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

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Abstract

Iodine is a naturally-occurring halogen in natural waters generally present in concentrations between 0.5 and 100 µg 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 I^- to HOI is rapid for most oxidants (apparent second-order rate constant, $k_{app} > 10^3$ $M^{-1}s^{-1}$ 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 µg L^{-1}), and 18% of exhibit concentrations > 10 µg L^{-1}. The most frequently

detected I-THM is $CHCl_2I$ followed by 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

360 applying conditions to effectively mitigate formation of regulated THMs and HAAs would also limit the
361 occurrence of many other known or unknown unregulated DBPs (Krasner, 2009; Hrudey and
362 Charrois, 2012). However, an application of alternative disinfectants to chlorine to minimize the
363 formation of the regulated DBPs can favor the formation of potentially more toxic emerging DBPs,
364 including iodinated compounds and nitrogenous compounds such as nitrosamines (Krasner, 2009;
365 Dong et al. 2019). It has been demonstrated for all classes of halogenated DBPs, that iodine-containing
366 species (I-DBPs) are generally the most toxic (Gonsioroski et al., 2020; Wagner and Plewa, 2017),
367 followed by bromine-containing and chlorine-containing analogues (Krasner, 2012).
368 Iodinated trihalomethanes (I-THMs) were the first studied I-DBPs due to concerns about a strong
369 medicinal taste and odor in drinking water (Hansson et al., 1987) and have received more attention
370 subsequently to improve the understanding of their formation (Bichsel and von Gunten, 2000a;
371 Krasner et al., 2006; Hua and Reckhow, 2007a; Jones et al., 2012; Allard et al., 2015).
372 After presenting the different iodine sources in the environment, this review paper analyses oxidation
373 pathways of iodide and reactive iodine species by selected oxidants used in drinking water treatment
374 and assesses second-order rate constants of the corresponding reactions. The aqueous iodine
375 chemistry is presented to better understand the fate of iodide and the formation of iodinated
376 disinfection by-products in drinking water. The available second-order rate constants for the reactions
377 of iodine with inorganic and organic compounds are also presented and discussed.
378 The different factors influencing the formation of I-DBPs are discussed and a modeling is provided to
379 explain the interplay between bromide concentration and pH. An assessment of the occurrence of I-
380 DBPs worldwide and a risk assessment related to I-DBP formation and mitigation strategies complete
381 this review.

382 2. Iodine in atmospheric, aqueous and terrestrial natural systems

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

385 environment (Preedy et al., 2009). Iodine occurs naturally as the stable isotope (^{127}I) and the
386 radioisotope (^{129}I), additionally, eight other synthetic radioisotopes exist (Risher et al., 2004).
387 The global cycling of iodine is presented in detail by Fuge and Johnson (2015) in a review of the role
388 of iodine environmental geochemistry on human health. The following discussion of the iodine cycle
389 will mainly focus on its transport and its role for water resources used for drinking purposes.
390 *Figure 1*

391 **2.1 The marine environment: The largest compartment of available iodine**

392 Despite only representing about 1% of the total iodine (Preedy et al., 2009), the ocean is the largest
393 compartment of accessible iodine corresponding to an average concentration of between 45 and 60
394 µg L^{-1} (Risher et al., 2004). By contrast, chlorine and bromine have an average seawater concentration
395 of 19.4 g L^{-1} and 67 mg L^{-1} respectively (Millero et al., 2008). In the open ocean, more than 95% of the
396 dissolved iodine is present as inorganic iodine (mainly iodide and iodate) (Preedy et al., 2009; Fuge
397 and Johnson, 2015). Iodate, is the most abundant species, as it is the thermodynamically stable form
398 in oxygenated, alkaline seawater (Fuge, 2013). However surface and shallow shelf waters are enriched
399 in iodide (up to 50%) (Fuge, 2013; Preedy et al., 2009). This is a result of the conversion of stable
400 iodate to metastable iodide, through the action of phytoplankton, some macroalgae, and possibly
401 through some abiotic processes such as photolysis (Figure 1) (Fuge and Johnson, 2015). Once formed,
402 iodide is slowly re-oxidised to iodate (Fuge, 2013), after a first oxidation step of iodide to iodine,
403 mediated by iodide-oxidising bacteria, followed by spontaneous hydrolysis to HOI, which finally
404 disproportionates to iodate (Bichsel and von Gunten, 2000b; Amachi, 2008).
405 Volatile organo-iodine species such as CH_3I, CH_2I_2 and CH_2ClI can be formed through biological activity
406 (Amachi, 2008). From the knowledge based on aqueous chemistry of halogenation of organic matter
407 and considering the formation of HOI as the key reactant in cells, it would be expected that iodoform
408 (CHI_3) is the first product formed through the haloform reaction. Subsequently, this may lead to the
409 formation of CH_3I by dehalogenation. However, this mechanism has never been confirmed in living
410 organisms. Organoiodine compounds, mainly iodoform, may also be formed by HOI and I_2 – produced

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

413 **2.2 Atmospheric iodine chemistry**

414 All the volatilized compounds photodissociate rapidly in the atmosphere (Figure 1) – with a lifetime of
415 a few seconds for I_2 up to 10 days for CH_3I – to generate the iodine atom (Keppler et al. 2003; Sherwen
416 et al. 2016). Subsequently, iodine atoms react mainly with ozone in the lower atmosphere to generate
417 iodine monoxide ($IO^{\bullet}$) (Preedy V. R. et al., 2009). Iodine and iodinated compounds are then an
418 important ozone-depleting family especially in the global marine upper troposphere (Saiz-Lopez et
419 al., 2014). Different atmospheric species were characterized, *e. g.*, OIO, I_2O_2, HOI, $IONO_2$, I_2O_2, I_2O_3,
420 I_2O_4 and I_2O_5. Polymerisation of oxides could also lead to the production of iodine oxide particles (IOPs)
421 (Figure 1) (Preedy V. R. et al., 2009). Iodine is transferred to the land surface through wet and dry
422 deposition (Risher et al., 2004). The iodine content of rainwater is usually in the range 0.5 to 2.5 µg L^{-}
423 ^{1} (Fuge and Johnson, 2015). Rainwater concentrations of iodine are higher near the coast, wherefore,
424 soils in the coastal zone are subjected to a greater input of iodine (Fuge and Johnson, 2015). However
425 further inland, there is apparently no significant correlation between the iodine content in the soil and
426 the distance from the sea because this also depends on total annual rainfall (Johnson, 2003). Over the
427 sea or along the coast, iodate has been found as the dominant species in several studies (Hou et al.,
428 2009; Truesdalea and Jones, 1996), whereas further inland, organo-iodine can become the most
429 dominant fraction, with lower fractions of iodate than iodide (Gilfedder et al., 2007).

430 **2.3 Iodine in soil**

431 In comprehensive worldwide databases of published iodine analysis, iodine concentrations varied from
432 < 0.1 to up to 660 mg kg^{-1}, with a median at 3 mg kg^{-1} (Johnson, 2003; Smyth and Johnson, 2011).
433 The input of iodine to soil occurs predominantly through transfer from the atmosphere (Risher J. et al.,
434 2004). The input of iodine to soil also occurs through weathering of recent marine sediments or
435 through the decay of vegetation or animals. Soil iodine is mainly in an organic form with variable
436 fractions of iodate and iodide (Fuge and Johnson, 2015). After transfer from the atmosphere,

437 dissolved inorganic iodine is rapidly transformed to organic forms – through abiotic or biotic processes
438 (Seki et al., 2013; Yamaguchi et al., 2010). For example, MnO_2 has been found to oxidise I^- to I_2 and
439 then to iodate (IO_3^-) or iodinated organic compounds in the presence of humic substances (Gallard et
440 al., 2009). Organic-rich soils have the highest iodine fixation potential, especially peat soils, and humus
441 may constitute the primary reservoir of iodine. Other components such as iron(III)- and/or
442 aluminium(III)-(hydr)oxides and clay minerals also enhance the iodine fixation potential (Johnson,
443 2003; Fuge and Johnson, 2015), due to anion exchange processes on their positively charged surfaces
444 (Preedy et al., 2009).

445 **2.4 Iodine in fresh waters**

446 Most natural surface waters have total iodine concentrations between 0.5 and 100 µg L^{-1} and often
447 below 20 µg L^{-1} (Table S1). In 807 samples taken in rivers across Europe, iodide concentrations ranged
448 from < 0.01 to 104 µg L^{-1} with a quite low median concentration (0.33 µg L^{-1}) (Salminen et al., 2005).
449 Central continental and mountainous areas in particular tend to have lower concentrations, typically
450 in the range 0.1 to 18 µg L^{-1} (Salminen et al., 2005).
451 Compared to surface waters, groundwaters are generally more enriched in iodine with concentrations
452 generally below sea concentrations (*i.e.* < 60 µg L^{-1}). Iodine in groundwaters mainly originates from
453 breakdown of iodine-containing organic matter, leaching from marine sediments in slow-moving
454 aquifers, and evapo-concentration in arid areas (Fuge and Johnson, 2015). The main species of iodine
455 in groundwater is generally iodide with a small proportion of iodate (Tang et al., 2013), but in some
456 cases organic iodine can also be important (Zhang et al., 2013).
457 Nevertheless, iodine concentrations higher than in sea water were reported in a some drinking waters,
458 with iodine levels in the mg L^{-1} range (Tang et al., 2013; Zhang et al., 2013). 72% of 950 water samples
459 in the southwestern Taiyuan Basin, China had iodine concentrations > 150 µg L^{-1} (Tang et al., 2013).
460 The iodine content of surface waters is also influenced by anthropogenic activities. Wastewaters from
461 hydraulic fracturing are characterized by high chloride, bromide and iodide concentrations (≤ 56 mg L^{-}
462 ^{1}). They may impact drinking water utilities downstream from disposal or accidental spill sites

463 (Harkness et al., 2015). Additional iodine may originate from agricultural activities by application of
464 pesticides or herbicides containing methyl iodide or via fertilizers with trace levels of iodine (Moran et
465 al., 2002; Salminen et al., 2005). Another source of iodide to surface and groundwaters is the
466 discharge of persistent iodinated pollutants such as iodinated X-ray contrast media (ICM), which are a
467 class of pharmaceuticals used in the medical imaging of soft tissues. Due to poor removal through
468 conventional wastewater treatment – in some cases as low as 10% – ICM concentrations in surface
469 waters can exceed 1 µg L^{-1} (Schulz et al., 2008; Duirk et al., 2011; Xu et al., 2017) (Table S2).
470 In some cases, iodine may be added directly to water to make it drinkable and/or to relieve endemic
471 goitre in certain regions (Maberly et al., 1981; Vigneri et al., 1993; Smith et al., 2010). However,
472 salt iodization for iodine supplementation to iodine-deficient populations remains the most
473 appropriate and widespread measure to relieve endemic goitre (Eastman and Zimmermann, 2000;
474 Bürgi et al., 2001). Iodine-based disinfectants (iodine solutions or iodine resins) have been a popular
475 option for point-of-use drinking water disinfection by campers, the military, and rural consumers in
476 developing countries (Goodyer and Behrens, 2000; Smith et al., 2010). However, use of iodination
477 for full-scale water disinfection has been rare, due to the high cost of elemental iodine (Smith et al.,
478 2010). Therefore, this source will not be a major contribution to iodine in fresh water systems.
479

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

482 ## 3.1. Specific removal of iodide

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

488 halide removal – may also remove bromide and iodide before a disinfection step. It has been shown
489 that membrane processes such as reverse osmosis, nanofiltration, ion exchange membranes,
490 electrodialysis have good to excellent halide removal efficiencies – with reverse osmosis being the
491 most effective (Watson et al., 2012). Studies on bromide and/or iodide removal using adsorption
492 techniques (layered double hydroxides, silver impregnated activated carbons and carbon aerogels, ion-
493 exchange resins, aluminium coagulation) – some of which are used in drinking water treatment –
494 showed varied results, as their efficiency was mainly limited by interference from competing anions
495 and DOM present in water resources (Sánchez-Polo et al., 2006; Watson et al., 2012).
496

497 **3.2. Oxidation of iodide and iodine**

498 During oxidative water treatment, I^- is first oxidised to reactive iodine species (usually HOI) which can
499 further react with oxidants and/or organic matter (Figure 2). The specific reactivity of iodide and iodine
500 with the main oxidants used in water treatment is decribed in this section. The reactivity of several
501 other oxidants (Mn(VII), MnO_2, Fe(VI) as well as peroxides HSO_5^-, $S_2O_8^{2-}$, H_2O_2 and their activation
502 processes) has been recently reviewed (Li et al., 2020), wherefore, only kinetic information will be
503 presented here for these oxidants (Table 1). A compilation of all oxidation processes is provided in
504 Table 1 and Figure 2, including those, which are not discussed in detail in this publication.
505 Overall, the reactivity of oxidants towards iodide increases in the following order: MnO_2 < MnO_4^- <
506 ClO_2 < NH_2Cl < $HFeVIO_4^-$ < HOCl < O_3 < HOBr (Table 1 and Figure 2). The oxidation of I^- to HOI is rapid
507 for most oxidants (k_{app} > 10^3 $M^{-1}s^{-1}$ at pH 7), but relatively slow for permanganate and MnO_2. For
508 chlorination, chloramination, ozonation and permanganate, HOI is the initial oxidation product in
509 oxidative drinking water treatment. In the case of chlorine dioxide, ferrate, sulfate radicals, hydrogen
510 peroxide and UV treatment, iodine atoms are formed which then can undergo various follow-up
511 transformations (Ye et al., 2012; Zhang et al., 2015; Kralchevska et al., 2016).
512 The further reactivity of iodine with various oxidants is also discussed with second-order rate
513 constants, the main products and half-life times being summarized in Table 1. At neutral pH, the

514 oxidants can be divided into three groups: (i) HOCl, HOBr, NH_2Cl, O_3 and $S_2O_8^-$ for which the second-
515 order rate constants for the reactions with I^- are higher than those for HOI; (ii) HSO_5^- and MnO_4^-, which
516 have similar second-order rate constants for the reactions both with I^- and HOI and (iii) $HFeO_4^-$, which
517 is more reactive towards HOI than towards I^-. In the later case, electrostatic repulsion has been
518 hypothetized to explain this paradox (Shin et al., 2018). Within the first group, the differences in
519 reactivities are high. The half-life times of reactive iodine species such as HOI during oxidative
520 treatment will determine the extent of the formation of iodinated organic compounds (see Figure 2
521 and section 5.1).

522 *Figure 2*

523 *Table 1*

524 **3.2.1. Chlorine**

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

529 $$HOCl + I^- \rightarrow HOI + Cl^- \quad (1)$$

530 $$OCl^- + I^- \rightarrow OI^- + Cl^- \quad (2)$$

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

536 A further oxidation of HOI by chlorine occurs through a combination of second- and third-order
537 reactions (Bichsel and von Gunten, 1999). There are two hypothetical pathways for HOI oxidation by
538 HOCl: (i) The I-atom in HOI is attacked by the O-atom of HOCl, leading to iodite (IO_2^-) formation, which
539 is quickly further oxidised by HOCl to IO_3^-; (ii) HOI is attacked by the Cl-atom of HOCl leading to the
540 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 $HOI(ClOH)_2$ which would quickly hydrolyse to IO_3^- (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.

$$2\ HOCl + HOI \rightarrow IO_3^- + 2\ Cl^- + 3H^+ \quad (3)$$

$$2\ OCl^- + HOI \rightarrow IO_3^- + 2\ Cl^- + H^+ \quad (4)$$

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^- (pK_a ($HOBr/OBr^-$) = 8.8) formed from the reaction between chlorine and bromide (Heeb et al., 2014) are also able to oxidise I^- to HOI or OI^- (Table 1) through an analogous reaction pathway. The formation of iodate is accelerated due to the relatively high reactivity of HOBr and OBr^- with HOI/OI^- (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_4^-) 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_2Cl transforms I^- into HOI/OI^- within < 15 minutes under typical drinking water treatment conditions (Bichsel and von Gunten, 1999) (Table 1).

$$NH_2Cl + H^+ + I^- + H_2O \rightarrow HOI + Cl^- + NH_4^+ \quad (5)$$

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_3Cl^+ 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 ($k = 2.0 \times 10^{-3}$ $M^{-1}s^{-1}$) 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 $I\text{-}OOO^-$ (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 ($^{\bullet}OH$) can be neglected (Allard et al., 2013b).

$$I^- + O_3 \rightarrow OI^- + O_2 \qquad (6)$$

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 $\leqslant$ 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^- of 0.35 or 0.92 s, respectively for pH 9 and 6 and 1 $mgO_3\ L^{-1}$. 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).

$$3\ O_3 + I^- \rightarrow IO_3^- + 3\ O_2 \qquad (7)$$

3.2.4. Chlorine dioxide

The chlorine dioxide (ClO_2) 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_2 has been shown to form I-atoms ($I^\bullet$) and finally I_2 via electron-transfer reactions (Eq. (8); $k(ClO_2/I^-) = 1.87 \times 10^3\ M^{-1}\ s^{-1}$(Fabian and Gordon, 1997). A further redox reaction between ClO_2^- and I^- 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).

$$2\ ClO_2 + 2\ I^- \rightarrow 2\ ClO_2^- + I_2 \qquad (8)$$

$$ClO_2^- + 4\ I^- + 4\ H^+ \rightarrow 2\ I_2 + Cl^- + 2\ H_2O \qquad (9)$$

A significant portion of ClO_2 degrades to free available chlorine upon reaction with DOM (about 20-25% under drinking water treatment conditions) which can oxidize I^- 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_2 (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).

$$I^- + h\nu \rightleftharpoons (I^{-*}) \rightarrow (I^\bullet + e^-) \qquad (10)$$

In the absence of electron scavengers, the back reaction predominates (Rahn, 1997). Enhancement of photoxidation 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 ($HOI^{-\bullet}$) which decomposes to $I^\bullet$ and HO^- or further reacts with iodide to a $I_2^{-\bullet}$ 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 10^8 to 3 x 10^9 M^{-1} s^{-1} (Hammaecher et al., 2011; Riffault et al., 2005). It is in the same order as the reactivity of $^\bullet OH$ with HOBr (2 x 10^9 M^{-1} 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^- ($k_{H2O2/HOI}$ = 9.8 $\times$ 10^3 $M^{-1}s^{-1}$), 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 ($SO_4^{-\bullet}$) 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).

645 **3.2.6. Fate of other iodine sources**

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

651 Chlorine poorly reacts with ICM, with iopamidol having the highest reactivity (*k*(HOCl + iopamidol) =
652 1.5 x 10^{-2} - 1.66 x 10^{-3} $M^{-1}s^{-1}$ and *k*(OCl^- + iopamidol) = 0.45 - 0.94 $M^{-1}s^{-1}$ (Wendel et al., 2014; Tian et
653 al. 2017a), releasing iodine at slightly alkaline pH (Duirk et al., 2011; Wendel et al., 2014).
654 Monochloramine does not degrade ICM (Duirk et al., 2011; Wendel et al., 2014). During ozonation
655 several ICM (iopamidol, iopromide, iomeprol, diatrizoate) are partially oxidized, mainly by the
656 secondarily formed hydroxyl radicals (Ternes et al., 2003). However, most studies used very high ozone
657 doses (10-16 mg L^{-1}) and degradation is not complete under more typical ozonation conditions (Huber
658 et al., 2005, 2003; Kovalova et al., 2013; Magdeburg et al., 2014; Ning and Graham, 2008; Ternes et al.,
659 2003). ICMs such as diatrizoate have also been reported to be degraded by zerovalent iron under
660 aerobic conditions (Stieber et al., 2011; Zhou et al., 2019) and by sulfate radicals (Hu et al., 2017; Wang
661 et al., 2019).

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

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

668 # 4. Aqueous iodine chemistry

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

672 **4.1. Speciation of aqueous iodine**

673 Once formed, HOI is in equilibrium with I_2, OI−, I_3^- and H_2OI^+ as described by Eqs. (11-13) (Table 2). At
674 low pH, I2 is the dominant species (Figure 3). At high pH, HOI dissociates to OI^- with a pKa = 10.4 ± 0.1
675 (Bichsel and von Gunten, 2000b). A pKa-value of 10.64 has been published by extrapolation to zero
676 ionic strength (Schmitz, 2004). Therefore, under typical drinking water conditions, HOI is the major
677 species and OI^- is less significant.

678 *Figure 3*
679 *Table 2:*
680
681 I_2 is in equilibrium with I_3^- and polyiodide anions, which is controlled by the iodide concentration (Eq.
682 14 in Table 2 and Figure S1). ICl (Eqs. 15-16, Table 2) has also been reported to be an important
683 iodinating agent in Cl^--rich waters (Rose and Roberts, 2019).
684

685 **4.2. Disproportionation of hypoiodous acid**

686 The disproportionation of HOI eventually leads to iodate formation (Eqs. 17-20, Table 2), with reactions
687 (17) and (18) being rate-determining. The disproportionation of HOI is catalysed by buffers such as
688 phosphate, borate or acetate and dominates the kinetics of HOI disproportionation (Bichsel and von
689 Gunten, 2000b; Opoku-Agyeman, 2010). A value of k = 0.3 M^{-1} s^{-1} has been proposed (Table 2) for Eq.
690 (17) in absence of buffers (Bichsel and von Gunten, 2000b). The value of Schmitz (2004) k= 25 M^{-1} s^{-1}
691 has been determined in presence of at least 5 x 10^{-2} M of perchloric acid which could be sufficient to
692 catalyse the disproportion reaction. The rate constants range from 50 to 5000 M^{-2} s^{-1} for the buffer
693 catalysed reaction (Bichsel and von Gunten, 2000b).
694 The overall reaction (Eq. (20)) remains very slow under typical drinking water conditions (pH 6-8, 0-5
695 mM carbonate, 1-10 µg L^{-1} iodine), with an initial half-life of HOI ranging from a few days to years.

696 Therefore, IO_3^- formation by this pathway is of minor importance during drinking water treatment
697 (Bichsel and von Gunten, 2000b). Ferrate and permanganate have been shown to catalyse the
698 disproportionation of HOI (at pH > 9 for ferrate (Shin et al., 2020) and pH > 8 for permanganate (Zhao
699 et al., 2017). Thus, the fate of iodine will depend on different parameters such as the reaction of HOI
700 with inorganic and organic compounds as well as the applied oxidants or reductants (*e.g.*, MnO_4^-, FeO_4^{2-}
701 H_2O_2).
702

703 **4.3. Hypoiodous acid reactivity with inorganic compounds**

704 Table 3 summarizes the published rate constants for reactions of iodine with inorganic compounds.
705 Unlike HOCl and HOBr, HOI is unreactive toward NH_3 (Bichsel and von Gunten, 1999). HOI/OI^- can
706 react with Cl^- and Br^- to form the intermediates ICl and IBr in a third-order reaction involving H^+, which
707 rapidly hydrolize back to HOI (2.4 x 10^6 s^{-1} and 8 x 10^5 s^{-1}, respectively) (Troy et al., 1991; Vogt et al.,
708 1999; Wang et al., 1989).
709 *Table 3*
710 Compared to HOCl or HOBr, the information on the HOI reactivity with inorganic compounds is scarce
711 (Deborde M. and von Gunten, U., 2008; Heeb et al., 2014). In particular, no rate constants are available
712 for the reactions with metals and metalloids of interest such as iron (Fe(II)) and manganese (Mn(II)),
713 or with other anions such as sulfite, cyanide, nitrite and thiocyanate. According to the literature, HOI
714 reaction with sulfite proceeds rapidly, forming sulfate and releasing iodide (Morgan, 1954). The
715 second-order rate constants for the reactions of HOI with sulfite and hydrogen sulfite were assumed
716 to be > 10^9 $M^{-1}s^{-1}$ (Pechtl et al., 2007; Xu, 2014).
717 Hydrogen peroxide has been shown to reduce HOI while it is able to oxidise I^-. These reactions
718 constitute one of the first oscillating reaction (Bray−Liebhafsky) described in literature (Bray, 1921).

719 **4.4. Hypoiodous acid reactivity with organic compounds**

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

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

726 *Table 4*

727

728 **4.4.1. Phenolic compounds**

729 Free iodine reacts with phenolic compounds via (i) electrophilic aromatic substitution (Wang et al.,
730 2017), or via (ii) electron transfer, leading to the formation of benzoquinones (Zhao et al., 2017). The
731 apparent second-order rate constants for the reactions of iodine with phenolic compounds (Table 4)
732 are pH-dependent (Bichsel and von Gunten, 2000a). The contribution of each reaction to the overall
733 reactivity is illustrated in Figure 4. Similarly to chlorine and bromine (Criquet et al., 2015), the
734 reactivity of iodine with phenolic compounds is high and is dominated by the reaction between
735 HOI and the phenolate (Eq. (24)) at circum neutral pH (Figure 4) with species-specific rate constants ≤
736 10^8 M^{-1} s^{-1} (Table 4). The reaction rate is minimal at pH 3 to 5 and increases to a maximum at the
737 mean of the pK_a values of phenol/phenolate and HOI/IO^- (*i.e.,* usually around pH 10). In this range,
738 the apparent second-order rate constant increases by a factor of 10 per pH unit increase (Bichsel
739 and von Gunten, 2000a). The apparent second-order rate constants also increase for pH below 3.
740 This was attributed to the reactivity of H_2OI^+ towards phenols (Eq. (21)) (Bichsel and von Gunten,
741 2000a; Rose and Roberts, 2019). Rose and Roberts (2019) introduced the additional reaction
742 between H_2OI^+ and the phenolate (Eq. (22)) in their modeling as it involves both the nucleophile
743 (H_2OI^+) and the electrophile (phenolate). This reaction shows a similar contribution to the reaction
744 between HOI and phenol and explains the differences observed between the apparent rate constant
745 calculation from pH 3 to 5 (Figure 4). However, the consideration of this fast reaction for the
746 determination of the other second-order rate constants does not modify substantially the
747 second-order rate constants of reactions 23 and 24 (Table 4) (Rose and Roberts, 2019) nor the
748 maximum pH (Figure 4).

749 H_2OI^+ + (substituted)phenol → products (21)

750 H_2OI^+ + (substituted)phenolate → products (22)

751 HOI + (substituted)phenol → products (23)

752 HOI + (substituted)phenolate → products (24)

753 A comparison of the species-specific second-order rate constants clearly shows the following trend:
754 $k_{HOI/PhO^-} > k_{H2OI+/PhOH} > k_{HOI/PhOH}$. The higher reactivity of H_2OI^+ compared to HOI towards phenol can be
755 explained by the higher electrophilicity of H_2OI^+ 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 $k(HOI/PhO^-)$ was estimated neglecting the other reactions and considering the
769 fraction of the phenolate species from its 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 $k(HOI/PhO^-)$ 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

775 could not be neglected in these cases. Thus, these compounds have been excluded from the
776 regression.
777 The slope obtained (-6.2) for the species-specific second-order rate constant $k_{HOI/phenolate}$ as a function
778 of the Hammett constant (σ) is lower than in a previous study (-7.0 (Lee et al., 2005)). Nevertheless,
779 the reactivity of HOI is more impacted by substituent moieties than for chlorine or bromine which
780 exibit similar and lower slopes (-3.0 and -3.5, respectively (Heeb et al., 2014)) (Figure 5).
781 The order of reactivity observed HOBr > HOI > HOCl is somehow not logical. Based on electronegativity
782 of halogens (Cl: 3.16; Br: 2.96; I: 2.66) the polarisation of the O-X bound increases from chlorine to
783 iodine. Then HOI, based on this aspect, should exhibit the highest reactivity. The steric hindrance due
784 to the bigger size of iodine atom could be affect its reactivity, however, the second-order rate
785 constants of o-, m- and p-bromophenols do not support this hypothesis; o-bromophenol should be
786 more reactive compared to p-bromophenol (Figure 5 and Table 4) if steric hindrance was an important
787 factor. Iodine atom is known to be more polarisable than other halogens, this could be an important
788 aspect in the specific reactivity, modifying the relative strength of O-X bonds, making OH a better
789 leaving group in HOBr than HOI. Likely, this factor overrules the effect of the electronegativity such
790 that HOI has an intermediate reactivity between HOCl and HOBr.
791 *Figure 5*
792 **4.4.2. Ketones and carboxylic acids**
793 Similarly to chlorine and bromine, the stoichiometry of the reaction between HOI and carbonyl
794 compounds is 3 to form a triiodomethyl group. At neutral pH, the enolization step is rate-determining
795 and the overall reaction depends only on the carbonyl concentration and the pH and not on the
796 concentration of HOI (Table 5). The triiodocarbonyl compound then hydrolyses with the formation of
797 CHI_3 and the corresponding carboxylic acid (RCOOH) (Bichsel and von Gunten, 2000a). The enolization
798 step is catalysed by OH^- and H_2O, and therefore, the rate of HOI consumption includes two rate
799 constants k_{H_2O} and k_{OH^-} $[OH^-]$ which reflects the pH dependence (Bichsel and von Gunten, 2000a).

800 3-oxopentanedioic acid exhibits a substantial reactivity towards HOI with an apparent second-order
801 rate constant of 4×10^3 M^{-1} s^{-1} at pH 7 (Zhao et al., 2017). This ketone may exhibit a different
802 mechanism without the enol-formation. The reactivity of carboxylic acids is low, the apparent second-
803 order rate constant for the reaction of iodine with citric acid at pH 8 has been reported as < 1 $M^{-1}s^{-1}$
804 (Zhao et al., 2017).

805 *Table 5*

806 **4.4.3. Other compounds**

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

812 Besides phenols and carbonyl compounds, other organic model compounds (allyl alcohol,
813 glucosamine, glycine, toluene, and oxalate) were tested for their reactivity with HOI. The
814 corresponding second-order rate constants were < 1 M^{-1} s^{-1} or even < 0.1 M^{-1} s^{-1} (Bichsel and von
815 Gunten, 2000a). Moderately nucleophilic aromatic compounds like dimethenamid exhibit a low
816 reactivity towards HOI (≤ (9.07 ± 1.95) × 10^{-4} M^{-1} s^{-1}), wherefore, in this case, the reactivity with H_2OI^+
817 ((6.53 ± 0.10) × 10^6 M^{-1} s^{-1}) is predominant under typical drinking water conditions (Rose and Roberts,
818 2019).

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

820 ## 5.1. Role of oxidant type/dose and residence time

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

826 concern when treating iodide-containing waters. In contrast, iodate has been shown to be a major sink
827 for iodide during ozonation, treatment with ferrate and peroxymonosulfate (Table 1). Overall, the yield
828 of iodinated DBPs for the main oxidants for typical water treatment conditions generally follows the
829 pattern summarized in Table 6.
830 In addition to the oxidant type also the oxidant dose needs to be considered. Low free chlorine residual
831 concentrations leads to higher organic I-DBPs concentrations (Ioannou et al., 2016) and higher doses
832 of chlorine reduce the formation of organic I-DBPs (Hua et al. 2006). Several studies have reported
833 that high residence times in distribution systems lead to higher organic I-DBPs concentrations in
834 chlorinated or chloraminated waters (Ioannou et al., 2016; Serrano et al., 2015).
835 *Table 6*

836 **5.2. Role of total iodine/iodide and bromide concentrations**

837 Generally, higher iodide concentrations are associated with higher concentrations and numbers of
838 organic I-DBPs during oxidation processes. This has been shown in several occurrence (Parsons et al.,
839 2009; Richardson et al., 2008) and laboratory studies (Bichsel and von Gunten, 2000a; Jones et al.,
840 2012; Kristiana et al., 2009; Zhang et al., 2015). A linear relationship has been established between I-
841 THM formation and iodide content (Parsons et al., 2009) but this could not be generalized (Postigo et
842 al., 2017; Richardson et al., 2008). (MacKeown et al., 2021) showed a linear correlation for low iodide
843 concentrations (< 8 µg L^{-1}), which was not observed anymore for higher iodide contents. For
844 chlorination at typical chlorine doses of 1-3 mg L^{-1}, 20% of the iodide was incorporated in organic I-
845 DBPs at pH < 8 in one study (Dillon et al., 2015). A similar trend of iodine and bromine incorporation
846 has been observed in other studies, ranging from 10 to 40% of halogen bound to DOM (Criquet et al.,
847 2015; Hua et al., 2006; Zhao et al., 2017). In some cases, even low levels of iodide (≤ 1 µg L^{-1}) can yield
848 measurable levels of organic I-DBPs (MacKeown et al., 2020; Richardson et al., 2008).
849 The formation of I-DBPs was also related to the presence of ICMs in source waters (Duirk et al., 2011;
850 Tugulea et al., 2018). MacKeown et al. (2020) showed a higher iodate formation after chlorination than
851 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 µg 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 ($k(HOBr/OI^-) = 1.9 \times 10^6\ M^{-1}\ s^{-1}$ and $k(OBr^-/OI^-) = 1.8 \times 10^3\ M^{-1}\ s^{-1}$) are much higher than the corresponding rate constants for chlorine ($k(HOCl/OI^-) = 8.2\ M^{-1}\ s^{-1}$ and $k(OCl^-/HOI) = 52\ M^{-1}\ s^{-1}$, 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 $CHCl_2I$ 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 $CHBr_2I$ 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 NHBrCl which may lead to more brominated precursors than NH_2Cl (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

904 and leaving less chlorine available for oxidation of HOI to iodate (Allard et al., 2015; Zhang et al.,
905 2016b). Considering the oxidation state of DOM, its partial pre-oxidation could change the production
906 of DBPs. This has been shown in the case of UV/H_2O_2 pretreatment before chloramination for which
907 the production of I-THM increased, due to the partial oxidation of the DOM, lowering its aromatic
908 structure and forming small molecular weight DOM fractions (Zhang et al., 2018).

909 **5.4. Role of pH**

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

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

920 Several studies reported that during chloramination the formation of I-THMs increases with increasing
921 pH in the pH range 6-8.5 for source waters spiked with either iodide or iopamidol (Duirk et al., 2011)
922 while TOI remained stable (Hua and Reckhow, 2008). However, only iodoform has been shown to
923 increase with a pH increase, while mixed Cl-Br-I-DBPs decreased (Wang et al., 2014; J. Zhang et al.,
924 2016b). The stability of monochloramine and the possible role of chlorine formed at lower pH has been
925 hypothetised to explain these results (Hua and Reckhow, 2008).

926 Finally, the pH also affects the stability of I-DBPs: similarly to TOCl or TOBr, TOI degradation – which
927 occurs faster than for TOBr and TOCl – increases with both increasing pH and temperature, notably
928 due to the dehalogenation of I-DBPs (Rahman, 2015; Abusallout et al., 2017). However, half–live
929 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 H_2OI^+ 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 moieities 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 µg L^{-1} of iodide has been assumed with bromide concentrations of up to 400 µg L^{-1} corresponding to a bromide:iodide molar ratio of ≤ 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

957 HOI to iodate by chlorine (note that 90% of iodide is converted either to iodate or bound to organic
958 matter for pH > 7.0 (Table S5)). At higher bromide levels, the competition of HOI with HOBr for phenolic
959 moieties leads to the formation of brominated phenolic compounds instead of iodinated compounds.
960 Therefore, the organic moieties become limiting and the residual HOI is either rapidly oxidised to
961 iodate by the residual HOBr, or when HOBr is depleted, slowly oxidised to iodate by HOCl.
962 As previously discussed (section 5.4), the optimal pH either for the formation of iodate or reaction with
963 phenolic moieties is > 9. However, the modeling shows that the decrease of pH favors the formation
964 of iodate, independently of the bromide level. For the selected conditions (DOC of 5 mgC/L and a
965 chlorine dose of 15 µM (*i.e.* about 1 $mgCl_2$/L, Figure 7a), pH ≤ 7.0 and [Br^-] ≥ 250 µg/L are needed for a
966 ≥ 50 % conversion of iodide to iodate.
967 Increasing chlorine doses relative to the phenolic moieties favors the formation of iodate. For example
968 at pH 7, the formation of iodate increases from 6 to 23% of the initial iodide concentration by
969 increasing the chlorine dose from 15 to 50 µM in the absence of bromide, and from 68 to 90% in
970 presence of 400 µg L^{-1} Br^-.
971

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

974 ## 6.1. Monitoring of individual I-DBPs

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

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

988 *Figure 8*

989 **6.1.1. Iodinated trihalomethanes (I-THMs)**

990 I-THMs are the main I-DBPs included in occurrence studies. The largest surveys focusing mainly on
991 chlorination were conducted in France (ANSES, 2018), China (Ding et al., 2013), Korea (Woo et al.,
992 2018), and Canada (Tugulea et al., 2018) and the largest focusing mainly on chloramination in the
993 US (Richardson et al., 2008). One third of the studies in literature show low levels of I-THMs (<1 µg L^{-1},
994 Figure S1 and Table S6), but a substantial number of studies showed larger concentrations of I-THMs,
995 with a third with concentrations between 1 and 5 µg L^{-1} and 18% of the studies showing concentrations
996 > 10 µg L^{-1}. The highest concentrations of I-THMs were found in North America and Pakistan, followed
997 by China and UK (Figure S2).

998 The most frequently quantified I-THMs are $CHCl_2I$ followed by CHBrClI (Table S6 and Figure S3) with
999 concentrations typically in the range 2 to 4 µg L^{-1}. In many laboratory studies on I-THM formation, CHI_3
1000 was found to be the major species. However, these studies were often conducted with low Br^-/I^- ratios
1001 and/or very high iodide concentrations, which favors the CHI_3 formation. In contrast, CHI_3 is the least
1002 occurring I-THM in most real water samples. Nevertheless, CHI_3 has been recently reported as the main
1003 I-THM in several distribution systems (Wei et al., 2013a; Tugulea et al., 2015, 2018), usually
1004 accompanied by high total I-THM concentrations. These waters had particularly high concentrations
1005 of iodide (20 -130 µg L^{-1}) and naturally occurring ammonium (0.6 to 3.3 mg L^{-1}). The concentration of
1006 I-THMs were shown to be higher than the regulated THMs in these particular waters.

1007 A tendency for higher I-THM concentrations during summer than during winter is generally observed
1008 (Parsons et al., 2009; Tugulea et al., 2018), which was related to rising iodide levels during summer in
1009 the different resources (surface and groundwaters). Weinberg et al. (2002), also showed some
1010 treatment plant-specific seasonal trends with more I-THMs formed in waters with higher
1011 temperatures. But the lack of data on iodide concentrations in most source waters makes it impossible
1012 to distinguish between possible seasonal effects in temperature and variations in iodide levels.
1013 A slight overall increase of I-THMs, limited compared to regulated THMs, has been observed in
1014 distribution systems either using chlorine or chloramines (Tugulea et al., 2018). A significant increase
1015 in the I-DBP concentrations can however be expected in distribution system, if iodide is not fully
1016 oxidized and/or already incorporated in the organic matrix during primary oxidation, especially
1017 considering a possible catalytic effect of pipe residues (Liu et al., 2014).
1018 Other iodinated halomethanes have also been detected (although not necessarily quantified) in water:
1019 chloroiodomethane was first reported in drinking water samples in the UK in the mid-1970's, but has
1020 not been often monitored since then (Rumsby et al., 2009). It has been reported both in chlorinated
1021 waters (Khan et al., 2018) and in laboratory chloraminated source waters (Postigo et al., 2016),
1022 Bromoiodomethane and diiodomethane were also identified in chloraminated water (Symons et al.,
1023 1998). The formation of iodinated mono or di-halomethanes is not possible based on the so-called
1024 haloform reaction involved in the formation of THMs. In this reaction the formation of a halomethane
1025 depends on three consecutive halogen incorporations at a methyl group in α-position of a ketone
1026 (Frimmel and Jahnel, 2003). The reactivity of the halogenated intermediate compound is increased by
1027 the presence of 1 or 2 halogens. In addition, the carbanion formed (X_3C^-) after hydrolysis is stabalized
1028 by the inductive effect of the halogens and constitutes a good leaving group. Mono- or di-halogenated
1029 compounds are typically formed from degradation of THMs or other compounds like HAAs by
1030 hydrolysis or biodegradation. Chloroiodomethane, bromoidomethane and diiodomethane have been
1031 identified as degradation products of I-THMs in spiked river water (Cancho et al., 2000).

1032 **6.1.2. Iodinated acids: haloacetic acids (I-HAAs) and others**

1033 In chlorinated and chloraminated drinking waters, four iodinated haloacetic acids (I-HAAs) were
1034 detected in different studies: (mono)iodoacetic acid (ICH_2CO_2H), chloroiodoacetic acid ($ClICHCO_2H$),
1035 bromoiodoacetic acid ($BrICHCO_2H$), and diiodoacetic acid (I_2CHCO_2H) (Plewa et al., 2004; Krasner et
1036 al., 2006; Richardson et al., 2008; Cuthbertson et al., 2020). The reported concentrations were in
1037 the low ng L^{-1} to low µg L^{-1} range with maximum concentrations of 1.7 µg L^{-1} for iodoacetic acid and
1038 approximately 0.5 µg L^{-1} for chloro- and bromoiodoacetic acid. So far, diiodoacetic acid has only been
1039 observed at < 1 ng L^{-1} in drinking waters. Triiodoacetic acid has been reported in several laboratory
1040 studies. However, tri-HAAs generally decompose very fast in drinking water at ambient temperature
1041 (Zhang and Minear, 2002), and it is unlikely to detect them in drinking water. The most frequently
1042 monitored I-HAA, until now, has been iodoacetic acid (ICH_2CO_2H) (Table S6). Other acids were
1043 identified in chloraminated drinking water in US nationwide DBP occurrence studies (Weinberg et al.,
1044 2002; Krasner et al., 2006) with concentrations < 1 µg L^{-1} for 23 drinking water treatment plants
1045 (Richardson et al., 2008)(Table S6). Another iodoacid, 3,5-diiodosalicylic acid was detected at
1046 concentrations in the 0.17-1.48 ng L^{-1} range in 9 tap waters in China (Hu et al. 2018a).

1047 **6.1.3. Other iodinated disinfection by-products**

1048 Among the 4 surveys that monitored iodinated haloacetonitriles (I-HANs) in drinking waters (Table S6),
1049 only Ding et al. (2013) detected iodoacetonitrile (0.2-4.2 µg L^{-1}) in only 4 out of 60 DWTPs applying
1050 chlorine in China. Considering acetamides, sampling of DWTPs showed that 3 out of 7 samples in China
1051 contained chloroiodoacetamide (<0.04 – 0.21 µg L^{-1}) and 3 out of 7 samples contained
1052 bromoiodoacetamide (<0.05 – 0.15 µg L^{-1}) (Chu et al., 2012).

1053 Iodobutanal was the first iodinated haloaldehyde (I-HAL) detected in a survey carried out in the US
1054 (Weinberg et al. 2002; Krasner et al. 2006). Subsequently, iodoacetaldehyde was detected at
1055 concentrations of 0.62 to 4.5 µg L^{-1} in 4 US drinking water treatment plants applying chloramination,
1056 even for iodide concentrations below the detection limit of 5 µg L^{-1} in the source waters (Jeong et al.,
1057 2015). While iodoacetaldehyde has not been further monitored in drinking water in other studies,

1058 disinfection experiments with river water have shown that its formation is possible during chlorination
1059 as well (Postigo et al. 2017).
1060 Various types of iodophenols have been quantified in tap water such as iodinated I-
1061 hydroxybenzaldehydes, I-hydroxybenzoic acids, and I-phenols (Wuilloud et al. 2003; Pan et al. 2016;
1062 Hu et al. 2018a). Their concentrations were < 1 ng L^{-1} in 18 Chinese tap waters (Pan et al. 2016; Hu
1063 et al. 2018a), except for 2,4-diiodo-6-nitrophenol, with a maximum concentration of 24 ng L^{-1} (Pan et
1064 al. 2016). Additionnally, 4 iodinated dipeptides (3-I-/3,5-di-I-Tyr-Ala and 3-I-/3,5-di-I-Tyr-Gly) have
1065 been identified in tap water samples (Huang et al., 2018).

1066 **6.2. Total (organic) iodine, Iodide, iodate and hypoiodous acid**

1067 Total iodine comprises of iodide, iodine, iodate and organic iodine for which inductively coupled
1068 plasma – mass spectrometry (ICP-MS) demonstrated superior sensitivity in comparison to other
1069 detection techniques (Tables S6-S8). However, considering the fate of iodine in water treatment,
1070 speciation is recommended. More than 60 methods for the determination of iodide and/or iodate by
1071 ion chromatography with various detection methods with detection limits that are often quite high for
1072 iodide, typically around 10 µg L^{-1}, and even higher for iodate (Table S7). A postcolumn reaction has
1073 been shown to lower the detection limits to 1 µg/L for iodate with high selectivity by a post-column
1074 reaction forming I_3^- which can be detected by a UV/Vis detector (Salhi and von Gunten, 1999;
1075 Weinberg and Yamada, 1998). Lately, HPLC or IC methods coupled to ICP-MS have been shown to be
1076 more sensitive, with detection limits of 0.2 µg L^{-1} (MacKeown et al., 2020) (Table S8). Other
1077 chromatographic techniques (Table S7) are time-consuming due to extensive sample pre-treatment,
1078 and suffer from possible interferences (Zhang et al. 2010) but they could be interesting for complex
1079 matrices such as seawater. Iodide specific electrodes were also developed, but they are not very
1080 sensitive (≥ 10 µg L^{-1}) (Criquet et al., 2012).
1081 Considering HOI, this species has been determined after reaction with phenol as the sum of o and p-
1082 iodophenol (Bichsel and von Gunten, 2000a; Shin et al., 2018). The DPD colorimetric method is also
1083 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 µg 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

1110 would help to develop and validate prediction models which would be useful for water utilities to
1111 estimate formation potentials for I-DBPs and improve the overall risk assessments.
1112

1113 7. Risk assessment and mitigation

1114 7.1. Toxicity of iodinated disinfection by-products and priorization

1115 Although toxicological evidence from *in vivo* assays and molecular epidemiology studies for I-DBPs is
1116 still lacking (Cortés and Marcos, 2018), different cytotoxicity and genototoxicity assays have been
1117 performed for various I-DBPs (Tables S10 and S11). Iodoacetic acid is the I-DBP which has been
1118 subjected to the highest number of different assays, allowing a comparison of hamster (CHO-AS52 and
1119 CHO-K1), mouse (NIH3T3, ovarian follicles), and human (HepG2, Caco-2, and CCD 841 CoN) cell lines
1120 (Table S10 and S11). The results show more than 2 orders of magnitude variability for cytotoxicity
1121 (Table S10), highlighting the difficulty in comparing different assays.
1122 A compilation of 103 DBPs providing the lowest cytotoxic concentrations, LC_{50} values (lethal
1123 concentration for 50% of a population), and other indices with CHO cells concluded that I-DBPs are
1124 more cytotoxic and genotoxic than their brominated and chlorinated analogues (Wagner and Plewa,
1125 2017). A more detailed discussion of the toxicity of each class of I-DBPs where the authors used
1126 mammalian cell cytotoxicity and genotoxicity data to provide a rank ordering of the relative toxicities
1127 is provided elsewhere (Dong et al., 2019).
1128 In contrast, iodate is considered non-toxic because it is quickly reduced *in vivo* to I^- and is therefore
1129 the desired sink for iodine during water treatment. In some countries it is even added to table salt as
1130 a prevention for goitre (Bürgi et al., 2001).
1131 To prioritize DBP classes, different methodologies have been proposed recently. A metric called "TIC-
1132 Tox" (Plewa et al., 2017) compares measured DBP concentrations – or semi-quantitative GC peak
1133 areas – weighted by metrics of toxic potency (cytotoxicity or genotoxicity index value) to determine
1134 chemical drivers of overall toxicity in water (Allard et al., 2015; Chuang et al., 2019; Dong et al., 2019;
1135 Jeong et al., 2012; Li and Mitch, 2018; Stalter et al., 2020). Based on this methodology,

1136 iodoacetaldehyde, iodoacetonitrile as well as iodoacetic acid could be important I-DBPs due to their
1137 high toxicities and significant concentrations (up to µg L^{-1} range). Iodophenols and iodoacetamides
1138 have reportedly high toxicites, especially the three iodoacetamides (iodoacetamide,
1139 bromoiodoacetamide, chloroiodoacetamide), however, only few occurences studies included these
1140 compounds and their concentration were far below the µg L^{-1} range (section 6.1).
1141 An indexing method based on 3 criteria (concentration level, reported frequency and toxicity) was also
1142 recently developed (Mian et al., 2018) to prioritize unregulated DBPs in three categories (*i.e.*, high,
1143 medium, and low priorities). The I-DBP group was categorized as low priority compared to other DBP
1144 classes, but, only iodoacetic acid and iodoform were considered. An earlier study (Hebert et al., 2010)
1145 gave scores to DBPs based on 4 criteria (toxicity, occurrence, US-EPA and/or IARC classification, and
1146 regulation). This procedure allowed the identification and ranking of three different groups of
1147 emerging DBPs: (i) moderate occurrence and high toxicity; (ii) moderate to elevated occurrence and
1148 relevant toxicity and (iii) low occurrence and unknown or little toxicity. From this study,
1149 dichloroidomethane and iodoacetonitrile were ranked in group (i) with compounds such nitrosamines
1150 or trichlorophenol, which are considered the most critical compounds. I-THMs as well as I-AAs and I-
1151 HAcAMs were categorized in group (ii) mainly due to their toxicity.
1152 There are some I-DBPs with no toxicity data as of yet, and more occurrence data is needed on I-DBPs
1153 in real drinking water systems to improve priorization of I-DBPs. Such priorization can provide useful
1154 information to develop control strategies to minimize human health risks resulting from the exposure
1155 of consumers to I-DBPs as compared to other DBPs, including the establishment of new drinking water
1156 standards.

1157 **7.2. Mitigation strategies**

1158 **7.2.1. Prevention of formation**

1159 Precursor abatement prior to disinfection is a common strategy for DBP minimisation, in that it non-
1160 specifically minimises all DBPs, both regulated and emerging (Watson et al., 2012). As DOM is the
1161 major precursor for the generation of organic DBPs, DOM removal prior to disinfection is an effective

1162 option. However, when focusing on I-DBPs, there may be also a need for iodide removal if more
1163 impaired water resources are used for drinking water production.
1164 Alternatively, the optimization of disinfection through the transformation of iodide to iodate, a safe
1165 iodine-derived end-product, has been proposed as a viable option. A pre-oxidation step with either
1166 ozone or ferrate(VI) before post-chlorination or especially post-chloramination to oxidize iodide to
1167 iodate is an efficient process to mitigate the formation of I-DBPs (Allard et al., 2013b, Zhang et al.,
1168 2016b, Wang et al., 2018, Jiang et al., 2019). Iodide oxidation by ozone is fast enough to avoid
1169 excessive formation of bromate, a regulated DBP linked to ozonation of bromide-containing waters
1170 (Allard et al., 2013b).
1171 Prechloration before chloramination also leads to a partial iodate formation, whereby reducing the
1172 subsequent formation of I-DBPs (Bichsel and von Gunten, 1999). Therefore, if chloramine is used as a
1173 disinfectant, it is recommended to increase free chlorine contact time before ammonia addition to
1174 reduce iodo-DBP formation (Richardson et al., 2008; Jones et al., 2011; Criquet et al., 2012; Allard
1175 et al., 2015). However, the formation of I-DBPs, and especially their speciation, in the pre-
1176 chlorination/post-chloramination process depends strongly on the concentration of bromide (Allard
1177 et al., 2015). It was demonstrated that pre-chlorination minimized iodoform formation, however,
1178 short pre-chlorination contact times form higher I-THM concentrations compared to pre-formed NH_2Cl
1179 due to a large increase in the formation of mixed Cl-Br-I-THM species (Jones et al., 2011; Criquet et
1180 al., 2012; Allard et al., 2015; Zhang et al., 2016b).
1181
1182 **7.2.2. Removal of I-DBPs after their formation**
1183 Activated carbon adsorption after pre- or intermediate chlorination or pre-chloramination in full-scale
1184 drinking water treatment plants has been shown to be beneficial to mitigate DBP concentrations in
1185 drinking waters (Cuthbertson et al., 2019, 2020; MacKeown et al., 2020). I-THMs showed particurlarly
1186 high removal efficiency in full-scale water treatment plants (Cancho et al., 2000; MacKeown et al.,
1187 2020). I-THMs were removed by 77 to 99 % (average of 3 campaigns for each compound), the efficiency

1188 increasing with the molecular weight and hydrophobicity of THMs. Iodoacetic acid had a removal
1189 efficiency > 90% in GAC filtration (around 20 000 bed volumes). The removal of these compounds was
1190 much more efficient than for the THM4 on the same filters (from 15 to 58%) (MacKeown et al., 2020).
1191 Cuthbertson et al. (2019; 2020) also demonstrated an overall decrease of TOI by (biological) activated
1192 carbon filtration and calculated geno- and cyto-toxicities. However, the assumptions were only based
1193 on a theoretical assessment of DBP related toxicities. Moreover, the assessment of different
1194 parameters such as GAC types, run time, age of filters and contact times would be needed to fully
1195 evaluate the potential of such a process.

1196 8. Conclusion

1197 The increasing demand on water resources will inevitably require increasing use of impaired water
1198 sources, containing higher concentrations of iodide/iodine especially in coastal areas. Reactive iodine
1199 species can be formed during oxidative water treatment of iodide-containing waters with various
1200 oxidants and they react with inorganic and organic compounds. HOI is generally the major reactive
1201 species for the reaction with dissolved organic matter. Iodine reactive species are similar to chlorine
1202 and bromine in terms of speciation, mechanism of reaction or binding to DOM. The few available
1203 second-order rate constants for the reactions of HOI with inorganic and organic compounds do not
1204 allow to draw final conclusions in terms of its reactivity, which however generally appears to be
1205 intermediate between chlorine and bromine. The largest difference consists of the further oxidation
1206 of HOI to iodate, which is a safe end-product for iodine. The formation of iodinated disinfection by-
1207 products is favored when the oxidant is not able to effectively oxidize HOI to iodate (mainly
1208 monochloramine). The incorporation of iodine depends strongly on the oxidant type, I^-, Br^- and DOM
1209 concentrations, DOM type, solution pH as well as on the ammonium concentration. Thus, disinfection
1210 practices intending to reduce THM4 levels may ultimately increase the formation of I-DBPs in the
1211 treated waters, especially in the case of chloramination. Enhanced detection methods will allow for
1212 detection of lower concentrations of I-DBPs in the sub ng L^{-1} range. Occurrence studies mainly detected
1213 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 exibit 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.

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Figure captions :

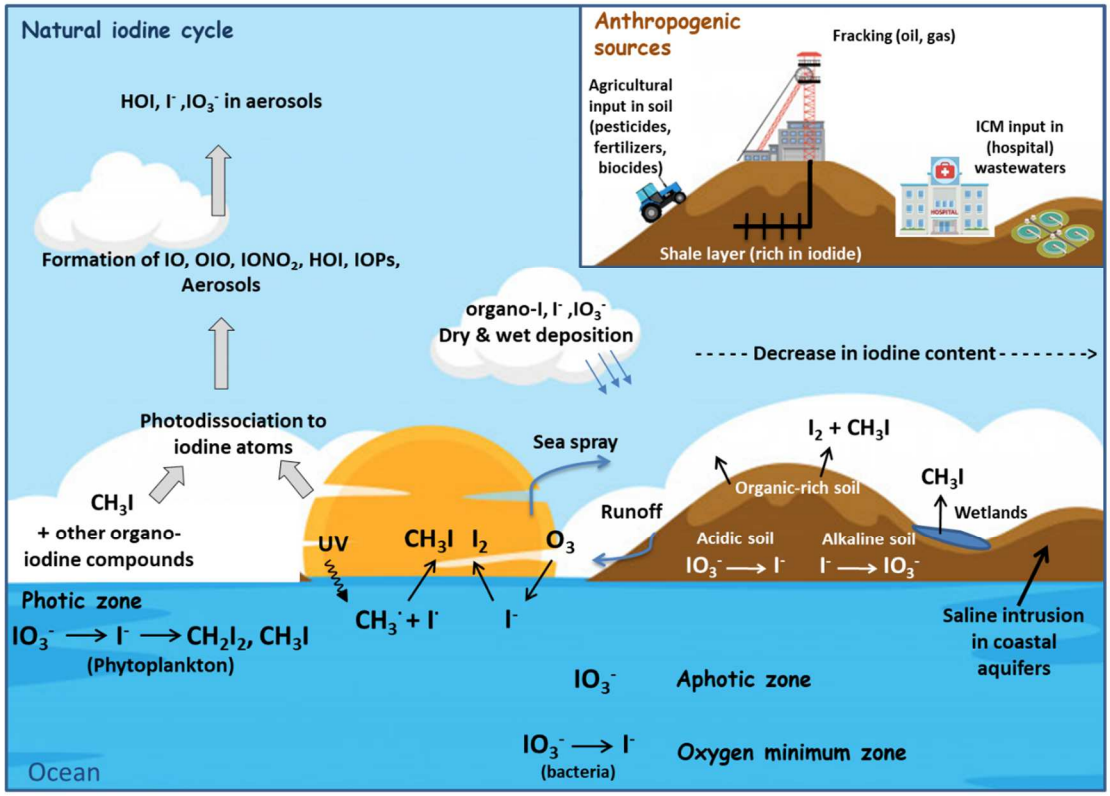

Figure 1: Schematic representation of the natural iodine cycle (adapted from Fuge and Johnson (2015) and Carpenter (2015)) and anthropogenic sources. ICM: iodinated contrast media; IOPs: iodine oxide particles; organo-I: organo-iodine.

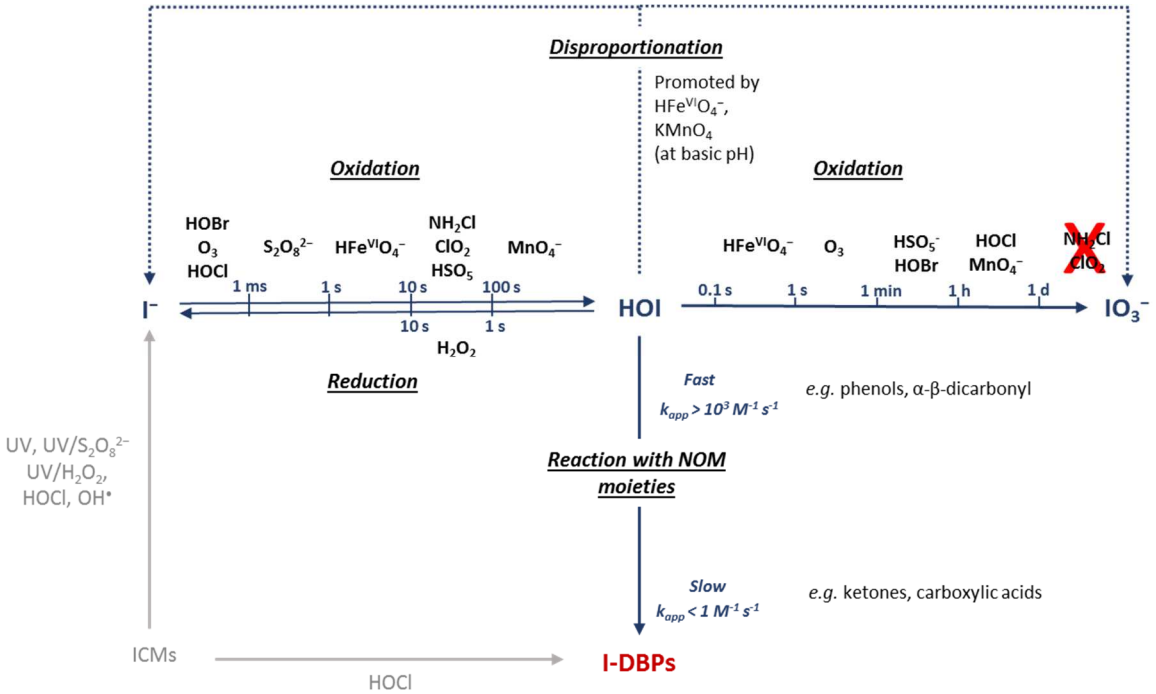

Figure 2: Scheme of the main reactions involving iodine-containing species in various oxidative processes. The indicated times are half-life times for oxidant/reductant concentrations of 10 µM (see Table 1).

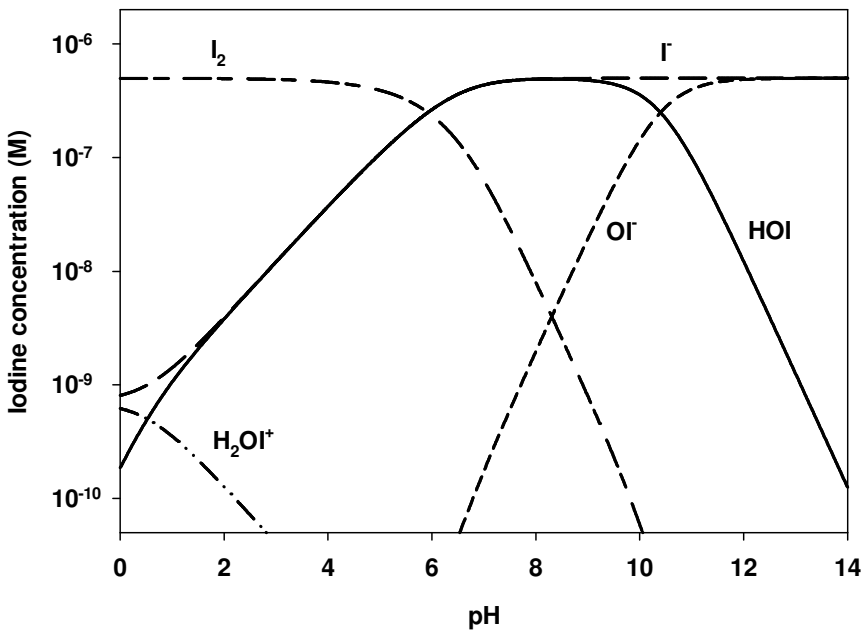

Figure 3: pH-dependent speciation of iodine (for a concentration of 1 µM I-). Calculations based on equilibria in Table 2.

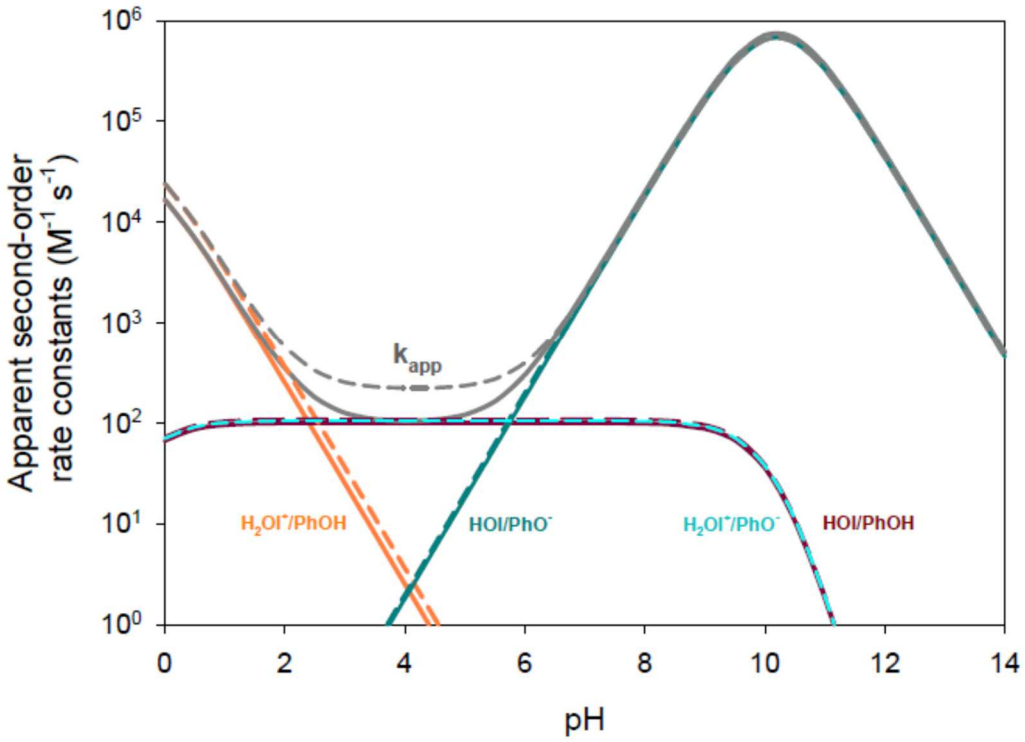

Figure 4: Apparent second order rate constants for the reactions of iodine with phenol as a function of pH. Solid lines considering reactions 21 and 23-24 using rate constants from (Bichsel and von Gunten, 2000a) (Table 4). Dashed lines considering reactions 21-24 using rate constants from (Rose and Roberts, 2019) (Table 4). pKa(H2OI+/HOI) = - 0.3 for both modelings. The contributions of each reaction are also shown as a function of the pH; apparent second-order rate constants calculated by multiplying the species specific second-order rate constant by the proportion of species for different pH.

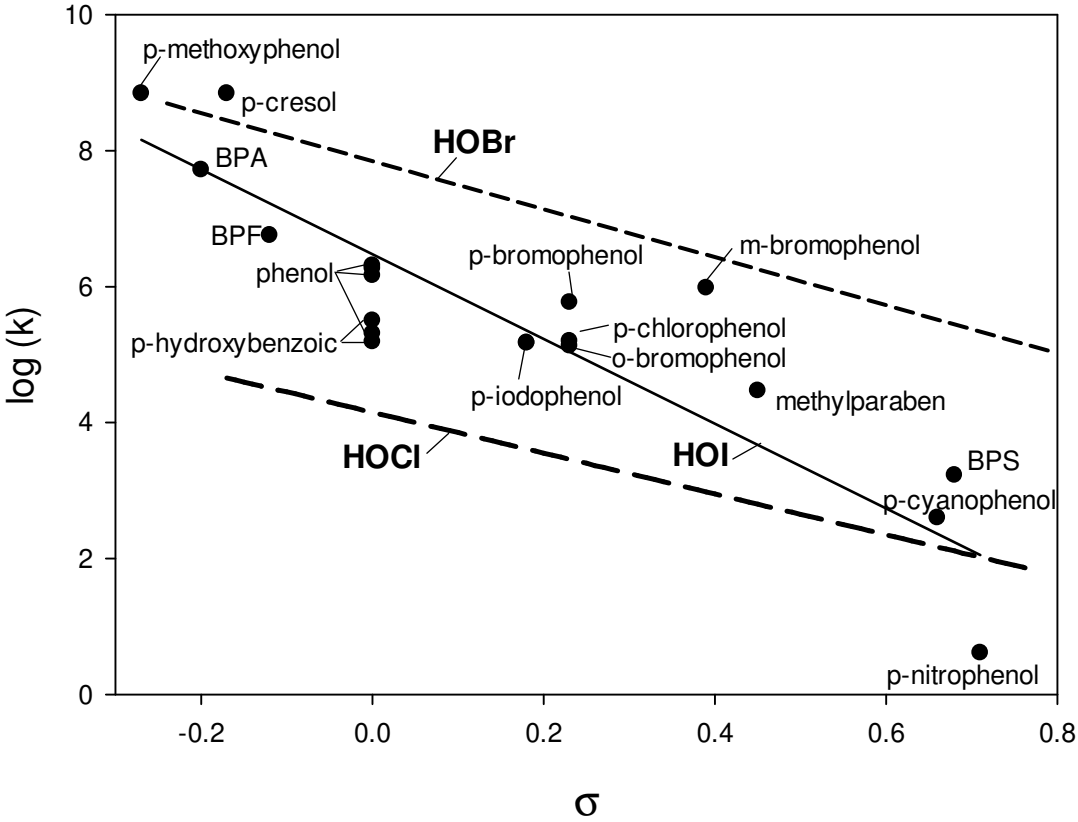

Figure 5: Correlation between the second-order rate constants (log (k)) for the reaction of HOI with dissociated phenols and the Hammett constant (sigma, σ) (Data in Table S3). Correlation log(kHOI/PhO-) = 6.5-6.2 ∑σ, R2 = 0.77. log(kHOBr/PhO-) = 7.8-3.5 ∑σ, R2 = 0.80 (Heeb et al., 2014); log(kHOCl/PhO-) = 4.15-3.0 ∑σ, R2 = 0.95 (Gallard and von Gunten, 2002).

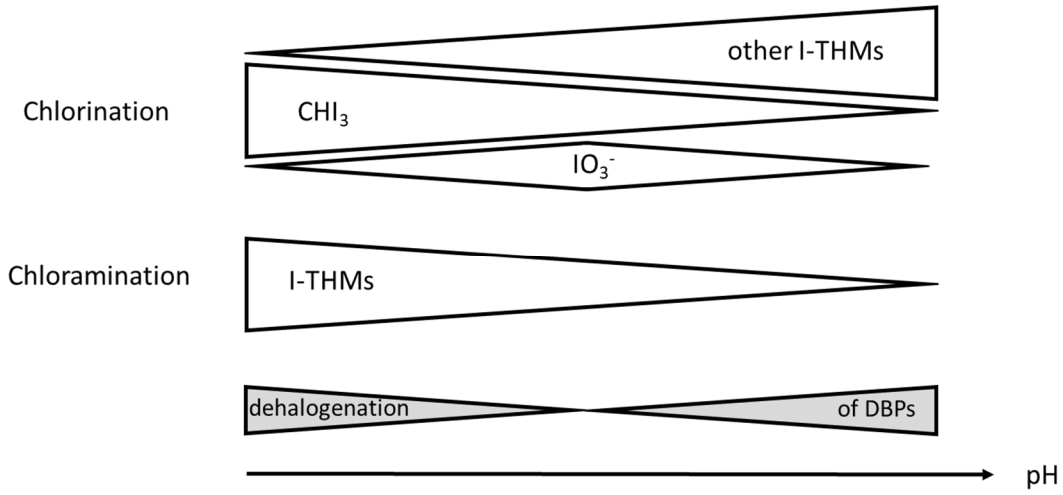

Figure 6. Shematic representation of the influence of pH on I-DBP and iodate formation during chlorination and chloramination and I-DBP dehalogenation.

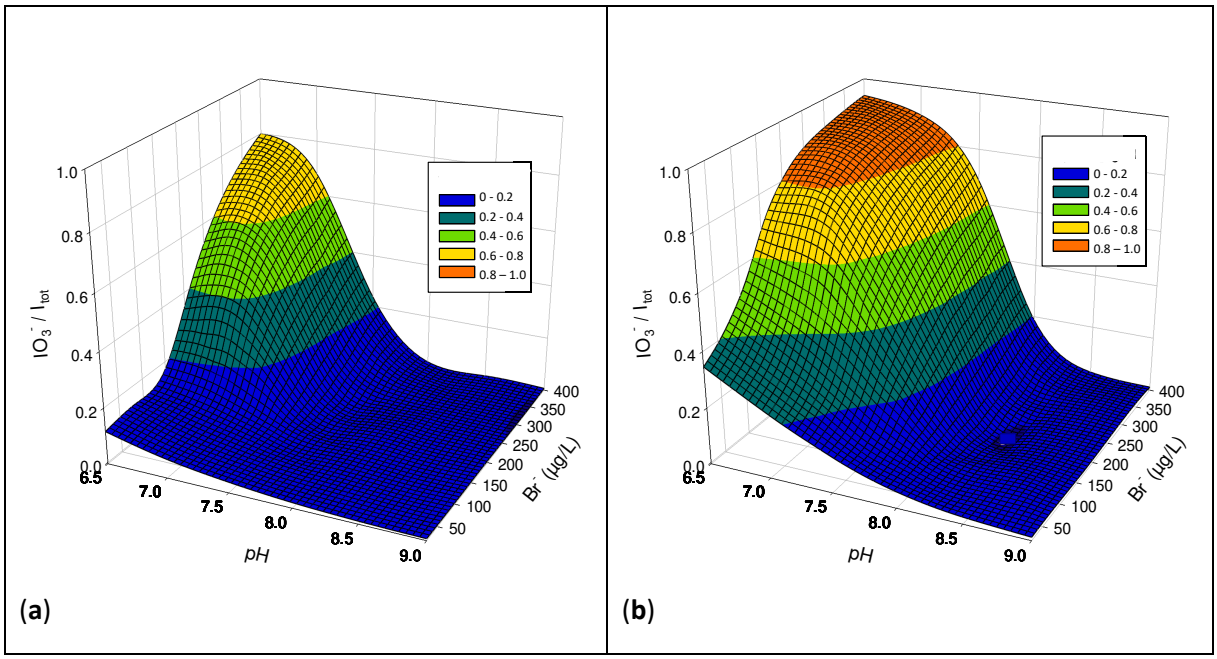

Figure 7: Modeling of the effect of pH and the bromide concentration on iodide speciation (IO3-/Itot) after chlorination of phenol-containing waters. The model run time was 4000 s, with initial concentrations of I– = 20 µg L-1 (0.16 µM), PhOH = 10 µM (so the number of fast reacting sites roughly matches the concentration of phenolic moieties in natural waters with 5 mgC L-1 of DOC (average of 2 mmol of phenolic moieties/gC in NOM extracts; (Önnby et al., 2018), (a) [HOCl]0= 15 µM, (b) [HOCl]0 =50 µM.

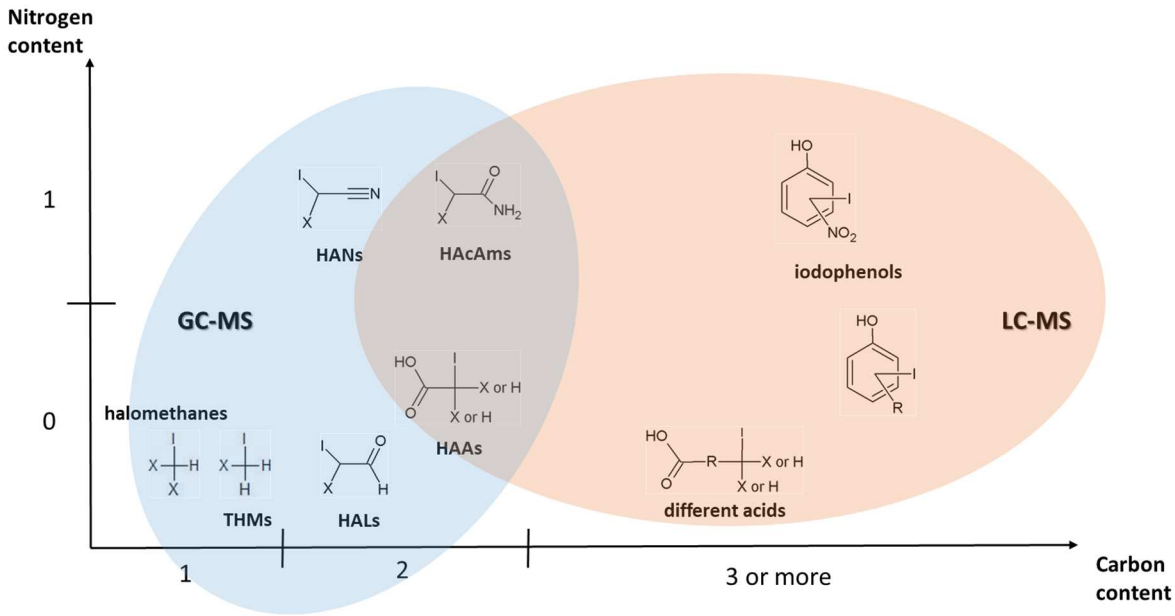

Figure 8: Main classes of I-DBPs analysed in previous studies as a function of carbon and nitrogen atom contents and the corresponding analytical methods.

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

	I^-				HOI/OI^-				
Oxidant	$k(I^-)$ ($M^{-1}s^{-1}$ unless otherwise stated)	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	4.3×10^8	HOI	2.1×10^{-4} s[i]	(Nagy et al. 1988)	8.2	-	IO_3^-	1.1 h	(Bichsel and von Gunten, 1999)
OCl^-	< 30			(Gerritsen and Margerum, 1990)	52	-			
HOBr	5.0×10^9	HOI	1.4×10^{-5} s[ii]	(Troy and Margerum 1991)	Not significant	1.9×10^6	IO_3^-	93 s[ii]	(Criquet et al., 2012)
OBr^-	6.8×10^5				-	1.8×10^3			
HOI (disproportionation)	-	-	-	-	0.3	15	IO_3^-	64 h	Bichsel (2000)
					0.6	9.3		32 h	(Opoku-Agyeman, 2010)
NH_2Cl	2.4×10^{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)
$NHCl_2$	9.3×10^5 $[H^+]$ $M^{-2}s^{-1}$	Unknown	8.6 d	(Kumar et al. 1986)	-	-	-	-	-
NCl_3	Higher than NH_2Cl and $NHCl_2$			(Kumar et al. 1986)					
O_3	1.2×10^9	HOI	5.8×10^{-5} s	(Liu et al. 2001)	3.6×10^4	1.6×10^6	IO_3^-	1.9 s	(Bichsel and von Gunten, 1999)
ClO_2	1.9×10^3	$I\cdot$	37 s	(Fabian and Gordon 1997)	-	-	-	-	-
ClO_2^-	$9.2\ 10^2$ $[H^+]$ $M^{-2}s^{-1}$	I_2	>1y[iii]	(Kern and Kim, 1965)					
$HClO_2$	5	IO^-							
$HFeO_4^-$	4.5×10^4	HOI	2.4 s[iv]	(Shin et al. 2018)	2.5×10^5	2.5×10^5	IO_3^-	0.3 s[iv]	(Shin et al. 2018)
	2.3×10^4	$I\cdot$ / $I_2^{\cdot-}$	4.8 s[iv]	(Kralchevska et al. 2016)	1.8×10^5	-		0.4 s[iv]	(Wang et al. 2018)
FeO_4^{2-}	-	-	-		7.7×10^3	-			
MnO_4^-	Not specified	HOI / I_2	2.8 h[v]	(Zhao et al. 2016)	Not specified		IO_3^-, I^-	2.8 h[vi]	(Zhao et al. 2016)
MnO_2	-	I_2[vii]	-	(Allard et al. 2009)	Not specified		IO_3^-	-	(Allard et al. 2009)
$S_2O_8^{2-}$	8.0×10^5	I_2	8.7×10^{-2} s	(House, 1962)	Negligible		IO_3^-, I^-	-	(Guan et al. 2017)
HSO_5^-	1.4×10^3	HOI	49 – 63 s [viii]	(Lente et al. 2009)	112	1.7×10^6	IO_3^- [viii]	88 s	(Li et al. 2017)
	1.1×10^3			(Li et al. 2017)					

SO_5^{2-}	2.2×10^2 3.0×10^2			(Li et al. 2017) (Lente et al. 2009)	≈ 0	1.5×10^5			
H_2O_2 HO_2^-	0.011	HOI -	2.4 - 58 months[ix]	(Milenković and Stanisavljev, 2012)	29 3.1×10^8	- 6.4×10^7	I^-	0.25 - 13 s[ix]	(Shin et al. 2020)
$^{\bullet}OH$	1.1×10^{10}	$HOI^{\bullet-}$ $I_2^{-\bullet}$	6.3×10^{-6} s	(Buxton et al., 1988)	4.7×10^8 3.0×10^9		-		(Riffault et al., 2005) (Hammaecher et al., 2011)
$SO_4^{-\bullet}$	unknown	HOI / I_2	-	(Wang et al. 2017)	Not specified		IO_3^-	-	(Wang et al. 2017)
Peracetic acid	422	HOI	164 s	(Awad et al. 2003)	-		-	-	-

[i] Calculated using pK_a ($HOCl/OCl^-$) = 7.53 (Martell 1976); [ii] Calculated using pK_a ($HOBr/OBr^-$) = 8.8 (Haag and Hoigné 1983); [iii] catalytic process not included (Kern and Kim 1965); [iv] Calculated using pK_a ($HFe^{VI}O_4^-/Fe^{VI}O_4^{2-}$) = 7.23 (Sharma 2011); [v] Calculated using k_{app} = 7.0 $M^{-1}s^{-1}$ (Zhao et al. 2016);[vi] Calculated using k_{app} = 6.9 $M^{-1}s^{-1}$ (Zhao et al. 2016); [vii] k_{app} = 71 $M^{-2}s^{-1}$ determined from (Allard et al. 2009); [viii] Calculated using pK_a (HSO_5^-/SO_5^{2-}) = 9.3; [ix] Calculated using pK_a (H_2O_2/HO_2^-) = 11.6

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) (Rose and Roberts 2019)
19	$I^- + I_2 \rightleftharpoons I_3^-$	$K = 698$ M^{-1}	(Palmer et al. 1984)
20	$HOI + Cl^- \rightleftharpoons ICl + H_2O$	$K = 22.4 \times 10^4$ M^{-1}	(Rose and Roberts 2019)
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)* (Schmitz 2004)
23	$HOI + OI^- \rightarrow IO_2^- + I^- + H^+$	$k = 15 \pm 2$ $M^{-1}s^{-1}$	*(Bichsel and von Gunten, 2000b)*
24	$HOI + IO_2^- \rightarrow IO_3^- + I^- + H^+$	Assumed to be fast	
25	$3\ HOI \rightarrow IO_3^- + 2I^- + 3H^+$	Overall reaction of HOI disproportionation	

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

Inorganic compounds	Rate constants	Main product	References
Reactivity of HOI			
Br^- ($+H^+$)	3.3×10^{12} $M^{-2}s^{-1}$	IBr	(Troy et al., 1991)
Cl^- ($+H^+$)	2.9×10^{10} $M^{-2}s^{-1}$	ICl	(Wang et al., 1989)
H_2O_2	29 ± 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^-	5.0×10^9 $M^{-1}s^{-1}$	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)
$N_2H_5^+$	4×10^9 $M^{-1}s^{-1}$	I^-	(Deane and Potter, 1985)
H_3AsO_3	7.4×10^8 $M^{-1}s^{-1}$	I^-	(Chen et al., 2021)
Reactivity of IO^-			
HO_2^-	$(6.4 \pm 1.4) \times 10^7$ $M^{-1}s^{-1}$	I^-	(Shin et al. 2020)

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

	second order rate constants ($M^{-1}s^{-1}$)				
Compounds	$k_{H2OI+/PhOH}$	$k_{HOI/PhOH}$	$k_{HOI/PhO-}$	k_{app} **(pH 7 or stated)**	**Reference**
p-chlorophenol	$(3 \pm 1) \times 10^3$	< 5	$(1.6 \pm 0.5) \times 10^5$	6.0×10^2	(Bichsel and von Gunten, 2000a)
	$(2.4 \pm 0.6) \times 10^3$	< 5	$(1.3 \pm 0.5) \times 10^5$	4.8×10^2	(Rose and Roberts, 2019)
	-	-	-	$(1.9 \pm 0.7) \times 10^3$	(Vikesland et al., 2013)
p-cresol	$(4.0 \pm 1.5) \times 10^4$	$(3 \pm 1) \times 10^2$	$(7 \pm 3) \times 10^8$	3.8×10^5	(Bichsel and von Gunten, 2000a)
	$(4.5 \pm 1.6) \times 10^4$	4×10^2	9.9×10^8	5.4×10^5	(Rose and Roberts, 2019)
p-cyanophenol	$(2 \pm 1) \times 10^2$	1.5 ± 0.5	$(4 \pm 2) \times 10^2$	5.0×10^1	(Bichsel and von Gunten, 2000a)
	$(3.1 \pm 1.1) \times 10^2$	1.4 ± 0.4	$(3.3 \pm 0.4) \times 10^2$	4.3×10^1	(Rose and Roberts, 2019)
p-iodophenol	$(4 \pm 1) \times 10^3$	20 ± 8	$(1.5 \pm 0.8) \times 10^5$	9.6×10^2	(Bichsel and von Gunten, 2000a)
	$(3.6 \pm 1.2) \times 10^3$	21 ± 7	$(9.8 \pm 1.9) \times 10^4$	6.5×10^2	(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	$(7 \pm 2) \times 10^8$	4.5×10^5	(Bichsel and von Gunten, 2000a)
	$(5.5 \pm 1.3) \times 10^4$	-	$(7.5 \pm 5.1) \times 10^8$	4.7×10^5	(Rose and Roberts, 2019)
phenol	$(5 \pm 2) \times 10^4$	$(1.0 \pm 0.3) \times 10^2$	$(2 \pm 1) \times 10^6$	2.1×10^3	(Bichsel and von Gunten, 2000a)
	$(7.2 \pm 2.9) \times 10^4$	$(1.1 \pm 0.3) \times 10^2$	$(1.8 \pm 0.2) \times 10^6$	2.0×10^3	(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)

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

Compounds	k_{H2O} (s^{-1})	k_{HO-} ($M^{-1}s^{-1}$)	k_{HOI} ($M^{-1}s^{-1}$)	k_{app} **at pH 7** (M^{-1} s^{-1})	**References**
acetaldehyde	$(9 \pm 1) \times 10^{-8}$	$(9.0 \pm 0.4) \times 10^{-1}$		5.1×10^{-6}	(Bichsel and von Gunten, 2000a)
acetate	$< 2 \times 10^{-10}$	$< 3 \times 10^{-6}$		$< 1 \times 10^{-8}$	
acetone	$(1.3 \pm 0.4) \times 10^{-8}$	$(2.5 \pm 0.3) \times 10^{-1}$		7.2×10^{-7}	
allyl alcohol				≤ 1	
citric acid	-	-		< 1 (pH 8)	(Zhao et al. 2017)
dimethenamid			$\leq (9.07 \pm 1.95) \times 10^{-4}$		(Rose and Roberts, 2019)
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	$(4 \pm 2) \times 10^{-9}$	$(3.7 \pm 0.2) \times 10^{-2}$		2.2×10^{-7}	

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

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).

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