances the formation of DBPs and shifts the speciation to more brominated species (Yang et al., 2013) including brominated I-THMs (Guo et al., 2014), despite the absence of reactivity between bromide and ClO<sub>2</sub> (Hoigné and Bader, 1994).

#### 3.2.5. Ultraviolet irradiation, advanced oxidation and other processes

Iodide can absorb UV light to form an excited state  $I_{aq}^{-*}$  which may relax back to the ground state or form an iodine atom and a solvated electron in close proximity (Eq. (10)). These radicals may combine once more in the cage or diffuse into the bulk (Eq. (10)) (Jortner et al., 1964).



In the absence of electron scavengers, the back reaction predominates (Rahn, 1997). Enhancement of photooxidation of As(III) has been found in the presence of iodide through the formation of iodine atoms (Yeo and Choi, 2009).

The reaction of hydroxyl radicals (formed during advanced oxidation) with iodide is diffusion limited (Table 1) and forms the hydroxyl iodide radical anion ( $HOI^{-*}$ ) which decomposes to  $I^{\bullet}$  and  $HO^{-}$  or further reacts with iodide to a  $I_2^{-*}$  radical (Yamaguchi, 2011). The further reaction of  $^{\bullet}OH$  with  $HOI$  is important in atmospheric chemistry with a second-order rate constants of  $k = 4.7 \times 10^8$  to  $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Hammaeher et al., 2011; Riffault et al., 2005). It is in the same order as the reactivity of  $^{\bullet}OH$  with  $HOBr$  ( $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ; (Buxton et al., 1988)). In presence of hydrogen peroxide ( $H_2O_2$ ) (present in AOPs such as  $UV/H_2O_2$  or  $O_3/H_2O_2$ ),  $HOI$  is quickly reduced to  $I^{-}$  ( $k_{H_2O_2/HOI} = 9.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ), which generally limits the formation of I-DBPs (Shin et al., 2020, 2018; Valent et al., 1998). This may have consequences for post-chlorination/-chloramination after the  $UV/H_2O_2$  process, because iodide will persist and may lead to the formation of I-DBPs (Shin et al., 2018).

While persulfate ( $S_2O_8^{2-}$ ) and peroxymonosulfate ( $HSO_5^{-}$ ) can oxidise iodide directly to  $I_2$  or  $HOI$  (Li et al., 2020), the sulfate radical ( $SO_4^{-*}$ ) formed from their activation has been suggested to lead to the iodine atom. Wang et al. (2017) hypothesized that iodide follows the same transformation pathway as bromide when oxidised by sulfate radicals to form radical iodine species, which undergo a self reaction to free iodine ( $I_2$ ). The second-order rate constant of the oxidation of iodide by sulfate radicals (Eq. (26)) is not yet known (Table 1).

Iron (III) has been reported to oxidise iodide, however, the mechanism has only been studied for high levels of iodide leading to the formation of  $I_3^{-}$  (Vrkljan et al., 2008). Nevertheless, the formation of I-DBPs has been highlighted during  $FeCl_3$ -based coagulation (Ding et al., 2019).

### 3.2.6. Fate of other iodine sources

Iodinated X-ray contrast media (ICM) are very recalcitrant compounds, wherefore, their degradation has gained some attention recently. ICM can be degraded by direct photolysis (254 nm), whereby  $I^-$  is released without formation of HOI or  $IO_3^-$  (Allard et al., 2016). Irradiation at 254 nm was shown to be quite effective in degrading diatrizoic acid, iotalamic acid, iohexol, iopromide and iopamidol (quantum yields  $0.034 - 0.071 \text{ mol} \times \text{Einstein}^{-1}$ ) (Tian et al., 2014; Allard et al., 2016).

Chlorine poorly reacts with ICM, with iopamidol having the highest reactivity ( $k(\text{HOCl} + \text{iopamidol}) = 1.5 \times 10^{-2} - 1.66 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$  and  $k(\text{OCl}^- + \text{iopamidol}) = 0.45 - 0.94 \text{ M}^{-1}\text{s}^{-1}$  (Wendel et al., 2014; Tian et al. 2017a), releasing iodine at slightly alkaline pH (Duirk et al., 2011; Wendel et al., 2014). Monochloramine does not degrade ICM (Duirk et al., 2011; Wendel et al., 2014). During ozonation several ICM (iopamidol, iopromide, iomeprol, diatrizoate) are partially oxidized, mainly by the secondarily formed hydroxyl radicals (Ternes et al., 2003). However, most studies used very high ozone doses ( $10\text{-}16 \text{ mg L}^{-1}$ ) and degradation is not complete under more typical ozonation conditions (Huber et al., 2005, 2003; Kovalova et al., 2013; Magdeburg et al., 2014; Ning and Graham, 2008; Ternes et al., 2003). ICMs such as diatrizoate have also been reported to be degraded by zerovalent iron under aerobic conditions (Stieber et al., 2011; Zhou et al., 2019) and by sulfate radicals (Hu et al., 2017; Wang et al., 2019).

$IO_3^-$  can be phototransformed to  $I^-$  during UV irradiation at 254 nm (Eqs. (13-15)) (Zhang et al., 2016a), with pseudo-first order kinetics and a quantum yield of  $0.0591 \text{ mol Einstein}^{-1}$  (Tian et al., 2017a).

However, phototransformation of iodate will not be important for typical UV disinfection in drinking water. It also has been shown that the reduction of  $IO_3^-$  to iodide by UV/ $H_2O_2$  is faster than with UV alone (Tian et al., 2019). This is probably due to the efficient reduction of the intermediate HOI by hydrogen peroxide (Shin et al., 2020).

## 4. Aqueous iodine chemistry

In oxidative water treatment, HOI formed from the oxidation of  $I^-$  can have various fates. The possible reactions of HOI – illustrated in Figure 2 – are (i) disproportionation, (ii) oxidation to iodate or (iii) reaction with DOM.

#### 4.1. Speciation of aqueous iodine

Once formed, HOI is in equilibrium with  $I_2$ ,  $OI^-$ ,  $I_3^-$  and  $H_2OI^+$  as described by Eqs. (11-13) (Table 2). At low pH,  $I_2$  is the dominant species (Figure 3). At high pH, HOI dissociates to  $OI^-$  with a  $pK_a = 10.4 \pm 0.1$  (Bichsel and von Gunten, 2000b). A  $pK_a$ -value of 10.64 has been published by extrapolation to zero ionic strength (Schmitz, 2004). Therefore, under typical drinking water conditions, HOI is the major species and  $OI^-$  is less significant.

Figure 3

Table 2:

$I_2$  is in equilibrium with  $I_3^-$  and polyiodide anions, which is controlled by the iodide concentration (Eq. 14 in Table 2 and Figure S1). ICI (Eqs. 15-16, Table 2) has also been reported to be an important iodinating agent in  $Cl^-$ -rich waters (Rose and Roberts, 2019).

#### 4.2. Disproportionation of hypiodous acid

The disproportionation of HOI eventually leads to iodate formation (Eqs. 17-20, Table 2), with reactions (17) and (18) being rate-determining. The disproportionation of HOI is catalysed by buffers such as phosphate, borate or acetate and dominates the kinetics of HOI disproportionation (Bichsel and von Gunten, 2000b; Opoku-Agyeman, 2010). A value of  $k = 0.3 \text{ M}^{-1} \text{ s}^{-1}$  has been proposed (Table 2) for Eq. (17) in absence of buffers (Bichsel and von Gunten, 2000b). The value of Schmitz (2004)  $k = 25 \text{ M}^{-1} \text{ s}^{-1}$  has been determined in presence of at least  $5 \times 10^{-2} \text{ M}$  of perchloric acid which could be sufficient to catalyse the disproportion reaction. The rate constants range from 50 to  $5000 \text{ M}^{-2} \text{ s}^{-1}$  for the buffer catalysed reaction (Bichsel and von Gunten, 2000b).

The overall reaction (Eq. (20)) remains very slow under typical drinking water conditions (pH 6-8, 0-5 mM carbonate, 1-10  $\mu\text{g L}^{-1}$  iodine), with an initial half-life of HOI ranging from a few days to years.

Therefore,  $\text{IO}_3^-$  formation by this pathway is of minor importance during drinking water treatment (Bichsel and von Gunten, 2000b). Ferrate and permanganate have been shown to catalyse the disproportionation of HOI (at  $\text{pH} > 9$  for ferrate (Shin et al., 2020) and  $\text{pH} > 8$  for permanganate (Zhao et al., 2017)). Thus, the fate of iodine will depend on different parameters such as the reaction of HOI with inorganic and organic compounds as well as the applied oxidants or reductants (*e.g.*,  $\text{MnO}_4^-$ ,  $\text{FeO}_4^{2-}$ ,  $\text{H}_2\text{O}_2$ ).

#### 4.3. Hypoiodous acid reactivity with inorganic compounds

Table 3 summarizes the published rate constants for reactions of iodine with inorganic compounds. Unlike HOCl and HOBr, HOI is unreactive toward  $\text{NH}_3$  (Bichsel and von Gunten, 1999). HOI/ $\text{OI}^-$  can react with  $\text{Cl}^-$  and  $\text{Br}^-$  to form the intermediates ICl and IBr in a third-order reaction involving  $\text{H}^+$ , which rapidly hydrolyze back to HOI ( $2.4 \times 10^6 \text{ s}^{-1}$  and  $8 \times 10^5 \text{ s}^{-1}$ , respectively) (Troy et al., 1991; Vogt et al., 1999; Wang et al., 1989).

Table 3

Compared to HOCl or HOBr, the information on the HOI reactivity with inorganic compounds is scarce (Deborde M. and von Gunten, U., 2008; Heeb et al., 2014). In particular, no rate constants are available for the reactions with metals and metalloids of interest such as iron (Fe(II)) and manganese (Mn(II)), or with other anions such as sulfite, cyanide, nitrite and thiocyanate. According to the literature, HOI reaction with sulfite proceeds rapidly, forming sulfate and releasing iodide (Morgan, 1954). The second-order rate constants for the reactions of HOI with sulfite and hydrogen sulfite were assumed to be  $> 10^9 \text{ M}^{-1}\text{s}^{-1}$  (Pechtl et al., 2007; Xu, 2014).

Hydrogen peroxide has been shown to reduce HOI while it is able to oxidise  $\text{I}^-$ . These reactions constitute one of the first oscillating reaction (Bray–Liebhafsky) described in literature (Bray, 1921).

#### 4.4. Hypoiodous acid reactivity with organic compounds

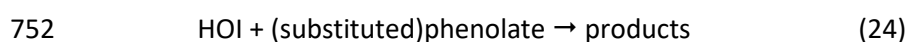
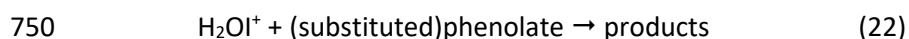
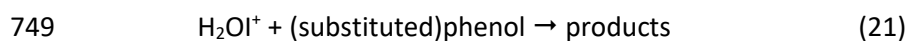
The two main types of moieties which have been investigated for HOI reactivity are phenols (Table 4) and  $\alpha$ -methyl carbonyl compounds (Table 5). These classes of compounds are known constituents of

NOM (Natural Organic Matter). NOM which contain  $\alpha$ -methyl carbonyl or phenol groups are known precursors of I-DBPs such as THMs, iodinated acids or iodinated phenols (Ding and Zhang, 2009). Recently, several other types of compounds have been studied including carboxylic acids and flavones (Zhao et al., 2017).

Table 4

#### 4.4.1. Phenolic compounds

Free iodine reacts with phenolic compounds via (i) electrophilic aromatic substitution (Wang et al., 2017), or via (ii) electron transfer, leading to the formation of benzoquinones (Zhao et al., 2017). The apparent second-order rate constants for the reactions of iodine with phenolic compounds (Table 4) are pH-dependent (Bichsel and von Gunten, 2000a). The contribution of each reaction to the overall reactivity is illustrated in Figure 4. Similarly to chlorine and bromine (Criquet et al., 2015), the reactivity of iodine with phenolic compounds is high and is dominated by the reaction between HOI and the phenolate (Eq. (24)) at circum neutral pH (Figure 4) with species-specific rate constants  $\leq 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (Table 4). The reaction rate is minimal at pH 3 to 5 and increases to a maximum at the mean of the  $\text{pK}_a$  values of phenol/phenolate and HOI/ $\text{IO}^-$  (*i.e.*, usually around pH 10). In this range, the apparent second-order rate constant increases by a factor of 10 per pH unit increase (Bichsel and von Gunten, 2000a). The apparent second-order rate constants also increase for pH below 3. This was attributed to the reactivity of  $\text{H}_2\text{OI}^+$  towards phenols (Eq. (21)) (Bichsel and von Gunten, 2000a; Rose and Roberts, 2019). Rose and Roberts (2019) introduced the additional reaction between  $\text{H}_2\text{OI}^+$  and the phenolate (Eq. (22)) in their modeling as it involves both the nucleophile ( $\text{H}_2\text{OI}^+$ ) and the electrophile (phenolate). This reaction shows a similar contribution to the reaction between HOI and phenol and explains the differences observed between the apparent rate constant calculation from pH 3 to 5 (Figure 4). However, the consideration of this fast reaction for the determination of the other second-order rate constants does not modify substantially the second-order rate constants of reactions 23 and 24 (Table 4) (Rose and Roberts, 2019) nor the maximum pH (Figure 4).



753 A comparison of the species-specific second-order rate constants clearly shows the following trend:

754  $k_{\text{HOI}/\text{PhO}^-} > k_{\text{H}_2\text{OI}^+/\text{PhOH}} > k_{\text{HOI}/\text{PhOH}}$ . The higher reactivity of  $\text{H}_2\text{OI}^+$  compared to HOI towards phenol can be

755 explained by the higher electrophilicity of  $\text{H}_2\text{OI}^+$  compared to HOI, whereas the different reactivities of

756 HOI towards phenol and phenolate can be explained by the higher nucleophilicity of the phenolate

757 compared to the phenol (Eqs. (23) and (24)) (Bichsel and von Gunten, 2000a). However, the impact of

758 buffers should also be considered as iodination of phenol is a buffer catalysed process (Berliner, 1951).

759 Zhao et al. (2017) showed a significant increase of the apparent second-order rate constants for the

760 reaction of iodine with phenol in the presence of increasing concentrations of phosphate and borate

761 buffers.

762 *Figure 4*

763 The reactivity of HOI with phenolic moieties lies between the reactivities of HOBr and HOCl. Its

764 reactivity varies significantly depending on the nature and location of the substituents on the phenol

765 (Figure 5). The QSAR modeling first presented in (Lee et al., 2005) from the data of Bichsel and von

766 Gunten (2000a) has been extended here with additional second-order rate constants from Table 4. For

767 cases for which only apparent second-order rate constants were available, the species-specific second-

768 order rate constant  $k(\text{HOI}/\text{PhO}^-)$  was estimated neglecting the other reactions and considering the

769 fraction of the phenolate species from its  $\text{pK}_a$  value. This approximation could be applied for the

770 apparent second-order rate constants available at pH 7 and 8 because, under these conditions,

771  $k(\text{HOI}/\text{PhO}^-)$  represents more than 95 and 99 % of the overall reactivity of iodine towards phenol,

772 respectively (Figure 4). However, it was not possible to determine the species-specific second-order

773 rate constants for resorcinol and phloroglucinol with this approach. The apparent second-order rate

774 constants are only available at pH 8 and the di-deprotonated forms which have much higher reactivity

could not be neglected in these cases. Thus, these compounds have been excluded from the regression.

The slope obtained (-6.2) for the species-specific second-order rate constant  $k_{\text{HOI/phenolate}}$  as a function of the Hammett constant ( $\sigma$ ) is lower than in a previous study (-7.0 (Lee et al., 2005)). Nevertheless, the reactivity of HOI is more impacted by substituent moieties than for chlorine or bromine which exhibit similar and lower slopes (-3.0 and -3.5, respectively (Heeb et al., 2014)) (Figure 5).

The order of reactivity observed  $\text{HOBr} > \text{HOI} > \text{HOCl}$  is somehow not logical. Based on electronegativity of halogens (Cl: 3.16; Br: 2.96; I: 2.66) the polarisation of the O-X bond increases from chlorine to iodine. Then HOI, based on this aspect, should exhibit the highest reactivity. The steric hindrance due to the bigger size of iodine atom could be affect its reactivity, however, the second-order rate constants of o-, m- and p-bromophenols do not support this hypothesis; o-bromophenol should be more reactive compared to p-bromophenol (Figure 5 and Table 4) if steric hindrance was an important factor. Iodine atom is known to be more polarisable than other halogens, this could be an important aspect in the specific reactivity, modifying the relative strength of O-X bonds, making OH a better leaving group in HOBr than HOI. Likely, this factor overrules the effect of the electronegativity such that HOI has an intermediate reactivity between HOCl and HOBr.

*Figure 5*

#### **4.4.2. Ketones and carboxylic acids**

Similarly to chlorine and bromine, the stoichiometry of the reaction between HOI and carbonyl compounds is 3 to form a triiodomethyl group. At neutral pH, the enolization step is rate-determining and the overall reaction depends only on the carbonyl concentration and the pH and not on the concentration of HOI (Table 5). The triiodocarbonyl compound then hydrolyses with the formation of  $\text{CHI}_3$  and the corresponding carboxylic acid ( $\text{RCOOH}$ ) (Bichsel and von Gunten, 2000a). The enolization step is catalysed by  $\text{OH}^-$  and  $\text{H}_2\text{O}$ , and therefore, the rate of HOI consumption includes two rate constants  $k_{\text{H}_2\text{O}}$  and  $k_{\text{OH}^-} [\text{OH}^-]$  which reflects the pH dependence (Bichsel and von Gunten, 2000a).

3-oxopentanedioic acid exhibits a substantial reactivity towards HOI with an apparent second-order rate constant of  $4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at pH 7 (Zhao et al., 2017). This ketone may exhibit a different mechanism without the enol-formation. The reactivity of carboxylic acids is low, the apparent second-order rate constant for the reaction of iodine with citric acid at pH 8 has been reported as  $< 1 \text{ M}^{-1} \text{ s}^{-1}$  (Zhao et al., 2017).

Table 5

#### 4.4.3. Other compounds

Second-order rate constants for the reactions of DOM with HOI have been determined to be in the range of  $0.1\text{-}0.4 \text{ M}^{-1} \text{ s}^{-1}$  on a C-atom concentration basis for DOM in two natural surface waters (Bichsel and von Gunten, 2000a). This reactivity is much lower than for HOBr which has been estimated to be in the range  $10^2\text{-}10^4 \text{ M}^{-1} \text{ s}^{-1}$  in the first phase and 100 times lower in the slow phase of reaction with DOM (Heeb et al., 2014).

Besides phenols and carbonyl compounds, other organic model compounds (allyl alcohol, glucosamine, glycine, toluene, and oxalate) were tested for their reactivity with HOI. The corresponding second-order rate constants were  $< 1 \text{ M}^{-1} \text{ s}^{-1}$  or even  $< 0.1 \text{ M}^{-1} \text{ s}^{-1}$  (Bichsel and von Gunten, 2000a). Moderately nucleophilic aromatic compounds like dimethenamid exhibit a low reactivity towards HOI ( $\leq (9.07 \pm 1.95) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ), wherefore, in this case, the reactivity with  $\text{H}_2\text{OI}^+$  ( $(6.53 \pm 0.10) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) is predominant under typical drinking water conditions (Rose and Roberts, 2019).

## 5. Factors influencing the formation of I-DBPs

### 5.1. Role of oxidant type/dose and residence time

Monochloramine unlike chlorine is unable to oxidise HOI to iodate leading to a longer lifetime of HOI and hence a potential increase of I-DBP formation compared to chlorination process. However, as shown previously, the kinetics of the formation of iodate by chlorine is also quite slow (Table 1). This life-time is reduced in presence of bromide (see section 3.1). Overall, due to the slow oxidation kinetics of HOI by chlorine, chlorine dioxide, permanganate, and chloramine, the formation of I-DBPs can be of

concern when treating iodide-containing waters. In contrast, iodate has been shown to be a major sink for iodide during ozonation, treatment with ferrate and peroxymonosulfate (Table 1). Overall, the yield of iodinated DBPs for the main oxidants for typical water treatment conditions generally follows the pattern summarized in Table 6.

In addition to the oxidant type also the oxidant dose needs to be considered. Low free chlorine residual concentrations leads to higher organic I-DBPs concentrations (Ioannou et al., 2016) and higher doses of chlorine reduce the formation of organic I-DBPs (Hua et al. 2006). Several studies have reported that high residence times in distribution systems lead to higher organic I-DBPs concentrations in chlorinated or chloraminated waters (Ioannou et al., 2016; Serrano et al., 2015).

Table 6

## 5.2. Role of total iodine/iodide and bromide concentrations

Generally, higher iodide concentrations are associated with higher concentrations and numbers of organic I-DBPs during oxidation processes. This has been shown in several occurrence (Parsons et al., 2009; Richardson et al., 2008) and laboratory studies (Bichsel and von Gunten, 2000a; Jones et al., 2012; Kristiana et al., 2009; Zhang et al., 2015). A linear relationship has been established between I-THM formation and iodide content (Parsons et al., 2009) but this could not be generalized (Postigo et al., 2017; Richardson et al., 2008). (MacKeown et al., 2021) showed a linear correlation for low iodide concentrations ( $< 8 \mu\text{g L}^{-1}$ ), which was not observed anymore for higher iodide contents. For chlorination at typical chlorine doses of  $1\text{--}3 \text{ mg L}^{-1}$ , 20% of the iodide was incorporated in organic I-DBPs at  $\text{pH} < 8$  in one study (Dillon et al., 2015). A similar trend of iodine and bromine incorporation has been observed in other studies, ranging from 10 to 40% of halogen bound to DOM (Criquet et al., 2015; Hua et al., 2006; Zhao et al., 2017). In some cases, even low levels of iodide ( $\leq 1 \mu\text{g L}^{-1}$ ) can yield measurable levels of organic I-DBPs (MacKeown et al., 2020; Richardson et al., 2008).

The formation of I-DBPs was also related to the presence of ICMs in source waters (Duirk et al., 2011; Tugulea et al., 2018). MacKeown et al. (2020) showed a higher iodate formation after chlorination than the initial iodide content in the raw water (70% increase), demonstrating an oxidation of other sources

of iodide. While ICMs could be important as anthropogenic micropollutants, their concentrations usually do not explain the formed TOI (MacKeown et al., 2020). It seems more likely that this deviation results from an underestimation of the iodide concentration due to iodide complexation by NOM (see section 5.4.2). Therefore, total iodine measurements in addition of iodide may be necessary.

Important amounts of iodide can be added during food preparation by the use of iodinated table salt. Up to several hundreds of  $\mu\text{g L}^{-1}$  of different I-DBPs were produced during cooking through the reaction with residual chlorine or chloramine from tap water, which increased the toxicity of the samples (Cao et al., 2022; Pan et al., 2016b; Yan et al., 2016).

Increasing the bromide concentrations in waters significantly enhances the rate and extent of iodate formation possibly reducing the yield of organic I-DBPs (Criquet et al., 2012). It has been shown that HOBr accelerates the oxidation of HOI to iodate during chlorination by a bromide-catalysed process. The second-order rate constants for the reaction of bromine with iodine ( $k(\text{HOBr/OI}^-) = 1.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $k(\text{OBr}^-/\text{OI}^-) = 1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ) are much higher than the corresponding rate constants for chlorine ( $k(\text{HOCl/OI}^-) = 8.2 \text{ M}^{-1} \text{ s}^{-1}$  and  $k(\text{OCl}^-/\text{HOI}) = 52 \text{ M}^{-1} \text{ s}^{-1}$ , Table 1). The effect of the bromide/iodide ratio on the formation and speciation of I-THMs by chlorine followed by ammonia addition showed that  $\text{CHCl}_2\text{I}$  is the main I-THM in the absence of bromide. At a molar bromide:iodide ratio of 10, mixed Cl-/Br-/I-THMs without any clear dominating species were formed. When the molar bromide:iodide ratio was increased to 50, Br-/I-THMs clearly became the major species with  $\text{CHBr}_2\text{I}$  being most important (Allard et al., 2015). This change in I-THM speciation is due to the formation of HOBr which is a better substituting agent than chlorine (Westerhoff et al., 2004; Acero et al., 2005). This may lead to higher concentrations of brominated precursors, which consecutively react with HOI to mixed Br-/I-THMs (Allard et al., 2015). In addition, increasing bromide concentrations in chloraminated solutions also lead to a significant decrease in the I-THM formation and changes in species distribution due to the formation of bromine and  $\text{NHBrCl}$  which may lead to more brominated precursors than  $\text{NH}_2\text{Cl}$  (Luh and Marinas, 2012; Jones et al. 2012; Liu et al. 2017).

### 5.3. Role of natural organic matter

878 Natural organic matter is the major precursor for the generation of organic DBPs during disinfection.  
879 DOM reacts with hypohalous acids (HOX) by electrophilic aromatic substitution leading to the  
880 incorporation of halogen atoms into the organic matrix or by redox processes leading to an oxidation  
881 of the DOM and the release of the halide ions (Criquet et al., 2015). The specific ultraviolet absorbance  
882 at 254 nm (SUVA) – with a high SUVA value generally indicating a high aromatic content (Reckhow et  
883 al. 1990) – has been widely used as an indicator of the DBP formation potential of DOM (Hua and  
884 Reckhow, 2007b; Jones et al., 2012; Hua et al., 2015; Liu et al., 2017). Liu et al. (2017) showed from the  
885 chloramination of model compounds that low SUVA substances favored the formation of I-DBPs  
886 compared to high SUVA substances. This could be related to the numbers of active sites, low SUVA  
887 waters exhibiting a limited number of active sites, while high SUVA DOM could incorporate iodine in  
888 many different sites favouring an increase of TOI in contrast to individual low molecular weight DBPs  
889 (Allard S. et al., 2015). The same behaviour has been observed with natural waters or NOM extracts in  
890 several studies (Jones et al., 2012; Liu et al., 2017), but the opposite was found in other studies (Wang  
891 et al., 2014; Zhang et al., 2016b). However, when TOI was measured, DOM with high SUVA shows the  
892 highest concentrations of unknown I-DBPs formed (Hua and Reckhow, 2007b) or lower iodate  
893 formation (Criquet et al., 2012). Consequently, the aromatic fraction seems to be more reactive with  
894 iodine to form TOI. Conversely, low SUVA DOM with aliphatic moieties, already containing smaller  
895 molecular weight (MW) precursors, could lead to the formation of measurable DBPs such as I-THMs.  
896 An analogue behaviour has been hypothesized for brominated DBPs (Hua and Reckhow, 2007b).  
897 However, these conclusions on I-DBPs are weakened by the fact that iodine incorporation into DOM  
898 depends on other factors (e.g. bromide concentration, oxidant exposure, iodate formation) that are  
899 not always well or clearly set and comparable in the different studies with NOM or natural waters. It  
900 has also to be noted that DBP formation potential tests (DBP-FP) are not appropriate in the case of I-  
901 DBPs due to the high extent of conversion of iodide to iodate in the presence of high concentrations  
902 of chlorine. For increasing SUVA and/or for high molecular weight fractions, a higher chlorine  
903 consumption is expected by direct reaction with the DOM, producing more chlorine-containing sites

and leaving less chlorine available for oxidation of HOI to iodate (Allard et al., 2015; Zhang et al., 2016b). Considering the oxidation state of DOM, its partial pre-oxidation could change the production of DBPs. This has been shown in the case of UV/H<sub>2</sub>O<sub>2</sub> pretreatment before chloramination for which the production of I-THM increased, due to the partial oxidation of the DOM, lowering its aromatic structure and forming small molecular weight DOM fractions (Zhang et al., 2018).

#### 5.4. Role of pH

The predominance of main iodine reactive species (*i.e.* HOI and IO<sup>-</sup>) depends on pH as well as chlorine and bromine speciation but also chloramine stability. Thus, the formation and speciation of I-DBPs is influenced by pH. The formation rate of iodate during chlorination (or bromination) has an optimal pH at the mean of pK<sub>a</sub> values of chlorine (or bromine) and iodine reactive species (Criquet et al., 2012), *i.e.*, 9.0 for chlorine and 9.6 for bromine. Therefore, the optimal pH for iodate formation lies between these two values and depends on the bromide level. This range of pH is also close to the optimal pH for the reactivity of phenolic moieties with HOX, and therefore potentially for the formation of I-DBPs (Figure 6).

It has been shown for chlorination that I-THM formation increases with increasing pH from 5.5 to 8.5, specifically for low MW fractions of DOM (Zhang et al., 2016b).

Several studies reported that during chloramination the formation of I-THMs increases with increasing pH in the pH range 6-8.5 for source waters spiked with either iodide or iopamidol (Duirk et al., 2011) while TOI remained stable (Hua and Reckhow, 2008). However, only iodoform has been shown to increase with a pH increase, while mixed Cl-Br-I-DBPs decreased (Wang et al., 2014; J. Zhang et al., 2016b). The stability of monochloramine and the possible role of chlorine formed at lower pH has been hypothesised to explain these results (Hua and Reckhow, 2008).

Finally, the pH also affects the stability of I-DBPs: similarly to TOCl or TOBr, TOI degradation – which occurs faster than for TOBr and TOCl – increases with both increasing pH and temperature, notably due to the dehalogenation of I-DBPs (Rahman, 2015; Abusallout et al., 2017). However, half-live times are quite high,  $t_{1/2} > 20$  days under realistic conditions (Rahman, 2015). Acidic conditions have

been shown to also increase the decomposition of certain I-DBPs such as iodophenols (Hu et al., 2018b).

*Figure 6*

### **5.5. Kinetic modeling to assess the effect of water quality parameters on I-DBP formation during chlorination**

Kinetic modeling was applied to assess the effects of various water quality parameters on I-DBP formation during chlorination. In this modeling (software Copasi, (Hoops et al., 2006)), 26 reactions (Table S4) were used to take into account the formation of different oxidants (bromine and iodine) with their pH-dependent speciation, and their reactivities towards phenol, which was chosen as a surrogate for natural organic matter. The second-order rate constants for the reaction of iodine with phenol determined by Bichsel and von Gunten (2000a) were used (Table 1), the reactivity of  $\text{H}_2\text{OI}^+$  with the phenolate species is negligible for the pH range of the modelling (pH 6.5 – 9.0). The species-specific second-order rate constants allow to take into account the kinetics of the selected reactions as a function of the pH. For this purpose, DOM was simulated by considering the acid-base speciation of phenolic moieties. Substituted phenol structures are associated with fast reacting DOM moieties controlling the rapid initial HOX consumption phase (Westerhoff et al., 2004). The slower phase for the reactions between HOI and other DOM moieties has not been taken into account in this modeling. A concentration of  $20 \mu\text{g L}^{-1}$  of iodide has been assumed with bromide concentrations of up to  $400 \mu\text{g L}^{-1}$  corresponding to a bromide:iodide molar ratio of  $\leq 32:1$ . 20% DOM-incorporation of halides has been considered to mimic the behaviour of chlorine, bromine and iodine reactive species with DOM (Criquet et al., 2015). The remaining 80% of the reaction of iodine reactive species with the organic moieties results in the release of iodide and the oxidation of the organic substance.

*Figure 7*

Figure 7 shows the modelled relative formation of iodate as a function of the bromide concentration and the pH for a reaction time of 4000 s (Table S5). At low bromide levels, low levels of iodate are formed and most of the HOI formed during chlorination is incorporated into organic moieties. This is due to the orders of magnitude higher reactivity of HOI with phenolate compared to the oxidation of

HOI to iodate by chlorine (note that 90% of iodide is converted either to iodate or bound to organic matter for pH > 7.0 (Table S5)). At higher bromide levels, the competition of HOI with HOBr for phenolic moieties leads to the formation of brominated phenolic compounds instead of iodinated compounds. Therefore, the organic moieties become limiting and the residual HOI is either rapidly oxidised to iodate by the residual HOBr, or when HOBr is depleted, slowly oxidised to iodate by HOCl. As previously discussed (section 5.4), the optimal pH either for the formation of iodate or reaction with phenolic moieties is > 9. However, the modeling shows that the decrease of pH favors the formation of iodate, independently of the bromide level. For the selected conditions (DOC of 5 mgC/L and a chlorine dose of 15 µM (*i.e.* about 1 mgCl<sub>2</sub>/L, Figure 7a), pH ≤ 7.0 and [Br<sup>-</sup>] ≥ 250 µg/L are needed for a ≥ 50 % conversion of iodide to iodate. Increasing chlorine doses relative to the phenolic moieties favors the formation of iodate. For example at pH 7, the formation of iodate increases from 6 to 23% of the initial iodide concentration by increasing the chlorine dose from 15 to 50 µM in the absence of bromide, and from 68 to 90% in presence of 400 µg L<sup>-1</sup> Br<sup>-</sup>.

## **6. Analysis and Occurrence of iodinated disinfection by-product classes in drinking water**

### **6.1. Monitoring of individual I-DBPs**

I-THMs were the first I-DBPs identified in drinking waters in 1976 (Shackelford and Keith, 1976). They were studied due to early concerns about medicinal taste and odours in drinking water (Hansson et al., 1987) with the lowest odour threshold of 0.03 µg L<sup>-1</sup> for iodoform (Cancho et al., 2001). The different classes of organic I-DBP can generally be grouped into two categories: aliphatic and aromatic compounds. To date, the reported aliphatic I-DBPs mainly comprise iodinated trihalomethanes (I-THMs), iodinated aliphatic acids, and iodinated haloacetamides. These compounds have quite diverse physical chemical properties and Figure 8 provides an overview of appropriate

methods for the detection of different target compounds. A majority of the first I-DBP species reported in drinking water were quantified by GC-MS (Hua and Reckhow, 2007a,b; Krasner et al., 2006; Plewa et al., 2004). Liquid chromatography has been also used subsequently to analyse haloacetamides (HAcAms) (Chu et al., 2012), different acids and iodophenols (Ding and Zhang, 2009; Pan et al., 2016a). So far, more than 650 drinking waters were analysed for organic I-DBPs in more than 40 studies worldwide (Table S6).

*Figure 8*

#### **6.1.1. Iodinated trihalomethanes (I-THMs)**

I-THMs are the main I-DBPs included in occurrence studies. The largest surveys focusing mainly on chlorination were conducted in France (ANSES, 2018), China (Ding et al., 2013), Korea (Woo et al., 2018), and Canada (Tugulea et al., 2018) and the largest focusing mainly on chloramination in the US (Richardson et al., 2008). One third of the studies in literature show low levels of I-THMs ( $<1 \mu\text{g L}^{-1}$ , Figure S1 and Table S6), but a substantial number of studies showed larger concentrations of I-THMs, with a third with concentrations between 1 and  $5 \mu\text{g L}^{-1}$  and 18% of the studies showing concentrations  $> 10 \mu\text{g L}^{-1}$ . The highest concentrations of I-THMs were found in North America and Pakistan, followed by China and UK (Figure S2).

The most frequently quantified I-THMs are  $\text{CHCl}_2\text{I}$  followed by  $\text{CHBrClI}$  (Table S6 and Figure S3) with concentrations typically in the range 2 to  $4 \mu\text{g L}^{-1}$ . In many laboratory studies on I-THM formation,  $\text{CHI}_3$  was found to be the major species. However, these studies were often conducted with low  $\text{Br}^-/\text{I}^-$  ratios and/or very high iodide concentrations, which favors the  $\text{CHI}_3$  formation. In contrast,  $\text{CHI}_3$  is the least occurring I-THM in most real water samples. Nevertheless,  $\text{CHI}_3$  has been recently reported as the main I-THM in several distribution systems (Wei et al., 2013a; Tugulea et al., 2015, 2018), usually accompanied by high total I-THM concentrations. These waters had particularly high concentrations of iodide ( $20 - 130 \mu\text{g L}^{-1}$ ) and naturally occurring ammonium ( $0.6$  to  $3.3 \text{ mg L}^{-1}$ ). The concentration of I-THMs were shown to be higher than the regulated THMs in these particular waters.

A tendency for higher I-THM concentrations during summer than during winter is generally observed (Parsons et al., 2009; Tugulea et al., 2018), which was related to rising iodide levels during summer in the different resources (surface and groundwaters). Weinberg et al. (2002), also showed some treatment plant-specific seasonal trends with more I-THMs formed in waters with higher temperatures. But the lack of data on iodide concentrations in most source waters makes it impossible to distinguish between possible seasonal effects in temperature and variations in iodide levels.

A slight overall increase of I-THMs, limited compared to regulated THMs, has been observed in distribution systems either using chlorine or chloramines (Tugulea et al., 2018). A significant increase in the I-DBP concentrations can however be expected in distribution system, if iodide is not fully oxidized and/or already incorporated in the organic matrix during primary oxidation, especially considering a possible catalytic effect of pipe residues (Liu et al., 2014).

Other iodinated halomethanes have also been detected (although not necessarily quantified) in water: chloriodomethane was first reported in drinking water samples in the UK in the mid-1970's, but has not been often monitored since then (Rumsby et al., 2009). It has been reported both in chlorinated waters (Khan et al., 2018) and in laboratory chloraminated source waters (Postigo et al., 2016), Bromiodomethane and diiodomethane were also identified in chloraminated water (Symons et al., 1998). The formation of iodinated mono or di-halomethanes is not possible based on the so-called haloform reaction involved in the formation of THMs. In this reaction the formation of a halomethane depends on three consecutive halogen incorporations at a methyl group in  $\alpha$ -position of a ketone (Frimmel and Jahnel, 2003). The reactivity of the halogenated intermediate compound is increased by the presence of 1 or 2 halogens. In addition, the carbanion formed ( $X_3C^-$ ) after hydrolysis is stabilized by the inductive effect of the halogens and constitutes a good leaving group. Mono- or di-halogenated compounds are typically formed from degradation of THMs or other compounds like HAAs by hydrolysis or biodegradation. Chloriodomethane, bromiodomethane and diiodomethane have been identified as degradation products of I-THMs in spiked river water (Cancho et al., 2000).

#### **6.1.2. Iodinated acids: haloacetic acids (I-HAAs) and others**

In chlorinated and chloraminated drinking waters, four iodinated haloacetic acids (I-HAAs) were detected in different studies: (mono)iodoacetic acid ( $\text{ICH}_2\text{CO}_2\text{H}$ ), chloroiodoacetic acid ( $\text{ClICHCO}_2\text{H}$ ), bromoiodoacetic acid ( $\text{BrICHCO}_2\text{H}$ ), and diiodoacetic acid ( $\text{I}_2\text{CHCO}_2\text{H}$ ) (Plewa et al., 2004; Krasner et al., 2006; Richardson et al., 2008; Cuthbertson et al., 2020). The reported concentrations were in the low  $\text{ng L}^{-1}$  to low  $\mu\text{g L}^{-1}$  range with maximum concentrations of  $1.7 \mu\text{g L}^{-1}$  for iodoacetic acid and approximately  $0.5 \mu\text{g L}^{-1}$  for chloro- and bromoiodoacetic acid. So far, diiodoacetic acid has only been observed at  $< 1 \text{ ng L}^{-1}$  in drinking waters. Triiodoacetic acid has been reported in several laboratory studies. However, tri-HAAs generally decompose very fast in drinking water at ambient temperature (Zhang and Minear, 2002), and it is unlikely to detect them in drinking water. The most frequently monitored I-HAA, until now, has been iodoacetic acid ( $\text{ICH}_2\text{CO}_2\text{H}$ ) (Table S6). Other acids were identified in chloraminated drinking water in US nationwide DBP occurrence studies (Weinberg et al., 2002; Krasner et al., 2006) with concentrations  $< 1 \mu\text{g L}^{-1}$  for 23 drinking water treatment plants (Richardson et al., 2008)(Table S6). Another iodoacid, 3,5-diiodosalicylic acid was detected at concentrations in the  $0.17\text{-}1.48 \text{ ng L}^{-1}$  range in 9 tap waters in China (Hu et al. 2018a).

### **6.1.3. Other iodinated disinfection by-products**

Among the 4 surveys that monitored iodinated haloacetonitriles (I-HANs) in drinking waters (Table S6), only Ding et al. (2013) detected iodoacetonitrile ( $0.2\text{-}4.2 \mu\text{g L}^{-1}$ ) in only 4 out of 60 DWTPs applying chlorine in China. Considering acetamides, sampling of DWTPs showed that 3 out of 7 samples in China contained chloroiodoacetamide ( $<0.04 - 0.21 \mu\text{g L}^{-1}$ ) and 3 out of 7 samples contained bromoiodoacetamide ( $<0.05 - 0.15 \mu\text{g L}^{-1}$ ) (Chu et al., 2012).

Iodobutanal was the first iodinated haloaldehyde (I-HAL) detected in a survey carried out in the US (Weinberg et al. 2002; Krasner et al. 2006). Subsequently, iodoacetaldehyde was detected at concentrations of  $0.62$  to  $4.5 \mu\text{g L}^{-1}$  in 4 US drinking water treatment plants applying chloramination, even for iodide concentrations below the detection limit of  $5 \mu\text{g L}^{-1}$  in the source waters (Jeong et al., 2015). While iodoacetaldehyde has not been further monitored in drinking water in other studies,

disinfection experiments with river water have shown that its formation is possible during chlorination as well (Postigo et al. 2017).

Various types of iodophenols have been quantified in tap water such as iodinated I-hydroxybenzaldehydes, I-hydroxybenzoic acids, and I-phenols (Wuilloud et al. 2003; Pan et al. 2016; Hu et al. 2018a). Their concentrations were  $< 1 \text{ ng L}^{-1}$  in 18 Chinese tap waters (Pan et al. 2016; Hu et al. 2018a), except for 2,4-diiodo-6-nitrophenol, with a maximum concentration of  $24 \text{ ng L}^{-1}$  (Pan et al. 2016). Additionally, 4 iodinated dipeptides (3-I-/3,5-di-I-Tyr-Ala and 3-I-/3,5-di-I-Tyr-Gly) have been identified in tap water samples (Huang et al., 2018).

## **6.2. Total (organic) iodine, iodide, iodate and hypiodous acid**

Total iodine comprises of iodide, iodine, iodate and organic iodine for which inductively coupled plasma – mass spectrometry (ICP-MS) demonstrated superior sensitivity in comparison to other detection techniques (Tables S6-S8). However, considering the fate of iodine in water treatment, speciation is recommended. More than 60 methods for the determination of iodide and/or iodate by ion chromatography with various detection methods with detection limits that are often quite high for iodide, typically around  $10 \text{ } \mu\text{g L}^{-1}$ , and even higher for iodate (Table S7). A postcolumn reaction has been shown to lower the detection limits to  $1 \text{ } \mu\text{g/L}$  for iodate with high selectivity by a post-column reaction forming  $\text{I}_3^-$  which can be detected by a UV/Vis detector (Salhi and von Gunten, 1999; Weinberg and Yamada, 1998). Lately, HPLC or IC methods coupled to ICP-MS have been shown to be more sensitive, with detection limits of  $0.2 \text{ } \mu\text{g L}^{-1}$  (MacKeown et al., 2020) (Table S8). Other chromatographic techniques (Table S7) are time-consuming due to extensive sample pre-treatment, and suffer from possible interferences (Zhang et al. 2010) but they could be interesting for complex matrices such as seawater. Iodide specific electrodes were also developed, but they are not very sensitive ( $\geq 10 \text{ } \mu\text{g L}^{-1}$ ) (Criquet et al., 2012).

Considering HOI, this species has been determined after reaction with phenol as the sum of o and p-iodophenol (Bichsel and von Gunten, 2000a; Shin et al., 2018). The DPD colorimetric method is also available, however, it is not specific. A compilation of methods for the total organic halogen including

iodine (TOI) measurement has been published previously (Chen et al., 2020; Kristiana et al., 2020). In addition to the classical technics, TOI can also be determined by measuring total iodine and total inorganic iodine (iodide + iodate) separately and then subtract inorganic from total iodine (Gilfedder et al. 2007) (Table S9). However, the uncertainties of both analyses should be taken into account and the impact of potential interferences of the iodide analysis due to complexation by DOM needs more investigation to not overestimate the organic fraction by this approach (MacKeown et al., 2020).

### 6.3. Research needs

Occurrence studies for real waters are not (well) distributed globally (Figure S2 and Table S6). For example, Australia has some data available for iodide showing very high concentrations in raw waters (up to several hundreds of  $\mu\text{g L}^{-1}$ , (Gruchlik et al., 2014). This may lead to potentially high I-DBP concentrations in the distributed waters. However, only data from 3 treated waters is reported in literature. In Europe, while not *a priori* an area rich in iodine, France shows a relatively high proportion of I-DBP occurrence (detection in 30% of the samples, (ANSES, 2018)). The highest concentrations of iodide occur in eastern Germany, The Netherlands and around the Mediterranean Sea (Salminen, R. et al., 2005), where no or only little information on I-DBPS is available. In contrast, the absence of either chlorination or chloramination processes in *e.g.*, The Netherlands is highly beneficial to mitigate I-DBPs formation (Rosario-Ortiz et al., 2016).

Overall, it remains difficult to compare occurrence and speciation of I-DBPs for different sites. Even for the most commonly reported I-THMs, many of the early studies did not measure all 6 I-THMs. Furthermore, some of the early studies used analytical methods with higher quantification limits and/or a lack of standards – especially for other I-DBP classes than I-THMs – making it difficult to obtain occurrence trends. Significant improvement has been made since the early 2000s, in the past 10 years also for more polar I-DBP classes. Nevertheless, many of the parameters which greatly influence I-DBP formation were not systematically measured. These parameters should be monitored in future studies if I-DBP occurrence is to be correlated to water characteristics and treatment processes. Such studies

would help to develop and validate prediction models which would be useful for water utilities to estimate formation potentials for I-DBPs and improve the overall risk assessments.

## **7. Risk assessment and mitigation**

### **7.1. Toxicity of iodinated disinfection by-products and prioritization**

Although toxicological evidence from *in vivo* assays and molecular epidemiology studies for I-DBPs is still lacking (Cortés and Marcos, 2018), different cytotoxicity and genotoxicity assays have been performed for various I-DBPs (Tables S10 and S11). Iodoacetic acid is the I-DBP which has been subjected to the highest number of different assays, allowing a comparison of hamster (CHO-AS52 and CHO-K1), mouse (NIH3T3, ovarian follicles), and human (HepG2, Caco-2, and CCD 841 CoN) cell lines (Table S10 and S11). The results show more than 2 orders of magnitude variability for cytotoxicity (Table S10), highlighting the difficulty in comparing different assays.

A compilation of 103 DBPs providing the lowest cytotoxic concentrations,  $LC_{50}$  values (lethal concentration for 50% of a population), and other indices with CHO cells concluded that I-DBPs are more cytotoxic and genotoxic than their brominated and chlorinated analogues (Wagner and Plewa, 2017). A more detailed discussion of the toxicity of each class of I-DBPs where the authors used mammalian cell cytotoxicity and genotoxicity data to provide a rank ordering of the relative toxicities is provided elsewhere (Dong et al., 2019).

In contrast, iodate is considered non-toxic because it is quickly reduced *in vivo* to  $I^-$  and is therefore the desired sink for iodine during water treatment. In some countries it is even added to table salt as a prevention for goitre (Bürgi et al., 2001).

To prioritize DBP classes, different methodologies have been proposed recently. A metric called “TIC-Tox” (Plewa et al., 2017) compares measured DBP concentrations – or semi-quantitative GC peak areas – weighted by metrics of toxic potency (cytotoxicity or genotoxicity index value) to determine chemical drivers of overall toxicity in water (Allard et al., 2015; Chuang et al., 2019; Dong et al., 2019; Jeong et al., 2012; Li and Mitch, 2018; Stalter et al., 2020). Based on this methodology,

iodoacetaldehyde, iodoacetonitrile as well as iodoacetic acid could be important I-DBPs due to their high toxicities and significant concentrations (up to  $\mu\text{g L}^{-1}$  range). Iodophenols and iodoacetamides have reportedly high toxicities, especially the three iodoacetamides (iodoacetamide, bromiodoacetamide, chloriodoacetamide), however, only few occurrence studies included these compounds and their concentration were far below the  $\mu\text{g L}^{-1}$  range (section 6.1).

An indexing method based on 3 criteria (concentration level, reported frequency and toxicity) was also recently developed (Mian et al., 2018) to prioritize unregulated DBPs in three categories (*i.e.*, high, medium, and low priorities). The I-DBP group was categorized as low priority compared to other DBP classes, but, only iodoacetic acid and iodoform were considered. An earlier study (Hebert et al., 2010) gave scores to DBPs based on 4 criteria (toxicity, occurrence, US-EPA and/or IARC classification, and regulation). This procedure allowed the identification and ranking of three different groups of emerging DBPs: (i) moderate occurrence and high toxicity; (ii) moderate to elevated occurrence and relevant toxicity and (iii) low occurrence and unknown or little toxicity. From this study, dichlorodimethane and iodoacetonitrile were ranked in group (i) with compounds such nitrosamines or trichlorophenol, which are considered the most critical compounds. I-THMs as well as I-AAs and I-HAcAMs were categorized in group (ii) mainly due to their toxicity.

There are some I-DBPs with no toxicity data as of yet, and more occurrence data is needed on I-DBPs in real drinking water systems to improve prioritization of I-DBPs. Such prioritization can provide useful information to develop control strategies to minimize human health risks resulting from the exposure of consumers to I-DBPs as compared to other DBPs, including the establishment of new drinking water standards.

## **7.2. Mitigation strategies**

### **7.2.1. Prevention of formation**

Precursor abatement prior to disinfection is a common strategy for DBP minimisation, in that it non-specifically minimises all DBPs, both regulated and emerging (Watson et al., 2012). As DOM is the major precursor for the generation of organic DBPs, DOM removal prior to disinfection is an effective

option. However, when focusing on I-DBPs, there may be also a need for iodide removal if more impaired water resources are used for drinking water production.

Alternatively, the optimization of disinfection through the transformation of iodide to iodate, a safe iodine-derived end-product, has been proposed as a viable option. A pre-oxidation step with either ozone or ferrate(VI) before post-chlorination or especially post-chloramination to oxidize iodide to iodate is an efficient process to mitigate the formation of I-DBPs (Allard et al., 2013b, Zhang et al., 2016b, Wang et al., 2018, Jiang et al., 2019). Iodide oxidation by ozone is fast enough to avoid excessive formation of bromate, a regulated DBP linked to ozonation of bromide-containing waters (Allard et al., 2013b).

Prechloration before chloramination also leads to a partial iodate formation, whereby reducing the subsequent formation of I-DBPs (Bichsel and von Gunten, 1999). Therefore, if chloramine is used as a disinfectant, it is recommended to increase free chlorine contact time before ammonia addition to reduce iodo-DBP formation (Richardson et al., 2008; Jones et al., 2011; Criquet et al., 2012; Allard et al., 2015). However, the formation of I-DBPs, and especially their speciation, in the pre-chlorination/post-chloramination process depends strongly on the concentration of bromide (Allard et al., 2015). It was demonstrated that pre-chlorination minimized iodoform formation, however, short pre-chlorination contact times form higher I-THM concentrations compared to pre-formed  $\text{NH}_2\text{Cl}$  due to a large increase in the formation of mixed Cl-Br-I-THM species (Jones et al., 2011; Criquet et al., 2012; Allard et al., 2015; Zhang et al., 2016b).

#### **7.2.2. Removal of I-DBPs after their formation**

Activated carbon adsorption after pre- or intermediate chlorination or pre-chloramination in full-scale drinking water treatment plants has been shown to be beneficial to mitigate DBP concentrations in drinking waters (Cuthbertson et al., 2019, 2020; MacKeown et al., 2020). I-THMs showed particularly high removal efficiency in full-scale water treatment plants (Cancho et al., 2000; MacKeown et al., 2020). I-THMs were removed by 77 to 99 % (average of 3 campaigns for each compound), the efficiency

increasing with the molecular weight and hydrophobicity of THMs. Iodoacetic acid had a removal efficiency > 90% in GAC filtration (around 20 000 bed volumes). The removal of these compounds was much more efficient than for the THM4 on the same filters (from 15 to 58%) (MacKeown et al., 2020). Cuthbertson et al. (2019; 2020) also demonstrated an overall decrease of TOI by (biological) activated carbon filtration and calculated geno- and cyto-toxicities. However, the assumptions were only based on a theoretical assessment of DBP related toxicities. Moreover, the assessment of different parameters such as GAC types, run time, age of filters and contact times would be needed to fully evaluate the potential of such a process.

## 8. Conclusion

The increasing demand on water resources will inevitably require increasing use of impaired water sources, containing higher concentrations of iodide/iodine especially in coastal areas. Reactive iodine species can be formed during oxidative water treatment of iodide-containing waters with various oxidants and they react with inorganic and organic compounds. HOI is generally the major reactive species for the reaction with dissolved organic matter. Iodine reactive species are similar to chlorine and bromine in terms of speciation, mechanism of reaction or binding to DOM. The few available second-order rate constants for the reactions of HOI with inorganic and organic compounds do not allow to draw final conclusions in terms of its reactivity, which however generally appears to be intermediate between chlorine and bromine. The largest difference consists of the further oxidation of HOI to iodate, which is a safe end-product for iodine. The formation of iodinated disinfection by-products is favored when the oxidant is not able to effectively oxidize HOI to iodate (mainly monochloramine). The incorporation of iodine depends strongly on the oxidant type,  $I^-$ ,  $Br^-$  and DOM concentrations, DOM type, solution pH as well as on the ammonium concentration. Thus, disinfection practices intending to reduce THM4 levels may ultimately increase the formation of I-DBPs in the treated waters, especially in the case of chloramination. Enhanced detection methods will allow for detection of lower concentrations of I-DBPs in the sub ng L<sup>-1</sup> range. Occurrence studies mainly detected I-THMs as well as several iodoacids. However, in recent years, more studies were carried out on

nitrogenous I-DBPs as well as other polar I-DBPs. One of the main analytical difficulty comprises the quantification of a large number of I-DBPs from different classes with different physical-chemical properties and at low levels.

I-DBPs are known to have generally higher toxicities than their chlorinated and brominated analogues. Iodoacetic acid and iodoacetamides exhibit particularly strong cytotoxicity and iodoacetic acid is still the most genotoxic DBP identified to-date and is shown to impair the endocrine system.

Processes which favor the formation of iodate are most efficient in I-DBP mitigation. In particular controlled ozonation allows to form iodate without formation of bromate and a pre-chlorination contact time before chloramination has been demonstrated to be efficient to control I-DBP formation.

## Acknowledgments

This study was supported by Interreg 2 Seas program via DOC2C's project - contract No 2S01-013. The authors also thank the Region "Hauts-de-France" through the CPER Climibio for support. Dr. Aurélien Moncomble is thanked for fruitful discussions.

## References

- Abusallout, I., Rahman, S., Hua, G., 2017. Effect of temperature and pH on dehalogenation of total organic chlorine, bromine and iodine in drinking water. *Chemosphere* 187, 11–18. <https://doi.org/10.1016/j.chemosphere.2017.07.149>
- Acero, J.L., Piriou, P., von Gunten, U., 2005. Kinetics and mechanisms of formation of bromophenols during drinking water chlorination: Assessment of taste and odor development. *Water Res.* 39, 2979–2993. <https://doi.org/10.1016/j.watres.2005.04.055>
- Allard, S., Criquet, J., Prunier, A., Falantin, C., Le Person, A., Yat-Man, Tang J., Croué, J-P., 2016. Photodecomposition of iodinated contrast media and subsequent formation of toxic iodinated moieties during final disinfection with chlorinated oxidants. *Water Res.* 103 15 453–461.
- Allard, S., Fouche, L., Dick, J., Heitz, A., von Gunten, U., 2013a. Oxidation of Manganese(II) during Chlorination: Role of Bromide. *Environ. Sci. Technol.* 47, 8716–8723. <https://doi.org/10.1021/es401304r>
- Allard, S., Nottle, C.E., Chan, A., Joll, C., von Gunten, U., 2013b. Ozonation of iodide-containing waters: Selective oxidation of iodide to iodate with simultaneous

1247 minimization of bromate and I-THMs. *Water Res.* 47, 1953–1960.  
1248 <https://doi.org/10.1016/j.watres.2012.12.002>

1249 Allard, S., Tan, J., Joll, C.A., von Gunten, U., 2015. Mechanistic Study on the Formation of Cl-  
1250 /Br-/I-Trihalomethanes during Chlorination/Chloramination Combined with a  
1251 Theoretical Cytotoxicity Evaluation. *Environ. Sci. Technol.* 49, 11105–11114.  
1252 <https://doi.org/10.1021/acs.est.5b02624>

1253 Allard, S., von Gunten, U., Salhi, E., Nicolau, R., Gallard, H., 2009. Oxidation of iodide and  
1254 iodine on birnessite ( $\delta$ -MnO<sub>2</sub>) in the pH range 4–8 - ScienceDirect. *Water Res.* Vol. 43  
1255 Issue 14 3417–3426.

1256 Amachi, S., 2008. Microbial Contribution to Global Iodine Cycling: Volatilization,  
1257 Accumulation, Reduction, Oxidation and Sorption of Iodine. *Microbes Env* 23, 269–  
1258 276.

1259 ANSES, 2018. Campagne nationale de mesures de l'occurrence de polluants émergents dans  
1260 les eaux destinées à la consommation humaine : Haloacétonitriles, Trihalométhanes  
1261 iodés, Halocétones, Chloropicrine, Alkylphénols, Bisphénols.

1262 Awad, M.I., Oritani, T., Ohsaka, T., 2003. Kinetic studies on the oxidation of iodide by  
1263 peroxyacetic acid. *Inorganica Chim. Acta* 344, 253–256.  
1264 [https://doi.org/10.1016/S0020-1693\(02\)01337-3](https://doi.org/10.1016/S0020-1693(02)01337-3)

1265 Becker, W., Stanford, B., Rosenfeldt, E. J., 2013. Guidance on Complying With Stage 2 D/DBP  
1266 Regulation. Water Research Foundation.

1267 Bellar, T. A., Lichtenberg, J. J., Kroner, R. C., 1974. The Occurrence of Organohalides in  
1268 Chlorinated Drinking Waters. U.S. Environmental Protection Agency, Office of  
1269 Research and Development, National Environmental Research Center.

1270 Berliner, E., 1951. Kinetics of the Iodination of Phenol. *J. Am. Chem. Soc.* 73, 4307–4311.  
1271 <https://doi.org/10.1021/ja01153a083>

1272 Bichsel, Y., von Gunten, U., 2000a. Formation of Iodo-Trihalomethanes during Disinfection  
1273 and Oxidation of Iodide-Containing Waters. *Environ. Sci. Technol.* 34, 2784–2791.  
1274 <https://doi.org/10.1021/es9914590>

1275 Bichsel, Y., von Gunten, U., 2000b. Hypoiodous acid: kinetics of the buffer-catalyzed  
1276 disproportionation. *Water Res.* 34, 3197–3203. [https://doi.org/10.1016/S0043-1354\(00\)00077-4](https://doi.org/10.1016/S0043-1354(00)00077-4)

1277 Bichsel, Y., von Gunten, U., 1999a. Oxidation of Iodide and Hypoiodous Acid in the  
1278 Disinfection of Natural Waters. *Environ. Sci. Technol.* 33, 4040–4045.  
1279 <https://doi.org/10.1021/es990336c>

1280 Bray, W.C., 1921. A periodic reaction in homogeneous solution and its relation to catalysis. *J.*  
1281 *Am. Chem. Soc.* 43, 1262–1267. <https://doi.org/10.1021/ja01439a007>

1282 Bruchet, A., Duguet, J.P., Suffe, I.H., 2004. Role of oxidants and disinfectants on the removal,  
1283 masking and generation of tastes and odours. *Rev. Environ. Sci. Biotechnol.* 3, 33–41.  
1284 <https://doi.org/10.1023/B:RESB.0000040011.81065.25>

1285 Bärli, H., Schaffner, T.H., Seiler, J.P., 2001. The toxicology of iodate: a review of the literature.  
1286 *Thyroid* 11, 449–456.

1287 Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical Review of rate  
1288 constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals  
1289 ( $\cdot\text{OH}/\cdot\text{O}-$ ) in Aqueous Solution. *J. Phys. Chem. Ref. Data* 17, 513–886.  
1290 <https://doi.org/10.1063/1.555805>

1291 Cancho, B., Fabrellas, C., Diaz, A., Ventura, F., 2001. Determination of the Odor Threshold  
1292 Concentrations Of Iodinated Trihalomethanes in Drinking Water. *J Agric Food Chem*  
1293 49 1881–1884.

Cancho, B., Ventura, F., Galceran, M., Diaz, A., Ricart, S., 2000. Determination, synthesis and survey of iodinated trihalomethanes in water treatment processes. *Water Res.* 34, 3380–3390.

Cao, Z., Ding, S., Deng, Y., Luan, X., Chu, W., 2022. Household cooking with seaweed salts and chloraminated tap water produce harmful iodinated disinfection by-products. *Chem. Eng. J.* 431, 133471. <https://doi.org/10.1016/j.cej.2021.133471>

Chen, B., Bu, Y., Yang, J., Nian, W., Hao, S., 2020. Methods for total organic halogen (TOX) analysis in water: Past, present, and future. *Chem. Eng. J.* 399, 125675. <https://doi.org/10.1016/j.cej.2020.125675>

Chen, Z., Li, J., Koh, K.Y., Du, Z., Ong, C.N., Chen, J.P., 2021. Kinetics and Mechanism Investigation of Selective Arsenite Oxidation by Reactive Iodine Species in Hydrogen Peroxide and Iodide ( $\text{H}_2\text{O}_2/\text{I}^-$ ) System. *ACS EST Water* 1, 1515–1523. <https://doi.org/10.1021/acsestwater.1c00062>

Chu, W., Gao, N., Yin, D., Krasner, S.W., Templeton, M.R., 2012. Trace determination of 13 haloacetamides in drinking water using liquid chromatography triple quadrupole mass spectrometry with atmospheric pressure chemical ionization. *J. Chromatogr. A* 1235, 178–181. <https://doi.org/10.1016/j.chroma.2012.02.074>

Chuang, Y.-H., Szczuka, A., Mitch, W.A., 2019. Comparison of Toxicity-Weighted Disinfection Byproduct Concentrations in Potable Reuse Waters and Conventional Drinking Waters as a New Approach to Assessing the Quality of Advanced Treatment Train Waters. *Environ. Sci. Technol.* 53, 3729–3738. <https://doi.org/10.1021/acs.est.8b06711>

Cortés, C., Marcos, R., 2018. Genotoxicity of disinfection byproducts and disinfected waters: A review of recent literature. *Mutat. Res. Toxicol. Environ. Mutagen.* 831, 1–12. <https://doi.org/10.1016/j.mrgentox.2018.04.005>

Criquet, J., Allard, S., Salhi, E., Joll, C.A., Heitz, A., von Gunten, U., 2012. Iodate and Iodo-Trihalomethane Formation during Chlorination of Iodide-Containing Waters: Role of Bromide. *Environ. Sci. Technol.* 46, 7350–7357. <https://doi.org/10.1021/es301301g>

Criquet, J., Rodriguez, E.M., Allard, S., Wellauer, S., Salhi, E., Joll, C.A., von Gunten, U., 2015. Reaction of bromine and chlorine with phenolic compounds and natural organic matter extracts – Electrophilic aromatic substitution and oxidation. *Water Res.* 85, 476–486. <https://doi.org/10.1016/j.watres.2015.08.051>

Cuthbertson, A., Kimura, S., Liberatore, H., Scott Summers, R., Knappe, D., D. Stanford, B., Clark Maness, J., Mulhern, R., Selbes, M., Richardson, S., 2019. Does GAC with Chlorination Produce Safer Drinking Water? From DBPs and TOX to Calculated Toxicity. *Environ. Sci. Technol.* <https://doi.org/10.1021/acs.est.9b00023>

Cuthbertson, A.A., Kimura, S.Y., Liberatore, H.K., Knappe, D.R.U., Stanford, B., Summers, R.S., Dickenson, E.R., Maness, J.C., Glover, C., Selbes, M., Richardson, S.D., 2020. GAC to BAC: Does it make chloraminated drinking water safer? *Water Res.* 172. <https://doi.org/10.1016/j.watres.2019.115432>

Deane, A.M., Potter, P.E., 1985. Proceedings of the specialists' workshop on iodine chemistry in reactor safety. *INIS* 17, 365.

Deborde, M., von Gunten, U., 2008. Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms: A critical review. *Water Res.* 42 1-2 13–51.

Dillon, G., Shepherd, D., Hall, T., Gee, R., Parker, J., Rumsby, P., 2015. CHAPTER 38: Risk-Based Approach to the Formation of DBPs of Concern in UK Drinking Water, in: *Disinfection By-Products in Drinking Water*. pp. 336–348. <https://doi.org/10.1039/9781782622710-00336>

- Ding, G., Zhang, X., 2009. A Picture of Polar Iodinated Disinfection Byproducts in Drinking Water by (UPLC/ESI-tqMS. *Environ. Sci. Technol.* 43, 9287–9293. <https://doi.org/10.1021/es901821a>
- Ding, H., Meng, L., Zhang, H., Yu, J., An, W., Hu, J., Yang, M., 2013. Occurrence, profiling and prioritization of halogenated disinfection by-products in drinking water of China. *Environ. Sci. Process. Impacts* 15, 1424. <https://doi.org/10.1039/c3em00110e>
- Ding, S., Deng, Y., Li, H., Fang, C., Gao, N., Chu, W., 2019. Coagulation of Iodide-Containing Resorcinol Solution or Natural Waters with Ferric Chloride Can Produce Iodinated Coagulation Byproducts. *Environ. Sci. Technol.* 53, 12407–12415. <https://doi.org/10.1021/acs.est.9b03671>
- Dong, H., Qiang, Z., Richardson, S.D., 2019. Formation of Iodinated Disinfection Byproducts (I-DBPs) in Drinking Water: Emerging Concerns and Current Issues. *Acc. Chem. Res.* 52, 896–905. <https://doi.org/10.1021/acs.accounts.8b00641>
- Duirk, S.E., Lindell, C., Cornelison, C.C., Kormos, J., Ternes, T.A., Attene-Ramos, M., Osiol, J., Wagner, E.D., Plewa, M.J., Richardson, S.D., 2011. Formation of Toxic Iodinated Disinfection By-Products from Compounds Used in Medical Imaging. *Environ. Sci. Technol.* 45, 6845–6854. <https://doi.org/10.1021/es200983f>
- Eastman, C.J., Zimmermann, M.B., 2000. The Iodine Deficiency Disorders, in: De Groot, L.J., Chrousos, G., Dungan, K., Feingold, K.R., Grossman, A., Hershman, J.M., Koch, C., Korbonits, M., McLachlan, R., New, M., Purnell, J., Rebar, R., Singer, F., Vinik, A. (Eds.), *Endotext*. MDText.com, Inc., South Dartmouth (MA).
- Fabian, I., Gordon, G., 1997. The Kinetics and Mechanism of the Chlorine Dioxide - Iodide Ion Reaction. *Inorg. Chem.* 36 2494–2497.
- Frimmel, F.H., Jernel, J.B., 2003 Formation of Haloforms in Drinking Water. In: Nikolaou A.D. (eds) *Haloforms and Related Compounds in Drinking Water. The Handbook of Environmental Chemistry (Water Pollution)*, vol 5 / 5G. Springer, Berlin, Heidelberg.
- Fuge, R., 2005. Soils and iodine deficiency, in: *Essentials of Medical Geology: Impacts of the Natural Environment on Public Health*. pp. 417–434.
- Fuge, R., Johnson, C. C., 2015. Iodine and human health, the role of environmental geochemistry and diet, a review. *Appl. Geochem.* 282–302.
- Gallard, H., Allard, S., Nicolau, R., von Gunten, U., Croué, J.P., 2009. Formation of Iodinated Organic Compounds by Oxidation of Iodide-Containing Waters with Manganese Dioxide. *Environ. Sci. Technol.* 43, 7003–7009. <https://doi.org/10.1021/es9010338>
- Gallard, H., von Gunten, U., 2002. Chlorination of natural organic matter: kinetics of chlorination and of THM formation. *Water Res.* 36, 65–74. [https://doi.org/10.1016/S0043-1354\(01\)00187-7](https://doi.org/10.1016/S0043-1354(01)00187-7)
- Gerritsen, C.M., Margerum, D.W., 1990. Non-metal redox kinetics: hypochlorite and hypochlorous acid reactions with cyanide. *Inorg. Chem.* 29, 2757–2762.
- Gilfedder, B.S., Petri, M., Biester, H., 2007. Iodine and bromine speciation in snow and the effect of orographically induced precipitation. *Atmospheric Chem. Phys.* 7, 2661–2669.
- Gonsioroski, A., Meling, D.D., Gao, L., Plewa, M.J., Flaws, J.A., 2020. Iodoacetic acid inhibits follicle growth and alters expression of genes that regulate apoptosis, the cell cycle, estrogen receptors, and ovarian steroidogenesis in mouse ovarian follicles. *Reprod. Toxicol.* 91, 101–108. <https://doi.org/10.1016/j.reprotox.2019.10.005>
- Goodyer, L., Behrens, R. H., 2000. Safety of Iodine Based Water Sterilization for Travelers. *J Travel Med* 7 38.
- Government of Newfoundland & Labrador, Department of Environment and Conservation, 2009. *Best Management Practices for the Control of Disinfection by-Products in Drinking Water Systems in Newfoundland and Labrador*.

1393 Gruchlik, Y., Tan, J., Allard, S., Heitz, A., Bowman, M., Halliwell, D., von Gunten, U., Criquet,  
 1394 J., Joll, C.A., 2014. Impact of bromide and iodide during drinking water disinfection  
 1395 and potential treatment processes for their removal or mitigation. *Water - J. Aust. Water*  
 1396 *Assoc.* 38–43.  
 1397 Guan, C., Jiang, J., Luo, C., Pang, S., Jiang, C., Ma, J., Jin, Y., Li, J., 2017. Transformation of  
 1398 Iodide by Carbon Nanotube Activated Peroxydisulfate and Formation of Iodoorganic  
 1399 Compounds in the Presence of Natural Organic Matter. *Environ. Sci. Technol.* 51, 479–  
 1400 487. <https://doi.org/10.1021/acs.est.6b04158>  
 1401 Guo, W., Shan, Y., Yang, X., 2014. Factors affecting the formation of iodo-trihalomethanes  
 1402 during oxidation with chlorine dioxide. *J. Hazard. Mater.* 264, 91–97.  
 1403 <https://doi.org/10.1016/j.jhazmat.2013.10.064>  
 1404 Haag, W.R., Hoigné, Juerg., 1983. Ozonation of bromide-containing waters: kinetics of  
 1405 formation of hypobromous acid and bromate. *Environ. Sci. Technol.* 17, 261–267.  
 1406 <https://doi.org/10.1021/es00111a004>  
 1407 Hammaecher, C., Canneaux, S., Louis, F., Cantrel, L., 2011. A theoretical study of the H-  
 1408 abstraction reactions from HOI by moist air radiolytic products (H, OH, and O (3P))  
 1409 and iodine atoms (  $2P_{3/2}$ ). *J. Phys. Chem. A* 115, 6664–6674.  
 1410 <https://doi.org/10.1021/jp202760u>  
 1411 Hansson, R. C., Henderson, M. J., Jack, P., Taylor, R. D., 1987. Iodoform taste complaints in  
 1412 chloramination. *Water Res.* 21 10 1265–1271. [https://doi.org/10.1016/0043-](https://doi.org/10.1016/0043-1354(87)90179-5)  
 1413 [1354\(87\)90179-5](https://doi.org/10.1016/0043-1354(87)90179-5)  
 1414 Harkness, J. S., Dwyer, G. S., Warner, N. R., Parker, K. M., Mitch, W. A., Vengosh, A., 2015.  
 1415 Iodide, Bromide, and Ammonium in Hydraulic Fracturing and Oil and Gas  
 1416 Wastewaters: Environmental Implications. *Env. Sci Technol* 49 1955–1963.  
 1417 Hebert, A., Forestier, D., Lenes, D., Benanou, D., Jacob, S., Arfi, C., Lambolez, L., Levi, Y.,  
 1418 2010. Innovative method for prioritizing emerging disinfection by-products (DBPs) in  
 1419 drinking water on the basis of their potential impact on public health. *Water Res.* 44,  
 1420 3147–3165. <https://doi.org/10.1016/j.watres.2010.02.004>  
 1421 Heeb, M. B., Kristiana, I., Trogolo, D., Arey, J. S., von Gunten, U., 2017. Formation and  
 1422 reactivity of inorganic and organic chloramines and bromamines during oxidative water  
 1423 treatment. *Water Res.* 110 91–101.  
 1424 Heeb, M.B., Criquet, J., Zimmermann-Steffens, S.G., von Gunten, U., 2014. Oxidative  
 1425 treatment of bromide-containing waters: Formation of bromine and its reactions with  
 1426 inorganic and organic compounds — A critical review. *Water Res.* 48, 15–42.  
 1427 <https://doi.org/10.1016/j.watres.2013.08.030>  
 1428 Hoigné, J., Bader, H., 1994. Kinetics of reactions of chlorine dioxide (OCIO) in water-I. Rate  
 1429 constants for inorganic and organic compounds. *Wat Res* 28, 45–55.  
 1430 Hoops, S., Sahle, S., Gauges, R., Lee, C., Pahle, J., Simus, N., Singhal, M., Xu, L., Mendes, P.,  
 1431 Kummer, U., 2006. COPASI--a COMplex PATHway SIMulator. *Bioinformatics* 22,  
 1432 3067–3074. <https://doi.org/10.1093/bioinformatics/btl485>  
 1433 Hou, X., Aldahan, A., Nielsen, S.P., Possnert, G., 2009. Time Series of 129I and 127I  
 1434 Speciation in Precipitation from Denmark. *Environ. Sci. Technol.* 43, 6522–6528.  
 1435 <https://doi.org/10.1021/es9012678>  
 1436 House, D.A., 1962. Kinetics and mechanism of oxidations by peroxydisulfate. *Chem. Rev.* 62,  
 1437 185–203. <https://doi.org/10.1021/cr60217a001>  
 1438 Hrudey, S. E., Charrois, J. W.A., 2012. Disinfection by-products and human health, IWA  
 1439 Publishing. ed.  
 1440 Hu, J., Dong, H., Qu, J., Qiang, Z., 2017. Enhanced degradation of iopamidol by  
 1441 peroxymonosulfate catalyzed by two pipe corrosion products (CuO and  $\delta$ -MnO<sub>2</sub>).  
 1442 *Water Res.* 112, 1–8. <https://doi.org/10.1016/j.watres.2017.01.025>

1443 Hu, S., Gong, T., Ma, J., Tao, Y., Xian, Q., 2018a. Simultaneous determination of iodinated  
 1444 haloacetic acids and aromatic iodinated disinfection byproducts in waters with a new  
 1445 SPE-HPLC-MS/MS method. *Chemosphere* 198, 147–153.  
 1446 <https://doi.org/10.1016/j.chemosphere.2018.01.124>  
 1447 Hu, S., Gong, T., Xian, Q., Wang, J., Ma, J., Li, Z., Yin, J., Zhang, B., Xu, B., 2018b. Formation  
 1448 of iodinated trihalomethanes and haloacetic acids from aromatic iodinated disinfection  
 1449 byproducts during chloramination. *Water Res.* 147, 254–263.  
 1450 <https://doi.org/10.1016/j.watres.2018.09.058>  
 1451 Hua, G., Reckhow, D.A., Kim, J., 2006. Effect of Bromide and Iodide Ions on the Formation  
 1452 and Speciation of Disinfection Byproducts during Chlorination. *Environ. Sci. Technol.*  
 1453 40, 3050–3056. <https://doi.org/10.1021/es0519278>  
 1454 Hua G., Reckhow D. A., 2007a. Comparison of disinfection byproduct formation from chlorine  
 1455 and alternative disinfectants. *Water Res.* 41 8 1667–1678.  
 1456 Hua, G., Reckhow, D.A., 2007b. Characterization of disinfection byproduct precursors based  
 1457 on hydrophobicity and molecular size. *Environ. Sci. Technol.* 41, 3309–3315.  
 1458 <https://doi.org/10.1021/es062178c>  
 1459 Hua, G., Reckhow, D.A., 2008. DBP formation during chlorination and chloramination: Effect  
 1460 of reaction time, pH, dosage, and temperature. *J. - Am. Water Works Assoc.* 100, 82–  
 1461 95. <https://doi.org/10.1002/j.1551-8833.2008.tb09702.x>  
 1462 Hua, G., Reckhow, D.A., Abusallout, I., 2015. Correlation between SUVA and DBP formation  
 1463 during chlorination and chloramination of NOM fractions from different sources.  
 1464 *Chemosphere* 130, 82–89. <https://doi.org/10.1016/j.chemosphere.2015.03.039>  
 1465 Huang, G., Jiang, P., Jmaiff Blackstock, L.K., Tian, D., Li, X.-F., 2018. Formation and  
 1466 Occurrence of Iodinated Tyrosyl Dipeptides in Disinfected Drinking Water. *Environ.*  
 1467 *Sci. Technol.* 52, 4218–4226. <https://doi.org/10.1021/acs.est.7b06276>  
 1468 Huber, M.M., Canonica, S., Park, G.-Y., von Gunten, U., 2003. Oxidation of Pharmaceuticals  
 1469 during Ozonation and Advanced Oxidation Processes. *Environ. Sci. Technol.* 37, 1016–  
 1470 1024. <https://doi.org/10.1021/es025896h>  
 1471 Huber, M.M., Göbel, A., Joss, A., Hermann, N., Löffler, D., Mc Ardell, C.S., Ried, A., Siegrist,  
 1472 H., Ternes, T.A., von Gunten, U., 2005. Oxidation of Pharmaceuticals during Ozonation  
 1473 of Municipal Wastewater Effluents: A Pilot Study. *Environ. Sci. Technol.* 39, 4290–  
 1474 4299. <https://doi.org/10.1021/es048396s>  
 1475 Ioannou, P., Charisiadis, P., Andra, S.S., Makris, K.C., 2016. Occurrence and variability of  
 1476 iodinated trihalomethanes concentrations within two drinking-water distribution  
 1477 networks. *Sci. Total Environ.* 543, 505–513.  
 1478 <https://doi.org/10.1016/j.scitotenv.2015.10.031>  
 1479 Jeong, C.H., Wagner, E.D., Siebert, V.R., Anduri, S., Richardson, S.D., Daiber, E.J., McKague,  
 1480 A.B., Kogevinas, M., Villanueva, C.M., Goslan, E.H., Luo, W., Isabelle, L.M., Pankow,  
 1481 J.F., Grazuleviciene, R., Cordier, S., Edwards, S.C., Righi, E., Nieuwenhuijsen, M.J.,  
 1482 Plewa, M.J., 2012. Occurrence and Toxicity of Disinfection Byproducts in European  
 1483 Drinking Waters in Relation with the HIWATE Epidemiology Study. *Environ. Sci.*  
 1484 *Technol.* 46, 12120–12128. <https://doi.org/10.1021/es3024226>  
 1485 Jeong, C.H., Postigo, C., Richardson, S.D., Simmons, J.E., Kimura, S.Y., Mariñas, B.J.,  
 1486 Barcelo, D., Liang, P., Wagner, E.D., Plewa, M.J., 2015. Occurrence and Comparative  
 1487 Toxicity of Haloacetaldehyde Disinfection Byproducts in Drinking Water. *Environ. Sci.*  
 1488 *Technol.* 49, 13749–13759. <https://doi.org/10.1021/es506358x>  
 1489 Johnson, C. C., 2003. The geochemistry of iodine and its application to environmental strategies  
 1490 for reducing the risks from iodine deficiency disorders (IDD) (Commissioned Report  
 1491 No. CR/03/057N). British Geological Survey.

1492 Jones, D.B., Saglam, A., Triger, A., Song, H., Karanfil, T., 2011. I-THM Formation and  
 1493 Speciation: Preformed Monochloramine versus Prechlorination Followed by Ammonia  
 1494 Addition. *Environ. Sci. Technol.* 45, 10429–10437. <https://doi.org/10.1021/es202745t>  
 1495 Jones, D. B., Saglam, A., Song, H., Karanfil, T., 2012. The impact of bromide/iodide  
 1496 concentration and ratio on iodinated trihalomethane formation and speciation. *Water*  
 1497 *Res.* 46 1 11–20.  
 1498 Jortner, J., Ottolenghi, M., Stein, G., 1964. On the photochemistry of aqueous solutions of  
 1499 chloride, bromide, and iodide ions. *J. Phys. Chem.* 68, 247–255.  
 1500 Kern, D.M., Kim, C.-H., 1965. Iodine Catalysis in the Chlorite-Iodide Reaction. *J. Am. Chem.*  
 1501 *Soc.* 87, 5309–5313.  
 1502 Khan, R., Hashmi, I., Nasir, H., Rasheed, S., Campos, L.C., 2018. Incidence of chlorination by-  
 1503 products in an institutional drinking water distribution network, Islamabad, Pakistan,  
 1504 using response surface methodology. *J. Water Sanit. Hyg. Dev.* 8, 740–751.  
 1505 <https://doi.org/10.2166/washdev.2018.047>  
 1506 Kovalova, L., Siegrist, H., von Gunten, U., Eugster, J., Hagenbuch, M., Wittmer, A., Moser,  
 1507 R., Mc Ardell, C.S., 2013. Elimination of Micropollutants during Post-Treatment of  
 1508 Hospital Wastewater with Powdered Activated Carbon, Ozone, and UV. *Environ. Sci.*  
 1509 *Technol.* 47, 7899–7908. <https://doi.org/10.1021/es400708w>  
 1510 Kralchevska, R. P., Sharma, V. K., Machala, L., Zboril, R., 2016. Ferrates (FeVI, FeV, and  
 1511 FeIV) oxidation of iodide: Formation of triiodide. *Chemosphere Vol 144* 1156–1161.  
 1512 Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Scilimenti, M.J.,  
 1513 Onstad, G.D., Thruston, A.D., 2006. Occurrence of a New Generation of Disinfection  
 1514 Byproducts. *Environ. Sci. Technol.* 40, 7175–7185. <https://doi.org/10.1021/es060353j>  
 1515 Krasner, S.W., 2009. The formation and control of emerging disinfection by-products of health  
 1516 concern. *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.* 367, 4077–4095.  
 1517 <https://doi.org/10.1098/rsta.2009.0108>  
 1518 Krasner, S.W., 2012. Halogenated DBPs and emerging issues, in: *Disinfection By-Products and*  
 1519 *Human Health*. pp. 59–71.  
 1520 Kristiana, I., Gallard, H., Joll, C., Croué, J.-P., 2009. The formation of halogen-specific TOX  
 1521 from chlorination and chloramination of natural organic matter isolates. *Water Res.* 43,  
 1522 4177–4186. <https://doi.org/10.1016/j.watres.2009.06.044>  
 1523 Kristiana, I., McDonald, S., Joll, C.A., 2020. The forest or the trees: a critical review on the  
 1524 analysis of total organic halogen (TOX) in drinking waters and its utility as a water  
 1525 quality parameter. *Environ. Sci. Water Res. Technol.* 6, 2313–2330.  
 1526 <https://doi.org/10.1039/D0EW00300J>  
 1527 Kumar, K., Day, R. A., Margerum, D. W., 1986. Atom-Transfer Redox Kinetics: General-  
 1528 Acid-Assisted Oxidation of Iodide by Chloramines and Hypochlorite. *Inorg. Chem.* 25  
 1529 4344–4350.  
 1530 Lee, Y., Yoon, J., von Gunten, U., 2005. Kinetics of the Oxidation of Phenols and Phenolic  
 1531 Endocrine Disruptors during Water Treatment with Ferrate (Fe(VI)). *Environ. Sci.*  
 1532 *Technol.* 39, 8978–8984. <https://doi.org/10.1021/es051198w>  
 1533 Lente, G., Kalmár, J., Baranyai, Z., Kun, A., Kék, I., Bajusz, D., Takács, M., Veres, L., Fábíán,  
 1534 I., 2009. One- Versus Two-Electron Oxidation with Peroxomonosulfate Ion: Reactions  
 1535 with Iron(II), Vanadium(IV), Halide Ions, and Photoreaction with Cerium(III). *Inorg.*  
 1536 *Chem.* 48, 1763–1773. <https://doi.org/10.1021/ic801569k>  
 1537 Li, J., Jiang, J., Zhou, Y., Pang, S.-Y., Gao, Y., Jiang, C., Ma, J., Jin, Y., Yang, Y., Liu, G.,  
 1538 Wang, L., Guan, C., 2017. Kinetics of Oxidation of Iodide (I<sup>-</sup>) and Hypoiodous Acid  
 1539 (HOI) by Peroxymonosulfate (PMS) and Formation of Iodinated Products in the  
 1540 PMS/I<sup>-</sup>/NOM System. *Environ. Sci. Technol. Lett.* 4, 76–82.  
 1541 <https://doi.org/10.1021/acs.estlett.6b00471>

- Li, X.-F., Mitch, W.A., 2018. Drinking Water Disinfection Byproducts (DBPs) and Human Health Effects: Multidisciplinary Challenges and Opportunities. *Environ. Sci. Technol.* 52, 1681–1689. <https://doi.org/10.1021/acs.est.7b05440>
- Li, J., Jiang, J., Pang, S., Zhou, Y., Gao, Y., Yang, Y., Sun, S., Liu, G., Ma, J., Jiang, C., Wang, L., 2018a. Transformation of Methylparaben by aqueous permanganate in the presence of iodide: Kinetics, modeling, and formation of iodinated aromatic products. *Water Res.* 135, 75–84. <https://doi.org/10.1016/j.watres.2018.02.014>
- Li, J., Pang, S., Zhou, Y., Sun, S., Wang, L., Wang, Z., Gao, Y., Yang, Y., Jiang, J., 2018b. Transformation of bisphenol AF and bisphenol S by manganese dioxide and effect of iodide. *Water Res.* 143, 47–55. <https://doi.org/10.1016/j.watres.2018.06.029>
- Li, J., Jiang, J., Pang, S.-Y., Cao, Y., Zhou, Y., Guan, C., 2020. Oxidation of iodide and hypiodous acid by non-chlorinated water treatment oxidants and formation of iodinated organic compounds: A review. *Chem. Eng. J.* 386. <https://doi.org/10.1016/j.cej.2019.123822>
- Liu, Q., Schurter, L. M., Muller, C. E., Aloisio, S., Francisco, J. S., Margerum D. W., 2001. Kinetics and Mechanisms of Aqueous Ozone Reactions with Bromide, Sulfite, Hydrogen Sulfite, Iodide, and Nitrite Ions. *Inorg. Chem.* 40 4436–4442.
- Liu, C., Salhi, E., Croué, J.-P., von Gunten, U., 2014. Chlorination of Iodide-Containing Waters in the Presence of CuO: Formation of Periodate. *Environ. Sci. Technol.* 48, 13173–13180. <https://doi.org/10.1021/es5032079>
- Liu, S., Li, Z., Dong, H., Goodman, B.A., Qiang, Z., 2017. Formation of iodo-trihalomethanes, iodo-acetic acids, and iodo-acetamides during chloramination of iodide-containing waters: Factors influencing formation and reaction pathways. *J. Hazard. Mater.* 321, 28–36. <https://doi.org/10.1016/j.jhazmat.2016.08.071>
- Luh, J., Mariñas, B.J., 2014. Kinetics of Bromochloramine Formation and Decomposition. *Environ. Sci. Technol.* 48, 2843–2852. <https://doi.org/10.1021/es4036754>
- Maberly, G. F., Eastman, C. J., Corcoran, J. M., 1981. Effect of Iodination of a village water-supply on goitre and thyroid function. *Lancet* Vol. 318 Issue 8258 1270–1272.
- Machek, Jr, E.J., 2015. Iopamidol as a Precursor to Iodinated Disinfection Byproduct (DBP) Formation as a Function of NOM concentration, pH, and Chlorinated Oxidants. University of Akron.
- MacKeown, H., Adusei Gyamfi, J., Schoutteten, K.V.K.M., Dumoulin, D., Verdickt, L., Ouddane, B., Criquet, J., 2020. Formation and removal of disinfection by-products in a full-scale drinking water treatment plant. *Sci. Total Environ.* 704. <https://doi.org/10.1016/j.scitotenv.2019.135280>
- MacKeown, H., Gyamfi, J.A., Delaporte, M., Schoutteten, K.V.K.M., Verdickt, L., Ouddane, B., Criquet, J., 2021. Removal of disinfection by-product precursors by ion exchange resins. *J. Environ. Chem. Eng.* 9, 104602. <https://doi.org/10.1016/j.jece.2020.104602>
- Magdeburg, A., Stalter, D., Schlüsener, M., Ternes, T., Oehlmann, J., 2014. Evaluating the efficiency of advanced wastewater treatment: Target analysis of organic contaminants and (geno-)toxicity assessment tell a different story. *Water Res.* 50, 35–47. <https://doi.org/10.1016/j.watres.2013.11.041>
- Martell, A. (Ed.), 1976. Critical Stability Constants: Inorganic Complexes. Springer US.
- Martino, M., Mills, G. P., Woeljen, J., Liss, P. S., 2009. A new source of volatile organoiodine compounds in surface seawater. *Geophys. Res. Lett.*
- Mian, H.R., Hu, G., Hewage, K., Rodriguez, M.J., Sadiq, R., 2018. Prioritization of unregulated disinfection by-products in drinking water distribution systems for human health risk mitigation: A critical review. *Water Res.* 147, 112–131. <https://doi.org/10.1016/j.watres.2018.09.054>

1591 Milenković, M.C., Stanisavljev, D.R., 2012. Role of Free Radicals in Modeling the Iodide–  
 1592 Peroxide Reaction Mechanism. *J. Phys. Chem. A* 116, 5541–5548.  
 1593 <https://doi.org/10.1021/jp303732u>

1594 Millero, F. J., Feistel, R., Wright, D. G., Mc Dougall T. J., 2008. The composition of Standard  
 1595 Seawater and the definition of the Reference-Composition Salinity Scale. *Deep Sea Res.*  
 1596 *Part Oceanogr. Res. Pap.* Vol. 55 Issue 1 50–72.

1597 Moran, J.E., Oktay, S.D., Santschi, P.H., 2002. Sources of iodine and iodine 129 in rivers.  
 1598 *Water Resour. Res.* 38, 24-1-24–10. <https://doi.org/10.1029/2001WR000622>

1599 Morgan, K.J., 1954. Some reactions of inorganic iodine compounds. *Q. Rev. Chem. Soc.* 8,  
 1600 123–146. <https://doi.org/10.1039/QR9540800123>

1601 Nagy, J. C., Kumar, K., Margerum, D. W., 1988. Non-Metal Redox Kinetics: Oxidation of  
 1602 Iodide by Hypochlorous Acid and by Nitrogen Trichloride Measured by the Pulsed-  
 1603 Accelerated-Flow Method. *Inorg. Chem.* Vol 27 No 16 2773–2780.

1604 National Research Council (US) Safe Drinking Water Committee, 1987. Disinfection Methods  
 1605 and Efficacy, in: *Drinking Water and Health: Disinfectants and Disinfectant By-*  
 1606 *Products: Volume 7.* National Academies Press (US).

1607 NHMRC, NRMCC, 2011. Australian Drinking Water Guidelines Paper 6 National Water  
 1608 Quality Management Strategy. National Health and Medical Research Council,  
 1609 National Resource Management Ministerial Council, Commonwealth of Australia,  
 1610 Canberra.

1611 Ning, B., Graham, N.J.D., 2008. Ozone Degradation of Iodinated Pharmaceutical Compounds.  
 1612 *J. Environ. Eng.* 43.

1613 Önnby, L., Salhi, E., McKay, G., Rosario-Ortiz, F.L., von Gunten, U., 2018. Ozone and chlorine  
 1614 reactions with dissolved organic matter - Assessment of oxidant-reactive moieties by  
 1615 optical measurements and the electron donating capacities. *Water Res.* 144, 64–75.  
 1616 <https://doi.org/10.1016/j.watres.2018.06.059>

1617 Opoku-Agyeman, B., 2010. New Method for the Synthesis of Iodohydrins. Indiana University  
 1618 of Pennsylvania.

1619 Palmer, D. A., Ramette, R. W., Mesmer, R. E., 1984. Triiodide Ion Formation Equilibrium and  
 1620 Activity Coefficients in Aqueous Solution. *J. Solut. Chem.* Vol 13 No 9.

1621 Pan, Y., Li, W., An, H., Cui, H., Wang, Y., 2016a. Formation and occurrence of new polar  
 1622 iodinated disinfection byproducts in drinking water. *Chemosphere* 144, 2312–2320.  
 1623 <https://doi.org/10.1016/j.chemosphere.2015.11.012>

1624 Pan, Y., Zhang, X., Li, Y., 2016b. Identification, toxicity and control of iodinated disinfection  
 1625 byproducts in cooking with simulated chlor(am)inated tap water and iodized table salt.  
 1626 *Water Res.* 88, 60–68. <https://doi.org/10.1016/j.watres.2015.10.002>

1627 Parsons, S.A., Goslan, E.H., Rocks, S.A., Holmes, P., Levy, L.S., Krasner, S.W., 2009. Study  
 1628 into the formation of disinfection by-products of chloramination, potential health  
 1629 implications and techniques for minimisation. Cranfield University.

1630 Pechtl, S., Schmitz, G., von Glasow, R., 2007. Modelling iodide? iodate speciation in  
 1631 atmospheric aerosol: Contributions of inorganic and organic iodine chemistry.  
 1632 *Atmospheric Chem. Phys.* 7, 1381–1393. <https://doi.org/10.5194/acp-7-1381-2007>

1633 Plewa, M. J., Wagner, E. D., Richardson, S. D., Thruston, A. D. JR., WOO Y-T., McKague A.  
 1634 B., 2004. Chemical and Biological Characterization of Newly Discovered Iodoacid  
 1635 Drinking Water Disinfection Byproducts. *Env. Sci Technol* 38 18 4713–4722.

1636 Plewa, M.J., Wagner, E.D., Richardson, S.D., 2017. TIC-Tox: A preliminary discussion on  
 1637 identifying the forcing agents of DBP-mediated toxicity of disinfected water. *J. Environ.*  
 1638 *Sci.* 58, 208–216. <https://doi.org/10.1016/j.jes.2017.04.014>

1639 Postigo, C., Cojocariu, C.I., Richardson, S.D., Silcock, P.J., Barcelo, D., 2016. Characterization  
 1640 of iodinated disinfection by-products in chlorinated and chloraminated waters using

Orbitrap based gas chromatography-mass spectrometry. *Anal. Bioanal. Chem.* 408, 3401–3411. <https://doi.org/10.1007/s00216-016-9435-x>

Postigo, C., Richardson, S.D., Barceló, D., 2017. Formation of iodo-trihalomethanes, iodo-haloacetic acids, and haloacetaldehydes during chlorination and chloramination of iodine containing waters in laboratory controlled reactions. *J. Environ. Sci.* 58, 127–134. <https://doi.org/10.1016/j.jes.2017.04.009>

Preedy, V. R., Burrow, G. N., Watson, R. R., 2009. *Comprehensive Handbook of Iodine: Nutritional, Biochemical, Pathological and Therapeutic Aspects*, Academic Press. ed. Elsevier.

Rahman, S.S., 2015. Effect of pH and Temperature on Halogenated DBPs (Master of Science (MS)). South Dakota State University.

Rahn, R.O., 1997. Potassium Iodide as a Chemical Actinometer for 254 nm Radiation: Use of Iodate as an Electron Scavenger. *Photochem. Photobiol.* 66, 450–455. <https://doi.org/10.1111/j.1751-1097.1997.tb03172.x>

Reckhow, D.A., Singer, P.C., Malcolm, R.L., 1990. Chlorination of humic materials: byproduct formation and chemical interpretations. *Environ. Sci. Technol.* 24, 1655–1664.

Richardson, S. D., Fasano, F., Ellington, J. J., Crumley, F. G., Buettner, K. M., Evans, J. J., Blount, B. C., Silva, L. K., Waite, T. J., Luther, G. W., McKague, A. B., Miltner, R. J., Wagner, E. D., Plewa, M. J., 2008. Occurrence and Mammalian Cell Toxicity of Iodinated Disinfection Byproducts in Drinking Water. *Env. Sci Technol* 42 8330–8338.

Richardson, S.D., Ternes, T.A., 2018. Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem.* 2018, 90, 1, 398–428 <https://doi.org/10.1021/acs.analchem.7b04577>

Riffault, V., Bedjanian, Y., Poulet, G., 2005. Kinetic and mechanistic study of the reactions of OH with IBr and HOI. *J. Photochem. Photobiol. Chem.* 176, 155–161. <https://doi.org/10.1016/j.jphotochem.2005.09.002>

Risher, J., Diamond, G., Swarts, S. G., Amata, R., 2004. Toxicological profile for iodine. Toxicological profile for iodine u.s. department of health and human services Public Health Service Agency for Toxic Substances and Disease Registry.

Rook, J. J., 1974. Formation of haloforms during chlorination of natural waters. *Water Treat Exam* 23 234–243.

Rosario-Ortiz, F., Rose, J., Speight, V., Von Gunten, U., Schnoor, J., 2016. How do you like your tap water? : Safe drinking water may not need to contain a residual disinfectant. *Science* 351, 912–914. <https://doi.org/10.1126/science.aaf0953>

Rose, M.R., Roberts, A.L., 2019. Iodination of Dimethenamid in Chloraminated Water: Active Iodinating Agents and Distinctions between Chlorination, Bromination, and Iodination. *Environ. Sci. Technol.* 53, 11764–11773. <https://doi.org/10.1021/acs.est.9b03645>

Rougé, V., Allard, S., Croué, J.-P., von Gunten, U., 2018. In Situ Formation of Free Chlorine During ClO<sub>2</sub> Treatment: Implications on the Formation of Disinfection Byproducts. *Environ. Sci. Technol.* 52, 13421–13429. <https://doi.org/10.1021/acs.est.8b04415>

Rumsby, P., Lawton, L., Ewence, A., Rockett, L., Hall, T., James, H., Jackson, P., 2009. REVIEW OF THE CURRENT TOXICOLOGICAL AND OCCURRENCE INFORMATION AVAILABLE ON IODINATED DISINFECTION BY-PRODUCTS (No. DEFRA 7883.03 (DWI 70/2/233)). WRc.

Saiz-Lopez, A., Fernandez, R.P., Ordóñez, C., Kinnison, D.E., Gómez Martín, J.C., Lamarque, J.-F., Tilmes, S., 2014. Iodine chemistry in the troposphere and its effect on ozone. *Atmospheric Chem. Phys.* 14, 13119–13143. <https://doi.org/10.5194/acp-14-13119-2014>

1689 Salhi, E., Von Gunten, U., 1999. Simultaneous determination of bromide, bromate and nitrite  
 1690 in low  $\mu\text{g l}^{-1}$  levels by ion chromatography without sample pretreatment. *Wat Res* 33,  
 1691 3239–3244.  
 1692 Salminen, R., Batista M. J., Bidovec M., Tarvainen T., 2005. Geochemical Atlas of Europe.  
 1693 Part 1 - Background Information, Methodology and Maps. Geological Survey of  
 1694 Finland, Otamedia Oy, Espoo.  
 1695 Sánchez-Polo, M., Rivera-Utrilla, J., Salhi, E., von Gunten, U., 2006. Removal of bromide and  
 1696 iodide anions from drinking water by silver-activated carbon aerogels. *J. Colloid*  
 1697 *Interface Sci.* 300, 437–441. <https://doi.org/10.1016/j.jcis.2006.03.037>  
 1698 Schmitz, G., 2004. Inorganic reactions of iodine(+1) in acidic solutions. *Int. J. Chem. Kinet.*  
 1699 36, 480–493. <https://doi.org/10.1002/kin.20020>  
 1700 Schulz, M., Löffler, D., Wagner, M., Ternes, T.A., 2008. Transformation of the X-ray Contrast  
 1701 Medium Iopromide In Soil and Biological Wastewater Treatment. *Environ. Sci.*  
 1702 *Technol.* 42, 7207–7217. <https://doi.org/10.1021/es800789r>  
 1703 Sedlak, D.S., von Gunten U., 2011. The Chlorine Dilemma. *Science* 331, 42–43.  
 1704 Seki, M., Oikawa, J., Taguchi, T., Ohnuki, T., Muramatsu, Y., Sakamoto, K., Amachi, S., 2013.  
 1705 Laccase-Catalyzed Oxidation of Iodide and Formation of Organically Bound Iodine in  
 1706 Soils. *Environ. Sci. Technol.* 47, 390–397. <https://doi.org/10.1021/es303228n>  
 1707 Serrano, M., Montesinos, I., Cardador, M.J., Silva, M., Gallego, M., 2015. Seasonal evaluation  
 1708 of the presence of 46 disinfection by-products throughout a drinking water treatment  
 1709 plant. *Sci. Total Environ.* 517, 246–258.  
 1710 <https://doi.org/10.1016/j.scitotenv.2015.02.070>  
 1711 Shackelford, W.M., Keith, L.H., 1976. Frequency of organic compounds identified in water.  
 1712 US Environmental Protection Agency, Athens, Georgia.  
 1713 Sharma, V.K., 2011. Oxidation of inorganic contaminants by ferrates (VI, V, and IV)–kinetics  
 1714 and mechanisms: A review. *J. Environ. Manage.* 92, 1051–1073.  
 1715 <https://doi.org/10.1016/j.jenvman.2010.11.026>  
 1716 Sherwen, T., Evans, M. J., Carpenter, L. J., Andrews, S. J., Lidster, R. T., Dix, B., Koenig, T.  
 1717 K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahakan,  
 1718 A. S., Ordonez, C., 2016. Iodine’s impact on tropospheric oxidants: a global model  
 1719 study in GEOS-Chem. *Atmos Chem Phys* 16 1161–1186.  
 1720 Shin, J., von Gunten, U., Reckhow, D.A., Allard, S., Lee, Y., 2018. Reactions of Ferrate(VI)  
 1721 with Iodide and Hypoiodous Acid: Kinetics, Pathways, and Implications for the Fate of  
 1722 Iodine during Water Treatment. *Environ. Sci. Technol.* 52, 7458–7467.  
 1723 <https://doi.org/10.1021/acs.est.8b01565>  
 1724 Shin, J., Lee, Y., von Gunten, U., 2020. Kinetics of the reaction between hydrogen peroxide  
 1725 and aqueous iodine: Implications for technical and natural aquatic systems. *Water Res.*  
 1726 179, 115852. <https://doi.org/10.1016/j.watres.2020.115852>  
 1727 Sigalla, J., 1961. N° 52. — Les réactions de l’iode en solution alcaline un nouveau composé  
 1728  $\text{I}_2\text{OH}^-$ . *J Chim Phys* 58 602–605.  
 1729 Smith, E. M., Plewa, M. J., Lindell, C. L., Richardson, S. D., Mitch, W. A., 2010. Comparison  
 1730 of Byproduct Formation in Waters Treated with Chlorine and Iodine: Relevance to  
 1731 Point-of-Use Treatment. *Env. Sci Technol* 44 8446–8452.  
 1732 Smyth, D., Johnson, C.C., 2011. Distribution of iodine in soils of Northern Ireland. *Geochem.*  
 1733 *Explor. Environ. Anal.* 11, 25–39. <https://doi.org/10.1144/1467-7873/09-015>  
 1734 Spellman, F.R., 2013. Handbook of Water and Wastewater Treatment Plant Operations, Third  
 1735 Edition. CRC Press.  
 1736 Stalter, D., O’Malley, E., Von Gunten, U., Escher, B.I., 2020. Mixture effects of drinking water  
 1737 disinfection by-products: Implications for risk assessment. *Environ. Sci. Water Res.*  
 1738 *Technol.* 6, 2341–2351. <https://doi.org/10.1039/c9ew00988d>

1739 Stieber, M., Putschew, A., Jekel, M., 2011. Treatment of Pharmaceuticals and Diagnostic  
1740 Agents Using Zero-Valent Iron – Kinetic Studies and Assessment of Transformation  
1741 Products Assay. *Environ. Sci. Technol.* 45, 4944–4950.  
1742 <https://doi.org/10.1021/es200034j>

1743 Symons, J.M., Xia, R., Jr, G.E.S., Diehl, A.C., Hwang, C.J., Krasner, S.W., Barrett, S.E., 1998.  
1744 Factors Affecting Disinfection By-Product Formation During Chloramination. *AWWA*  
1745 *Res. Found. Am. Water Works Assoc.* 330.

1746 Tang, Q., Xu, Q., Zhang, F., Huang, Y., Liu, J., Wang, X., Yang, Y., Liu, X., 2013.  
1747 Geochemistry of iodine-rich groundwater in the Taiyuan Basin of central Shanxi  
1748 Province, North China. *J. Geochem. Explor., Arsenic, Fluoride and Iodine in*  
1749 *Groundwater of China* 135, 117–123. <https://doi.org/10.1016/j.gexplo.2012.08.019>

1750 Terhalle, J., Kaiser, P., Jütte, M., Buss, J., Yasar, S., Marks, R., Uhlmann, H., Schmidt, T.C.,  
1751 Lutze, H.V., 2018. Chlorine Dioxide—Pollutant Transformation and Formation of  
1752 Hypochlorous Acid as a Secondary Oxidant. *Environ. Sci. Technol.* 52, 9964–9971.  
1753 <https://doi.org/10.1021/acs.est.8b01099>

1754 Ternes, T.A., Stüber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M., Teiser, B.,  
1755 2003. Ozonation: a tool for removal of pharmaceuticals, contrast media and musk  
1756 fragrances from wastewater? *Water Res.* 37, 1976–1982.

1757 Tian, F.-X., Xu, B., Lin, Y.-L., Hu, C.-Y., Zhang, T.-Y., Gao, N.-Y., 2014. Photodegradation  
1758 kinetics of iopamidol by UV irradiation and enhanced formation of iodinated  
1759 disinfection by-products in sequential oxidation processes. *Water Res.* 58, 198–208.  
1760 <https://doi.org/10.1016/j.watres.2014.03.069>

1761 Tian, F.-X., Hu, X.-J., Xu, B., Zhang, T.-Y., Gao, Y.-Q., 2017a. Phototransformation of iodate  
1762 by UV irradiation: Kinetics and iodinated trihalomethane formation during subsequent  
1763 chlor(am)ination. *J. Hazard. Mater.* 326, 138–144.  
1764 <https://doi.org/10.1016/j.jhazmat.2016.12.012>

1765 Tian, F.-X., Xu, B., Lin, Y.-L., Hu, C.-Y., Zhang, T.-Y., Xia, S.-J., Chu, W.-H., Gao, N.-Y.,  
1766 2017b. Chlor(am)ination of iopamidol: Kinetics, pathways and disinfection by-products  
1767 formation. *Chemosphere* 184, 489–497.  
1768 <https://doi.org/10.1016/j.chemosphere.2017.06.012>

1769 Tian, F.-X., Ma, S.-X., Xu, B., Hu, X.-J., Xing, H.-B., Liu, J., Wang, J., Li, Y.-Y., Wang, B.,  
1770 Jiang, X., 2019. Photochemical degradation of iodate by UV/H<sub>2</sub>O<sub>2</sub> process: Kinetics,  
1771 parameters and enhanced formation of iodo-trihalomethanes during chloramination.  
1772 *Chemosphere* 221, 292–300. <https://doi.org/10.1016/j.chemosphere.2019.01.014>

1773 Trofe, T.W., Inman, G.W.Jr., Johnson, J.D., 1980. Kinetics of Monochloramine Decomposition  
1774 in the Presence of Bromide. *Environ. Sci. Technol.* 14, 544–549.

1775 Trogolo, D., Arey, J.S., 2017. Equilibria and Speciation of Chloramines, Bromamines, and  
1776 Bromochloramines in Water. *Environ. Sci. Technol.* 51, 128–140.  
1777 <https://doi.org/10.1021/acs.est.6b03219>

1778 Troy, R.C., Kelley, M.D., Nagy, J.C., Margerum, D.W., 1991. Non-Metal Redox Kinetics:  
1779 Iodine Monobromide Reaction with Iodide Ion and the Hydrolysis of IBr. *Inorg. Chem.*  
1780 30, 4838–4845. <https://doi.org/10.1021/ic00025a030>

1781 Troy, R.C., Margerum, D.W., 1991. Non-metal redox kinetics: Hypobromite and hypobromous  
1782 acid reactions with iodide and with sulfite and the hydrolysis of bromosulfate. *Inorg.*  
1783 *Chem.* 30, 3538–3543.

1784 Truesdalea, V.W., Jones, S.D., 1996. The variation of iodate and total iodine in some UK  
1785 rainwaters during 1980–1981. *J. Hydrol.* 179, 67–86. [https://doi.org/10.1016/0022-1694\(95\)02873-0](https://doi.org/10.1016/0022-1694(95)02873-0)

1787 Tugulea, A.-M., Aranda-Rodriguez, R., Bérubé, D., Giddings, M., Lemieux, F., Hnatiw, J.,  
1788 Dabeka, L., Breton, F., 2018. The influence of precursors and treatment process on the

1789 formation of Iodo-THMs in Canadian drinking water. *Water Res.* 130, 215–223.  
1790 <https://doi.org/10.1016/j.watres.2017.11.055>

1791 Tugulea, A.-M., Aranda-Rodriguez, R., Giddings, M., Lemieux, F., Hnatiw, J., 2015. Iodo-  
1792 THM Formation During Chlorination of Source Waters With Naturally Occurring  
1793 Ammonium and High Sodium Content, in: *Disinfection By-Products in Drinking Water*,  
1794 The Royal Society of Chemistry. Thompson K. Clive, Gillespie Simon, Goslan Emma,  
1795 pp. 46–58.

1796 Valent, I., L'ubica A., and Ševčík, P., 1998. Simulations of the Iodine Interphase Transport  
1797 Effect on the Oscillating Bray- Liebhafsky Reaction. *J. Phys. Chem. A* 102, 7576–7579.  
1798 <https://doi.org/10.1021/jp982323b>

1799 Varga, D., Nagypál, I., Horváth, A.K., 2010. Complex Kinetics of a Landolt-Type Reaction:  
1800 The Later Phase of the Thiosulfate–Iodate Reaction. *J. Phys. Chem. A* 114, 5752–5758.  
1801 <https://doi.org/10.1021/jp101458e>

1802 Vigneri, R., Catalfamo, R., Freni, V., Ippolito, A., La Rosa, G. L., Regalbuto, C., 1993. Iodine  
1803 supplementation to a public water supply: An efficient method for correcting iodine  
1804 deficiency, in: *Iodine Deficiency in Europe: A Continuing Concern*, NATO Science  
1805 Series A: Life Sciences. Delange F., Dunn J. T., Glinoe D., pp. 275–281.

1806 Vikesland, P.J., Fiss, E.M., Wigginton, K.R., McNeill, K., Arnold, W.A., 2013. Halogenation  
1807 of Bisphenol-A, Triclosan, and Phenols in Chlorinated Waters Containing Iodide.  
1808 *Environ. Sci. Technol.* 47, 6764–6772. <https://doi.org/10.1021/es304927j>

1809 Vogt, R., Sander, R., Glasow, R.V., Crutzen, P.J., 1999. Iodine Chemistry and its Role in  
1810 Halogen Activation and Ozone Loss in the Marine Boundary Layer: A Model Study. *J.*  
1811 *Atmospheric Chem.* 375–395.

1812 von Gunten, U., 2018. Oxidation Processes in Water Treatment: Are We on Track? *Environ.*  
1813 *Sci. Technol.* 52, 5062–5075. <https://doi.org/10.1021/acs.est.8b00586>

1814 von Gunten, U., 2003. Ozonation of drinking water: Part I. Oxidation kinetics and product  
1815 formation. *Water Res.* 37, 1443–1467. [https://doi.org/10.1016/S0043-1354\(02\)00457-](https://doi.org/10.1016/S0043-1354(02)00457-8)  
1816 8

1817 von Gunten, U., 2003. Ozonation of drinking water: Part II. Disinfection and by-product  
1818 formation in presence of bromide, iodide or chlorine. *Water Res.* 37 7 1469–1487.

1819 von Sonntag, C., von Gunten, U., 2012. *Chemistry of Ozone in Water and Waste-water*  
1820 *Treatment: From Basic Principles to Applications*.

1821 Vrkljan, P.B.A., Bauer, J., Tomisic, V., 2008. Kinetics and Mechanism of Iodide Oxidation by  
1822 Iron(III): A Clock Reaction Approach. *J. Chem. Educ.* 85, 1123.  
1823 <https://doi.org/10.1021/ed085p1123>

1824 Wagner, E.D., Plewa, M.J., 2017. CHO cell cytotoxicity and genotoxicity analyses of  
1825 disinfection by-products: An updated review. *J. Environ. Sci., water treatment and*  
1826 *disinfection by-products* 58, 64–76. <https://doi.org/10.1016/j.jes.2017.04.021>

1827 Wang, Y.L., Nagy, J.C., Margerum, D.W., 1989. Kinetics of Hydrolysis of Iodine  
1828 Monochloride Measured by the Pulsed-Accelerated-Flow Method. *J. Am. Chem. Soc.*  
1829 111, 7838–7844. <https://doi.org/10.1021/ja00202a026>

1830 Wang, Z., Xu, B., Lin, Y.-L., Hu, C.-Y., Tian, F.-X., Zhang, T.-Y., Gao, N.-Y., 2014. A  
1831 comparison of iodinated trihalomethane formation from iodide and iopamidol in the  
1832 presence of organic precursors during monochloramination. *Chem. Eng. J.* 257, 292–  
1833 298. <https://doi.org/10.1016/j.cej.2014.07.084>

1834 Wang, L., Kong, D., Ji, Y., Lu, J., Yin, X., Zhou, Q., 2017. Transformation of iodide and  
1835 formation of iodinated by-products in heat activated persulfate oxidation process.  
1836 *Chemosphere* 181, 400–408. <https://doi.org/10.1016/j.chemosphere.2017.04.076>

1837 Wang, X., Liu, Y., Huang, Z., Wang, L., Wang, Y., Li, Y., Li, J., Qi, J., Ma, J., 2018. Rapid  
1838 oxidation of iodide and hypoiodous acid with ferrate and no formation of iodoform and

1839 monoiodoacetic acid in the ferrate/I – /HA system. *Water Res.* 144.  
1840 <https://doi.org/10.1016/j.watres.2018.07.061>

1841 Wang, X., Wang, Z., Tang, Y., Xiao, D., Zhang, D., Huang, Y., Guo, Y., Liu, J., 2019.  
1842 Oxidative degradation of iodinated X-ray contrast media (iomeprol and iohexol) with  
1843 sulfate radical: An experimental and theoretical study. *Chem. Eng. J.* 368, 999–1012.  
1844 <https://doi.org/10.1016/j.cej.2019.02.194>

1845 Watson, K., Farré, M. J., Knight, N., 2012. Strategies for the removal of halides from drinking  
1846 water sources, and their applicability in disinfection by-product minimisation: A critical  
1847 review. *J. Environ. Manage.* 276–298.

1848 Wei, X., Chen, X., Wang, X., Zheng, W., Zhang, D., Tian, D., Jiang, S., Ong, C.N., He, G., Qu,  
1849 W., 2013. Occurrence of Regulated and Emerging Iodinated DBPs in the Shanghai  
1850 Drinking Water. *PLoS ONE* 8, e59677. <https://doi.org/10.1371/journal.pone.0059677>

1851 Weinberg, H.S., Yamada, H., 1998. Post-Ion-Chromatography Derivatization for the  
1852 Determination of Oxyhalides at Sub-PPB Levels in Drinking Water. *Anal. Chem.* 70,  
1853 1–6. <https://doi.org/10.1021/ac970651m>

1854 Weinberg, H. S., Krasner, S. W., Richardson, S. D., Thruston, A. D. JR., 2002. The Occurrence  
1855 of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a  
1856 Nationwide DBP Occurrence Study (U.S. Environmental Protection Agency, National  
1857 Exposure Research Laboratory: Athens, GA).

1858 Wendel, F.M., Lütke Eversloh, C., Machek, E.J., Duirk, S.E., Plewa, M.J., Richardson, S.D.,  
1859 Ternes, T.A., 2014. Transformation of Iopamidol during Chlorination. *Environ. Sci.*  
1860 *Technol.* 48, 12689–12697. <https://doi.org/10.1021/es503609s>

1861 Westerhoff, P., Chao, P., Mash, H., 2004. Reactivity of natural organic matter with aqueous  
1862 chlorine and bromine. *Water Res.* 38, 1502–1513.  
1863 <https://doi.org/10.1016/j.watres.2003.12.014>

1864 Woo, B., Park, J.-H., Kim, S., Lee, J., Choi, J.-H., Pyo, H., 2018. Determination of six  
1865 iodotrihalomethanes in drinking water in Korea. *Sci. Total Environ.* 640–641, 581–590.  
1866 <https://doi.org/10.1016/j.scitotenv.2018.05.329>

1867 Wuilloud, R.G., de Wuilloud, J.C.A., Vonderheide, A.P., Caruso, J.A., 2003. Determination of  
1868 iodinated phenol species at parts-per-trillion concentration levels in different water  
1869 samples by solid-phase microextraction/offline GC-ICP-MS. *J Anal Spectrom* 18,  
1870 1119–1124. <https://doi.org/10.1039/B300911B>

1871 Xie, Y. F., 2016. Disinfection Byproducts in Drinking Water: Formation, Analysis, and  
1872 Control. CRC Press.

1873 Xu, L., 2014. Kinetics and Mechanism of the Reactions of Pentathionate Ion by Different  
1874 Halogen-Containing Oxidizing Agents (Ph.D. dissertation). UNIVERSITY OF PÉCS  
1875 Doctoral School of Chemistry, Pécs.

1876 Xu, Z., Li, X., Hu, X., Yin, D., 2017. Distribution and relevance of iodinated X-ray contrast  
1877 media and iodinated trihalomethanes in an aquatic environment. *Chemosphere* 184,  
1878 253–260. <https://doi.org/10.1016/j.chemosphere.2017.05.048>

1879 Yamaguchi, N., Nakano, M., Takamatsu, R., Tanida, H., 2010. Inorganic iodine incorporation  
1880 into soil organic matter: evidence from iodine K-edge X-ray absorption near-edge  
1881 structure. *J. Environ. Radioact.* 101, 451–457.  
1882 <https://doi.org/10.1016/j.jenvrad.2008.06.003>

1883 Yamaguchi, M., 2011. Hemibonding of Hydroxyl Radical and Halide Anion in Aqueous  
1884 Solution. *J. Phys. Chem. A* 115, 14620–14628. <https://doi.org/10.1021/jp2063386>

1885 Yan, M., Li, M., Han, X., 2016. Behaviour of I/Br/Cl-THMs and their projected toxicities under  
1886 simulated cooking conditions: Effects of heating, table salt and residual chlorine. *J.*  
1887 *Hazard. Mater.* 314, 105–112. <https://doi.org/10.1016/j.jhazmat.2016.04.025>

1888 Yang, X., Guo, W., Lee, W., 2013. Formation of disinfection byproducts upon chlorine dioxide  
1889 preoxidation followed by chlorination or chloramination of natural organic matter.  
1890 Chemosphere 91, 1477–1485. <https://doi.org/10.1016/j.chemosphere.2012.12.014>

1891 Ye T., Lin Y.-L., Hu C.-Y., Xia S.-J., Lin L., Mwakagenda S.A., Gao N.-Y., 2012. Formation of  
1892 iodinated disinfection by-products during oxidation of iodide-containing water with  
1893 potassium permanganate. J. Hazard. Mater. 241–242 348–354.

1894 Yeo, J., Choi, W., 2009. Iodide-Mediated Photooxidation of Arsenite under 254 nm Irradiation.  
1895 Environ. Sci. Technol. 43, 3784–3788. <https://doi.org/10.1021/es900602n>

1896 Yu, W., Campos, L., Shi, T., Li, G., Graham, N., 2015. Enhanced removal of manganese in  
1897 organic-rich surface water by combined sodium hypochlorite and potassium  
1898 permanganate during drinking water treatment. RSC Adv. 5, 27970–27977.  
1899 <https://doi.org/10.1039/C5RA01643F>

1900 Zhai, H., Zhang, X., Zhu, X., Liu, J., Ji, M., 2014. Formation of Brominated Disinfection  
1901 Byproducts during Chloramination of Drinking Water: New Polar Species and Overall  
1902 Kinetics. Environ. Sci. Technol. 48, 2579–2588. <https://doi.org/10.1021/es4034765>

1903 Zhang, X., Minear, R.A., 2002. Decomposition of trihaloacetic acids and formation of the  
1904 corresponding trihalomethanes in drinking water. Water Res. 36, 3665–3673.  
1905 [https://doi.org/10.1016/S0043-1354\(02\)00072-6](https://doi.org/10.1016/S0043-1354(02)00072-6)

1906 Zhang, S., Schwehr, K.A., Ho, Y.-F., Xu, C., Roberts, K.A., Kaplan, D.I., Brinkmeyer, R.,  
1907 Yeager, C.M., Santschi, P.H., 2010. A Novel Approach for the Simultaneous  
1908 Determination of Iodide, Iodate and Organo-Iodide for 127I and 129I in Environmental  
1909 Samples Using Gas Chromatography–Mass Spectrometry. Environ. Sci. Technol. 44,  
1910 9042–9048. <https://doi.org/10.1021/es102047y>

1911 Zhang, E., Wang, Y., Qian, Y., Ma, T., Zhang, D., Zhan, H., Zhang, Z., Fei, Y., Wang, S., 2013.  
1912 Iodine in groundwater of the North China Plain: Spatial patterns and hydrogeochemical  
1913 processes of enrichment. J. Geochem. Explor., Arsenic, Fluoride and Iodine in  
1914 Groundwater of China 135, 40–53. <https://doi.org/10.1016/j.gexplo.2012.11.016>

1915 Zhang, T.-Y., Xu, B., Hu, C.-Y., Lin, Y.-L., Lin, L., Ye, T., Tian, F.-X., 2015. A comparison of  
1916 iodinated trihalomethane formation from chlorine, chlorine dioxide and potassium  
1917 permanganate oxidation processes. Water Res. 68 394–403.

1918 Zhang, T.-Y., Lin, Y.-L., Wang, A.-Q., Tian, F.-X., Xu, B., Xia, S.-J., Gao, N.-Y., 2016a.  
1919 Formation of iodinated trihalomethanes during UV/chloramination with iodate as the  
1920 iodine source. Water Res. 98, 199–205. <https://doi.org/10.1016/j.watres.2016.04.012>

1921 Zhang, J., Chen, D.-D., Li, L., Li, W.-W., Mu, Y., Yu, H.-Q., 2016b. Role of NOM molecular  
1922 size on iodo-trihalomethane formation during chlorination and chloramination. Water  
1923 Res. 102, 533–541. <https://doi.org/10.1016/j.watres.2016.07.007>

1924 Zhang, J., Liu, J., He, C.-S., Qian, C., Mu, Y., 2018. Formation of iodo-trihalomethanes (I-  
1925 THMs) during disinfection with chlorine or chloramine: Impact of UV/H<sub>2</sub>O<sub>2</sub> pre-  
1926 oxidation. Sci. Total Environ. 640–641, 764–771.  
1927 <https://doi.org/10.1016/j.scitotenv.2018.05.306>

1928 Zhao, X., Salhi, E., Liu, H., Ma, J., von Gunten, U., 2016. Kinetic and Mechanistic Aspects of  
1929 the Reactions of Iodide and Hypoiodous Acid with Permanganate: Oxidation and  
1930 Disproportionation. Env. Sci Technol 50 4358–4365.

1931 Zhao, X., Ma, J., von Gunten, U., 2017. Reactions of hypoiodous acid with model compounds  
1932 and the formation of iodoform in absence/presence of permanganate. Water Res. 119,  
1933 126–135. <https://doi.org/10.1016/j.watres.2017.04.033>

1934 Zhou, X., Zheng, L., Chen, S., Du, H., Gakoko Raphael, B.M., Song, Q., Wu, F., Chen, J., Lin,  
1935 H., Hong, H., 2019. Factors influencing DBPs occurrence in tap water of Jinhua Region  
1936 in Zhejiang Province, China. Ecotoxicol. Environ. Saf. 171, 813–822.  
1937 <https://doi.org/10.1016/j.ecoenv.2018.12.106>

Zhu, X., Zhang, X., 2016. Modeling the formation of TOCl, TOBr and TOI during chlor(am)ination of drinking water. Water Res. 96 166–176.

Figure captions :

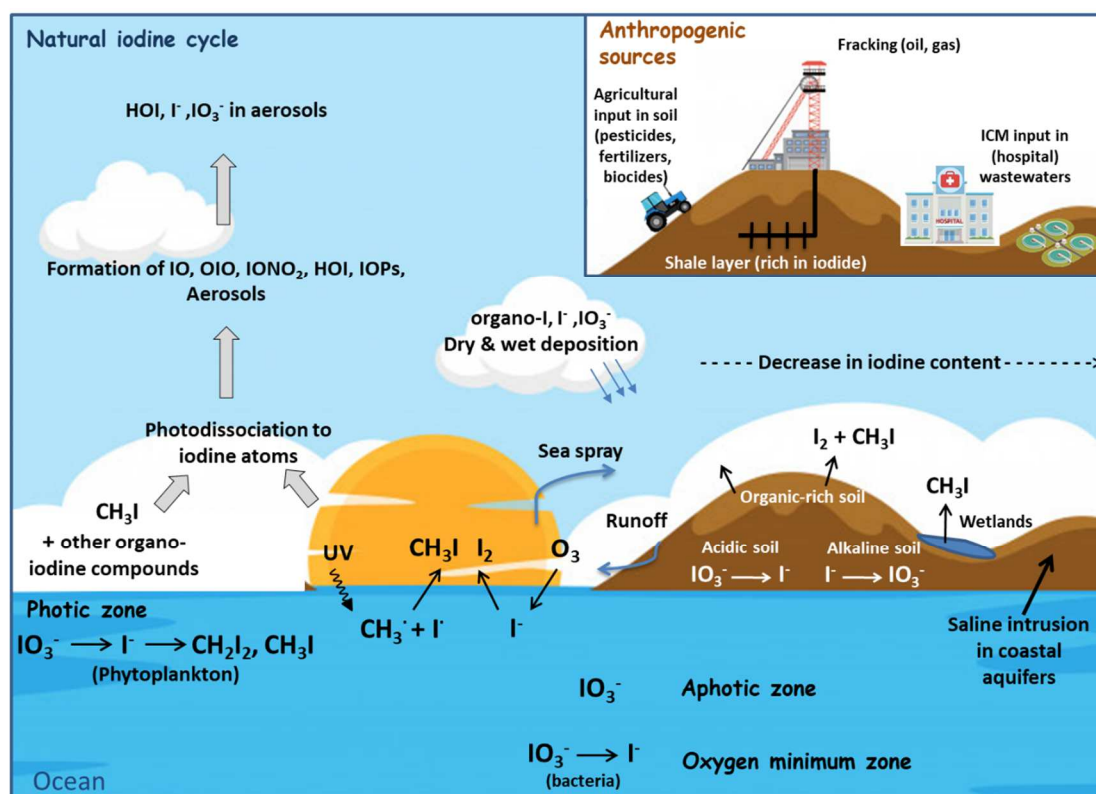


Figure 1: Schematic representation of the natural iodine cycle (adapted from Fuge and Johnson (2015) and Carpenter (2015)) and anthropogenic sources. ICM: iodinated contrast media; IOPs: iodine oxide particles; organo-I: organo-iodine.

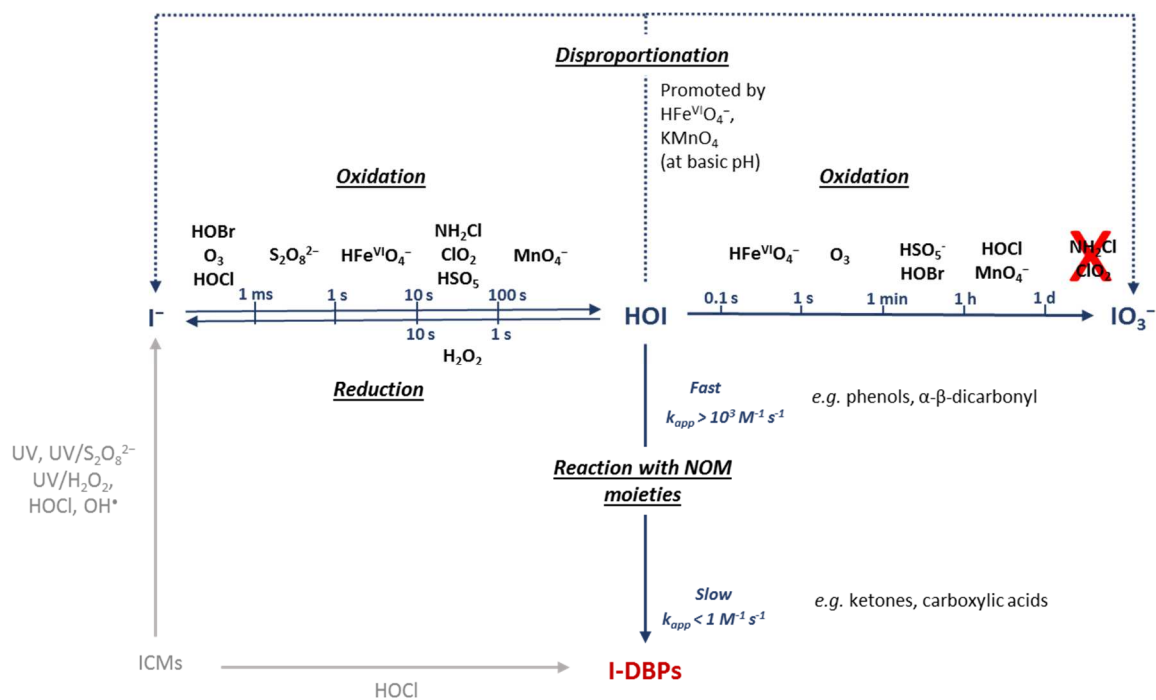


Figure 2: Scheme of the main reactions involving iodine-containing species in various oxidative processes. The indicated times are half-life times for oxidant/reductant concentrations of 10  $\mu\text{M}$  (see Table 1).

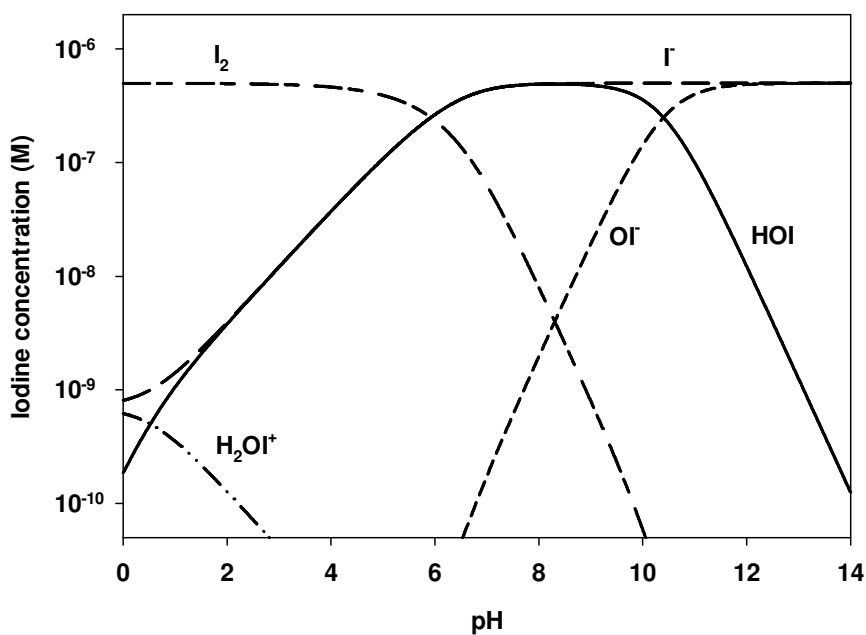
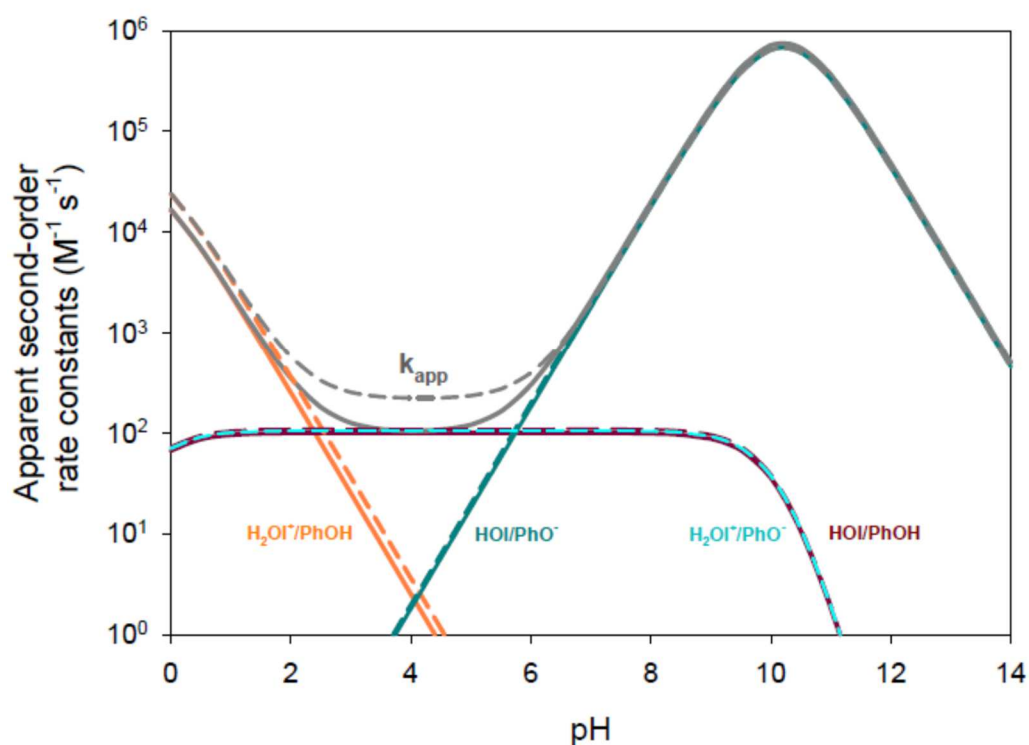
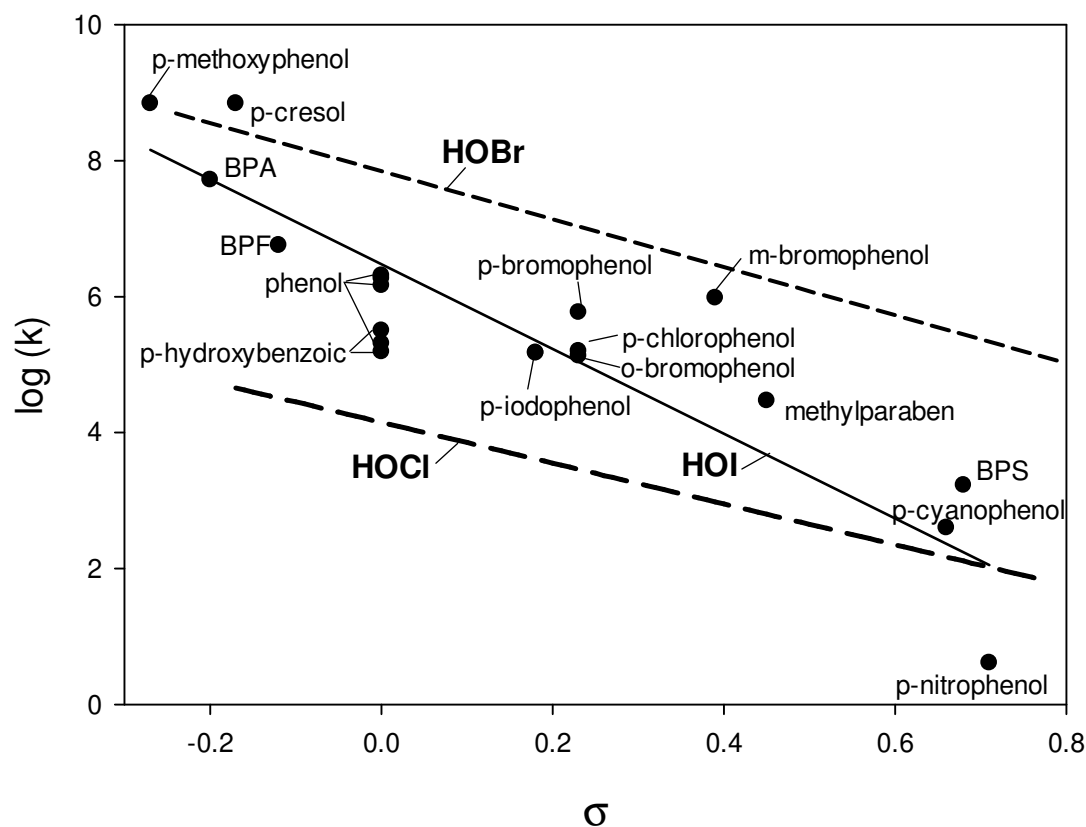


Figure 3: pH-dependent speciation of iodine (for a concentration of 1  $\mu\text{M}$   $\text{I}^-$ ). Calculations based on equilibria in Table 2.

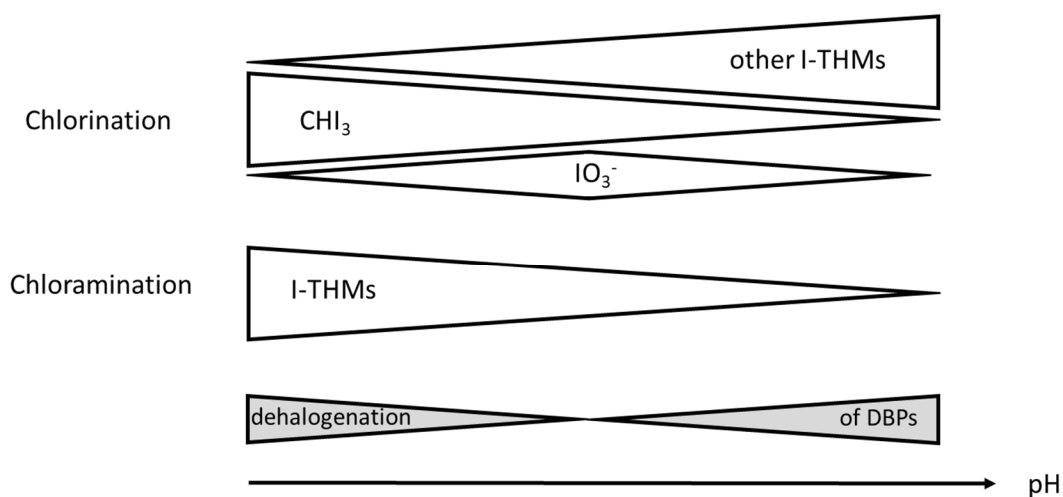


1955  
 1956 Figure 4: Apparent second order rate constants for the reactions of iodine with phenol as a function of  
 1957 pH. Solid lines considering reactions 21 and 23-24 using rate constants from (Bichsel and von Gunten,  
 1958 2000a) (Table 4). Dashed lines considering reactions 21-24 using rate constants from (Rose and Roberts,  
 1959 2019) (Table 4).  $\text{pK}_a(\text{H}_2\text{OI}^+/\text{HOI}) = -0.3$  for both modelings. The contributions of each reaction are also  
 1960 shown as a function of the pH; apparent second-order rate constants calculated by multiplying the  
 1961 species specific second-order rate constant by the proportion of species for different pH.



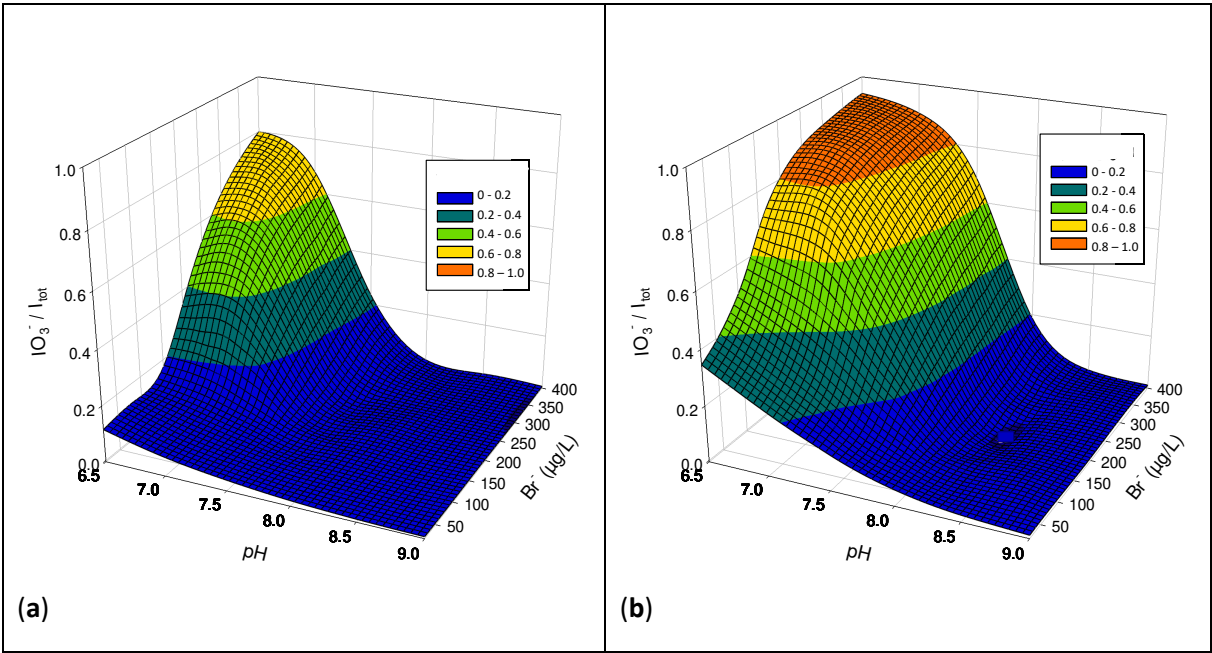
1962

1963 Figure 5: Correlation between the second-order rate constants ( $\log(k)$ ) for the reaction of HOI with  
 1964 dissociated phenols and the Hammett constant ( $\sigma$ ) (Data in Table S3). Correlation  
 1965  $\log(k_{\text{HOI/PhO}^-}) = 6.5 - 6.2 \sum \sigma$ ,  $R^2 = 0.77$ .  $\log(k_{\text{HOBr/PhO}^-}) = 7.8 - 3.5 \sum \sigma$ ,  $R^2 = 0.80$  (Heeb et al., 2014);  
 1966  $\log(k_{\text{HOCl/PhO}^-}) = 4.15 - 3.0 \sum \sigma$ ,  $R^2 = 0.95$  (Gallard and von Gunten, 2002).

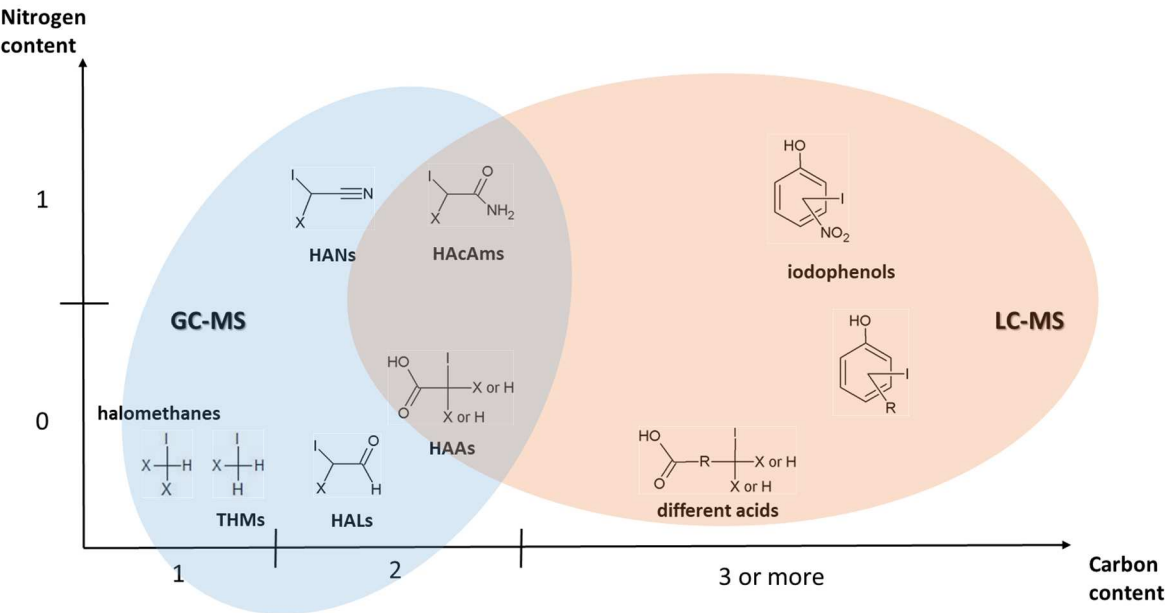


1967

1968 Figure 6. Schematic representation of the influence of pH on I-DBP and iodate formation during chlorination and chloramination and I-DBP dehalogenation.  
1969



1970  
1971 Figure 7: Modeling of the effect of pH and the bromide concentration on iodide speciation ( $\text{IO}_3^-/\text{I}_{\text{tot}}$ )  
1972 after chlorination of phenol-containing waters. The model run time was 4000 s, with initial  
1973 concentrations of  $\text{I}^- = 20 \mu\text{g L}^{-1}$  ( $0.16 \mu\text{M}$ ),  $\text{PhOH} = 10 \mu\text{M}$  (so the number of fast reacting sites roughly  
1974 matches the concentration of phenolic moieties in natural waters with  $5 \text{ mgC L}^{-1}$  of DOC (average of 2  
1975 mmol of phenolic moieties/gC in NOM extracts; Önnby et al., 2018), (a)  $[\text{HOCl}]_0 = 15 \mu\text{M}$ , (b)  $[\text{HOCl}]_0$   
1976  $= 50 \mu\text{M}$ .



1977  
1978 Figure 8: Main classes of I-DBPs analysed in previous studies as a function of carbon and nitrogen atom  
1979 contents and the corresponding analytical methods.

1980  
1981

Table 1: Compilation of rate constants and half-life times for the oxidation of iodide and hypiodous acid by various oxidants under typical drinking water treatment conditions (pH 7.0 and with an oxidant concentration of 10  $\mu$ M).

Oxidant	$k(I^-)$ ( $M^{-1}s^{-1}$ unless otherwise stated)	$I^-$			$HOI/OI^-$				
		Main Product	Half-life time	Reference	$k(HOI)$ ( $M^{-1}s^{-1}$ )	$k(OI^-)$ ( $M^{-1}s^{-1}$ )	Final product	Half-life time	Reference
HOCl	$4.3 \times 10^8$	HOI	$2.1 \times 10^{-4}$ s <sup>i</sup>	(Nagy et al. 1988) (Gerritsen and Margerum, 1990)	8.2	-	$IO_3^-$	1.1 h	(Bichsel and von Gunten, 1999)
$OCl^-$	< 30				52	-			
HOB <sup>r</sup>	$5.0 \times 10^9$	HOI	$1.4 \times 10^{-5}$ s <sup>ii</sup>	(Troy and Margerum 1991)	Not significant	$1.9 \times 10^6$	$IO_3^-$	93 s <sup>ii</sup>	(Criquet et al., 2012)
$OBr-}}$	$6.8 \times 10^5$				-	$1.8 \times 10^3$			
HOI	-	-	-	-	0.3	15	$IO_3^-$	64 h	Bichsel (2000)
(disproportionation)	-				0.6	9.3		32 h	(Opoku-Agyeman, 2010)
NH <sub>2</sub> Cl	$2.4 \times 10^{10} [H^+] M^{-2}s^{-1}$	HOI	29 s	(Kumar et al. 1986)	$< 2 \times 10^{-3}$	< 3	unknown	8.4 months	(Bichsel and von Gunten, 1999)
NHCl <sub>2</sub>	$9.3 \times 10^5 [H^+] M^{-2}s^{-1}$	Unknown	8.6 d	(Kumar et al. 1986)	-	-	-	-	-
NCl <sub>3</sub>	Higher than NH <sub>2</sub> Cl and NHCl <sub>2</sub>			(Kumar et al. 1986)					
O <sub>3</sub>	$1.2 \times 10^9$	HOI	$5.8 \times 10^{-5}$ s	(Liu et al. 2001)	$3.6 \times 10^4$	$1.6 \times 10^6$	$IO_3^-$	1.9 s	(Bichsel and von Gunten, 1999)
ClO <sub>2</sub>	$1.9 \times 10^3$	I <sup>•</sup>	37 s	(Fabian and Gordon 1997)	-	-	-	-	-
ClO <sub>2</sub> <sup>-</sup>	$9.2 \cdot 10^2 [H^+] M^{-2}s^{-1}$	I <sub>2</sub>	>1y <sup>iii</sup>	(Kern and Kim, 1965)					
HClO <sub>2</sub>	5	IO <sup>•</sup>							
HFeO <sub>4</sub> <sup>-</sup>	$4.5 \times 10^4$	HOI	2.4 s <sup>iv</sup>	(Shin et al. 2018)	$2.5 \times 10^5$	$2.5 \times 10^5$		0.3 s <sup>iv</sup>	(Shin et al. 2018)
	$2.3 \times 10^4$	I <sup>•</sup> / I <sub>2</sub> <sup>-</sup>	4.8 s <sup>iv</sup>	(Kralchevska et al. 2016)	$1.8 \times 10^5$	-	$IO_3^-$	0.4 s <sup>iv</sup>	(Wang et al. 2018)
FeO <sub>4</sub> <sup>2-</sup>	-	-	-		$7.7 \times 10^3$	-			
MnO <sub>4</sub> <sup>-</sup>	Not specified	HOI / I <sub>2</sub>	2.8 h <sup>v</sup>	(Zhao et al. 2016)	Not specified		$IO_3^-$ , I <sup>-</sup>	2.8 h <sup>vi</sup>	(Zhao et al. 2016)
MnO <sub>2</sub>	-	I <sub>2</sub> <sup>vii</sup>	-	(Allard et al. 2009)	Not specified		$IO_3^-$	-	(Allard et al. 2009)
S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	$8.0 \times 10^5$	I <sub>2</sub>	$8.7 \times 10^{-2}$ s	(House, 1962)	Negligible		$IO_3^-$ , I <sup>-</sup>	-	(Guan et al. 2017)
HSO <sub>5</sub> <sup>-</sup>	$1.4 \times 10^3$	HOI	49 – 63 s <sup>viii</sup>	(Lente et al. 2009)	112	$1.7 \times 10^6$	$IO_3^-$ <sup>viii</sup>	88 s	(Li et al. 2017)
	$1.1 \times 10^3$			(Li et al. 2017)					

1982  
1983  
1984  
1985

SO <sub>5</sub> <sup>2-</sup>	2.2 x 10 <sup>2</sup> 3.0 x 10 <sup>2</sup>			(Li et al. 2017) (Lente et al. 2009)	≈ 0	1.5 x 10 <sup>5</sup>			
H <sub>2</sub> O <sub>2</sub>	0.011	HOI	2.4 - 58 months <sup>ix</sup>	(Milenković and Stanisavljev, 2012)	29	-	I <sup>-</sup>	0.25 - 13 s <sup>ix</sup>	(Shin et al. 2020)
HO <sub>2</sub> <sup>-</sup>		-			3.1 x 10 <sup>8</sup>	6.4 x 10 <sup>7</sup>			(Riffault et al., 2005)
•OH	1.1 x 10 <sup>10</sup>	HOI•• I <sub>2</sub> ••	6.3 X 10 <sup>-6</sup> s	(Buxton et al., 1988)	4.7 x 10 <sup>8</sup> 3.0 x 10 <sup>9</sup>		-		(Hammaecher et al., 2011)
SO <sub>4</sub> ••	unknown	HOI / I <sub>2</sub>	-	(Wang et al. 2017)	Not specified		IO <sub>3</sub> <sup>-</sup>	-	(Wang et al. 2017)
Peracetic acid	422	HOI	164 s	(Awad et al. 2003)	-		-	-	-

<sup>i</sup> Calculated using pK<sub>a</sub> (HOCl/OCl<sup>-</sup>) = 7.53 (Martell 1976); <sup>ii</sup> Calculated using pK<sub>a</sub> (HOBr/OBr<sup>-</sup>) = 8.8 (Haag and Hoigné 1983); <sup>iii</sup> catalytic process not included (Kern and Kim 1965); <sup>iv</sup> Calculated using pK<sub>a</sub> (HFe<sup>VI</sup>O<sub>4</sub><sup>-</sup>/Fe<sup>VI</sup>O<sub>4</sub><sup>2-</sup>) = 7.23 (Sharma 2011); <sup>v</sup> Calculated using k<sub>app</sub> = 7.0 M<sup>-1</sup>s<sup>-1</sup> (Zhao et al. 2016); <sup>vi</sup> Calculated using k<sub>app</sub> = 6.9 M<sup>-1</sup>s<sup>-1</sup> (Zhao et al. 2016); <sup>vii</sup> k<sub>app</sub> = 71 M<sup>-2</sup>s<sup>-1</sup> determined from (Allard et al. 2009); <sup>viii</sup> Calculated using pK<sub>a</sub> (HSO<sub>5</sub><sup>-</sup>/SO<sub>5</sub><sup>2-</sup>) = 9.3; <sup>ix</sup> Calculated using pK<sub>a</sub> (H<sub>2</sub>O<sub>2</sub>/HO<sub>2</sub><sup>-</sup>) = 11.6

1986

Table 2: Equilibria and kinetics of reactions for iodine speciation in oxidative water treatment processes

Eq. number	Equation	Equilibrium constant ( $K$ or $pK_a$ ) or rate constant ( $k$ )	References
16	$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$	$K = 3 \times 10^{-13} - 5.4 \times 10^{-13} M^2$	(Sigalla 1961)
17	$HOI \rightleftharpoons OI^- + H^+$	$pK_a = 10.4$	(Bichsel and von Gunten, 2000b)
18	$H_2OI^+ \rightleftharpoons HOI + H^+$	$pK_a = -0.3$	(Anslyn and Dougherty 2006)
19	$I^- + I_2 \rightleftharpoons I_3^-$	$K = 698 M^{-1}$	(Rose and Roberts 2019)
20	$HOI + Cl^- \rightleftharpoons ICl + H_2O$	$K = 22.4 \times 10^4 M^{-1}$	(Palmer et al. 1984)
21	$ICl + Cl^- \rightleftharpoons ICl_2^-$	$K = 77.6 M^{-1}$	(Rose and Roberts 2019)
22	$HOI + HOI \rightarrow IO_2^- + I^- + 2H^+$	$k = 0.3 \pm 0.2 M^{-1}s^{-1}$ $k = 25 M^{-1}s^{-1}$	(Bichsel and von Gunten, 2000b)
23	$HOI + OI^- \rightarrow IO_2^- + I^- + H^+$	$k = 15 \pm 2 M^{-1}s^{-1}$	(Schmitz 2004)
24	$HOI + IO_2^- \rightarrow IO_3^- + I^- + H^+$	Assumed to be fast	(Bichsel and von Gunten, 2000b)
25	$3 HOI \rightarrow IO_3^- + 2I^- + 3H^+$	Overall reaction of HOI disproportionation	

1987

1988

1989

Table 3: Summary of rate constants for hypoiodous acid reactions with various inorganic compounds.

Inorganic compounds	Rate constants	Main product	References
<i>Reactivity of HOI</i>			
$Br^- (+H^+)$	$3.3 \times 10^{12} M^{-2}s^{-1}$	$IBr$	(Troy et al., 1991)
$Cl^- (+H^+)$	$2.9 \times 10^{10} M^{-2}s^{-1}$	$ICl$	(Wang et al., 1989)
$H_2O_2$	$29 \pm 5 M^{-1}s^{-1}$	$I^-$	(Shin et al. 2020)
$HO_2^-$	$(3.1 \pm 0.3) \times 10^8 M^{-1}s^{-1}$	$I^-$	(Shin et al. 2020)
$I^-$	$5.0 \times 10^9 M^{-1}s^{-1}$	$I_2OH^-$	(Deane and Potter, 1985)
$S_2O_3^{2-}$	$(3.2 \pm 0.2) \times 10^{10} M^{-1}s^{-1}$ $(9.4 \pm 0.6) \times 10^9 M^{-1}s^{-1}$	$I^-$ $S_2O_3I^-$	(Varga et al. 2010)
$N_2H_5^+$	$4 \times 10^9 M^{-1}s^{-1}$	$I^-$	(Deane and Potter, 1985)
$H_3AsO_3$	$7.4 \times 10^8 M^{-1}s^{-1}$	$I^-$	(Chen et al., 2021)
<i>Reactivity of <math>IO^-</math></i>			
$HO_2^-$	$(6.4 \pm 1.4) \times 10^7 M^{-1}s^{-1}$	$I^-$	(Shin et al. 2020)

1990

1991

1992  
1993

Table 4: Species-specific or apparent second-order rate constants for the reactions of phenolic compounds or flavone with iodine

Compounds	second order rate constants (M <sup>-1</sup> s <sup>-1</sup> )				Reference
	$k_{\text{H}_2\text{OI}^+/\text{PhOH}}$	$k_{\text{HOI}/\text{PhOH}}$	$k_{\text{HOI}/\text{PhO}^-}$	$k_{\text{app}}$ (pH 7 or stated)	
p-chlorophenol	$(3 \pm 1) \times 10^3$	< 5	$(1.6 \pm 0.5) \times 10^5$	$6.0 \times 10^2$	(Bichsel and von Gunten, 2000a)
	$(2.4 \pm 0.6) \times 10^3$	< 5	$(1.3 \pm 0.5) \times 10^5$	$4.8 \times 10^2$	(Rose and Roberts, 2019)
	-	-	-	$(1.9 \pm 0.7) \times 10^3$	(Vikesland et al., 2013)
p-cresol	$(4.0 \pm 1.5) \times 10^4$	$(3 \pm 1) \times 10^2$	$(7 \pm 3) \times 10^8$	$3.8 \times 10^5$	(Bichsel and von Gunten, 2000a)
	$(4.5 \pm 1.6) \times 10^4$	$4 \times 10^2$	$9.9 \times 10^8$	$5.4 \times 10^5$	(Rose and Roberts, 2019)
p-cyanophenol	$(2 \pm 1) \times 10^2$	$1.5 \pm 0.5$	$(4 \pm 2) \times 10^2$	$5.0 \times 10^1$	(Bichsel and von Gunten, 2000a)
	$(3.1 \pm 1.1) \times 10^2$	$1.4 \pm 0.4$	$(3.3 \pm 0.4) \times 10^2$	$4.3 \times 10^1$	(Rose and Roberts, 2019)
p-iodophenol	$(4 \pm 1) \times 10^3$	$20 \pm 8$	$(1.5 \pm 0.8) \times 10^5$	$9.6 \times 10^2$	(Bichsel and von Gunten, 2000a)
	$(3.6 \pm 1.2) \times 10^3$	$21 \pm 7$	$(9.8 \pm 1.9) \times 10^4$	$6.5 \times 10^2$	(Rose and Roberts, 2019)
	-	-	-	$(9.5 \pm 0.6) \times 10^2$	(Vikesland et al., 2013)
p-methoxyphenol	$(5 \pm 1) \times 10^4$	< 100	$(7 \pm 2) \times 10^8$	$4.5 \times 10^5$	(Bichsel and von Gunten, 2000a)
	$(5.5 \pm 1.3) \times 10^4$	-	$(7.5 \pm 5.1) \times 10^8$	$4.7 \times 10^5$	(Rose and Roberts, 2019)
phenol	$(5 \pm 2) \times 10^4$	$(1.0 \pm 0.3) \times 10^2$	$(2 \pm 1) \times 10^6$	$2.1 \times 10^3$	(Bichsel and von Gunten, 2000a)
	$(7.2 \pm 2.9) \times 10^4$	$(1.1 \pm 0.3) \times 10^2$	$(1.8 \pm 0.2) \times 10^6$	$2.0 \times 10^3$	(Rose and Roberts, 2019)
	-	-	-	$(1.5 \pm 0.2) \times 10^3$	(Vikesland et al., 2013)
	-	-	-	$(2.1 \pm 0.2) \times 10^3$ (pH 8)	(Zhao et al. 2017)
	-	-	-	$(1.9 \pm 0.1) \times 10^3$	(Li et al. 2018a)
bisphenol A	-	-	-	$(8.7 \pm 0.5) \times 10^4$	(Li et al. 2018b)
bisphenol F	-	-	-	$(8.3 \pm 0.5) \times 10^3$	(Li et al. 2018b)
bisphenol S	-	-	-	$(6.4 \pm 0.3) \times 10^2$	(Li et al. 2018b)
o-bromophenol	-	-	-	$(4.8 \pm 0.4) \times 10^3$	(Li et al. 2018a)
m-bromophenol	-	-	-	$(1.54 \pm 0.09) \times 10^4$	(Li et al. 2018a)
p-bromophenol	-	-	-	$(4.0 \pm 0.3) \times 10^3$	(Li et al. 2018a)
flavone	-	-	-	$(2.5 \pm 0.2) \times 10^3$ (pH 8)	(Zhao et al. 2017)
p-hydroxybenzoic acid	-	-	-	$(7.8 \pm 0.1) \times 10^3$ (pH 8)	(Zhao et al. 2017)
	-	-	-	$(1.6 \pm 0.2) \times 10^3$	(Li et al. 2018a)
methylparaben	-	-	-	$(1.02 \pm 0.03) \times 10^3$	(Li et al. 2018a)
p-nitrophenol	-	-	-	$(2.6 \pm 0.4) \times 10^1$ (pH 8)	(Zhao et al. 2017)
phloroglucinol	-	-	-	$(3.1 \pm 0.5) \times 10^7$ (pH 8)	(Zhao et al. 2017)
resorcinol	-	-	-	$(4.2 \pm 0.3) \times 10^6$ (pH 8)	(Zhao et al. 2017)

1994  
1995

Table 5: Species-specific and apparent second-order rate constants for the reactions of various compounds containing divers functional groups with HOI.

Compounds	$k_{\text{H}_2\text{O}}$ (s <sup>-1</sup> )	$k_{\text{HO}}$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_{\text{HOI}}$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_{\text{app}}$ at pH 7 (M <sup>-1</sup> s <sup>-1</sup> )	References
acetaldehyde	$(9 \pm 1) \times 10^{-8}$	$(9.0 \pm 0.4) \times 10^{-1}$		$5.1 \times 10^{-6}$	(Bichsel and von Gunten, 2000a)
acetate	< $2 \times 10^{-10}$	< $3 \times 10^{-6}$		< $1 \times 10^{-8}$	
acetone	$(1.3 \pm 0.4) \times 10^{-8}$	$(2.5 \pm 0.3) \times 10^{-1}$		$7.2 \times 10^{-7}$	
allyl alcohol				≤ 1	(Zhao et al. 2017)
citric acid	-	-		< 1 (pH 8)	
dimethenamid			≤ $(9.07 \pm 1.95) \times 10^{-4}$		
glucosamine				< 1	(Bichsel and von Gunten, 2000a)
glycine				< 0.1	
oxalate				< 0.1	
3-oxopentanedioic acid	-	-		$(4.0 \pm 0.3) \times 10^3$	(Zhao et al. 2017)
pinacolone	$(4 \pm 2) \times 10^{-9}$	$(3.7 \pm 0.2) \times 10^{-2}$		$2.2 \times 10^{-7}$	

toluene				< 1	(Bichsel and von Gunten, 2000a)
---------	--	--	--	-----	---------------------------------

1996

1997

Table 6: Relative anticipated yields of I-DBPs for the main oxidants and under drinking water treatment conditions (excluding iodate which is a safe end-product).

1998

High I-DBP yields	Intermediate I-DBP yields	Low I-DBP yields
Chloramines Chlorine dioxide Persulfate	Permanganate Chlorine	Peroxymonosulfate Ozone Ferrate

1999