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Influence of bromide and iodide on the formation of disinfection by-products in drinking water treatment

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Abstract

The speciation of disinfection by-products (DBPs) formed during oxidative processes strongly depends on the presence of bromide and iodide. These ubiquitous elements can be found in water at various concentrations, Br^- from a few $\mu\text{g L}^{-1}$ to a few mg L^{-1} and I^- typically from 0.5 to 100 $\mu\text{g L}^{-1}$. The hypohalous acid (HOX) formed during oxidative treatment is the key intermediate. The formation of DBPs will depend on the ability of the oxidant to form HOX from the oxidation of halides and its further stability in the treated water. The reactivity of Br^- , I^- , HOBr , BrO^- , HOI and IO^- with various oxidants (chlorine, bromine, ozone, chloramines and chlorine dioxide) and corresponding rate constants are compiled and compared in this paper to explain the propensity of various disinfection processes to form halogenated DBPs. The detrimental effects (*i.e.* enhanced toxicity of the treated waters due to the higher toxicity of I-DBPs and Br-DBPs compared to their chlorinated analogues, and enhanced NDMA formation in presence of bromide) and the beneficial effects of the presence of halides (bromide catalysis of iodate formation, enhanced micropollutant removal in presence of bromide) are presented and discussed. Finally, strategies to avoid/mitigate the formation of DBPs or to remove DBPs are presented.

Keywords: halides, halogenated disinfection by-products, chlorination, chloramination, bromate

1. Introduction

Climate change, expanding populations and drought have resulted in water scarcity in many urban and regional centres and effective water resources management during periods of drying climate is of crucial importance. Scarcity of water has led to an increasing need for water utilities to rely on lower quality source waters, which often contain elevated concentrations of bromide/iodide and DOM. Increasingly stringent guidelines for maximum DBP concentrations place additional pressure on water utilities to access good quality source water or, in its absence, to identify better methods to treat and manage poorer quality sources. The formation of iodinated and brominated disinfection by-products (Br-DBPs) is of concern, since these compounds have been shown to be more toxic than their chlorinated analogues and generally an increased toxicity has been observed in chlorinated waters containing bromide or iodide[1–5] (Figure 1). Iodoacetic acid is the most genotoxic compound identified to-date[4]. In addition, I-DBPs are associated with a medicinal taste and odor in distributed waters. I-THMs have a low odor threshold ranging from 0.03 to 8.9 $\mu\text{g L}^{-1}$, iodoform being the most problematic compound[6,7]. Hence, in the last decade, the behaviour of bromide/iodide along the treatment train and distribution system has been extensively studied. The knowledge gained from these studies allowed to develop new treatment strategies to mitigate the impact of bromide/iodide on the formation and toxicity of DBPs.

Bromide and iodide are naturally occurring at various concentrations worldwide. In fresh waters, bromide concentrations are in the range of a few $\mu\text{g L}^{-1}$ to a few mg L^{-1} [8,9], while iodide concentrations are much lower, usually in the range 0.5 to 100 $\mu\text{g L}^{-1}$ and often below 20 $\mu\text{g L}^{-1}$ [10,11]. The highest concentrations encountered are usually due to the impacts of seawater through direct salt-water intrusion or bedrocks formed from marine sediments. The concentrations of bromide and iodide in seawater are relatively constant, with a Br/I ratio slightly higher than 1000. The concentration of bromide is around 67 mg L^{-1} and iodine (mostly in the form of iodate in seawater) is between 45 and 60 $\mu\text{g L}^{-1}$ [12,13]. However, in fresh water, no particular trend can be observed[9]. In most cases iodide is not detected while in some regions, a large proportion of water samples contained high concentration of iodide > 150 $\mu\text{g L}^{-1}$ (72% of 950 samples in [14]).

Anthropogenic activities have also been found to increase the concentrations of bromide[15] and iodide in fresh waters[16]. Especially, environmental impact studies on hydraulic fracturing have shown high halide concentration in their effluent (I^- up to 54 mg L^{-1} and Br^- up to 1.9 g L^{-1})[17]. Overall, increasing halide concentrations due to climate change and increasing pressure on water resources are expected (sea water intrusion in coastal aquifers and lower dilution rates due to water scarcity) and may affect the type and concentrations of DBPs formed and their associated toxicity.

2. Hypohalous acid: a key intermediate in the formation of DBPs

In this chapter, chlorine, bromine or iodine will be used to refer to both corresponding hypohalous acid (HOX) and/or hypohalite (XO^-) species.

Chlorine is the most commonly used drinking water disinfectant worldwide. Therefore, understanding the chemistry of HOCl is crucial in water treatment processes. Chlorine participates in numerous reactions during drinking water treatment, including oxidation/disinfection and halogenation of dissolved organic matter (DOM), to form chlorinated organic disinfection by-products (DBPs) (Figure 1). In the presence of bromide and iodide, HOBr and HOI may be formed by various oxidants and react, similar to chlorine, with DOM to form Br-DBPs and I-DBPs (Figure 1). Therefore, it is important to understand and control the formation and reactivity of HOX since it is a key intermediate in the formation of DBPs. In fact, the formation of HOBr and HOI strongly depends on the type of oxidant used for disinfection.

Figure 1

Bromide is rapidly oxidized by HOCl with a second order rate constant (k) of $1550 \text{ M}^{-1}\text{s}^{-1}$ while ClO^- is not reactive with bromide (Table 1)[18]. Ozone reacts slowly with bromide to form HOBr with k of $160 \text{ M}^{-1}\text{s}^{-1}$. ClO_2 is unreactive with bromide and therefore does not form HOBr. In the case of chloramination, bromide reacts slowly with NH_2Cl to form brominated amines and not HOBr (a discussion is provided in the following section).

The reactivity of the different oxidants with iodide is different from bromide. Iodide is quickly oxidised by HOCl ($k = 4.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) but much more slowly by ClO^- ($k < 30 \text{ M}^{-1}\text{s}^{-1}$). Ozone oxidises iodide quickly with $k = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. Both processes lead to the formation of HOI. In contrast, the oxidation of iodide by ClO_2 is possible under typical drinking water treatment conditions ($k = 1870 \text{ M}^{-1}\text{s}^{-1}$). However, it does not form HOI but the iodine radical I^\bullet [19]. Compared to bromide, iodide is oxidised by monochloramine to HOI ($k = 2.4 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ at pH 7) (Table 1). If HOBr/ BrO^- are present in solution, these species are also able to oxidise iodide to HOI at a high rate with k of $5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $6.8 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ respectively (Table 2).

The formation and speciation of DBPs will depend on the competition between the different oxidants and the DOM reactive sites for reaction with HOBr and HOI. If the hypohalous acids are stable in solution, they will have sufficient time to react with DOM and form organic DBPs. If the hypohalous acid are reacting quickly with the oxidant, inorganic DBPs such as bromate (BrO_3^-) or iodate (IO_3^-) will be formed.

Table 1

2.1. Inorganic disinfection by-product formation

As mentioned previously, once HOX is formed, one option is that it is further oxidised by the oxidants present in solution (Figure 1). As shown in Table 2, only ozone is able to further oxidize reactive bromine and more precisely BrO^- with a k of $110 \text{ M}^{-1}\text{s}^{-1}$. The reactivity of other oxidants as well as the disproportionation of HOBr are negligible under typical drinking water treatment conditions[26]. The oxidation of BrO^- by ozone leads to the formation of bromate[28], which is a potential human carcinogen and is regulated in most of countries with a drinking water guideline of $10 \mu\text{gL}^{-1}$.

In comparison to HOBr, HOI may be oxidised by a wide range of oxidants and leads to the formation of iodate (IO_3^-), which in contrast to bromate is a non-toxic and a stable form of iodine in drinking water[29]. HOCl/ ClO^- are able to oxidize HOI (but not OI^-) to IO_3^- at a low rate with k of $8.2 \text{ M}^{-1}\text{s}^{-1}$ and $52 \text{ M}^{-1}\text{s}^{-1}$, respectively. The half-life of HOI in presence of chlorine at pH 7 is ~ 40 min, which means that HOI is quite stable in solution (Table 2). However, in presence of HOBr/ BrO^- the half-life of HOI is drastically reduced to ~ 2 min with k of $1.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $1.8 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$, for the reaction of OI^-

with HOBr/BrO⁻, respectively[30]. The oxidation of HOBr/BrO⁻ by HOI is not significant. Ozone reacts quickly with HOI/OI⁻ with k of $3.6 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ and $1.6 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, respectively. Finally, chloramine is not able to oxidize reactive iodine to iodate. Therefore, HOI/OI⁻ will be stable in solution during chloramination and be able to react with any DOM present.

Table 2

2.2. Organic disinfection by-product formation

If HOX is not oxidised to oxyhalides, then it reacts with DOM, to form organic halogenated DBPs. As shown in Table 2, only ozone is able to oxidise BrO⁻ to bromate and at a slow rate. Therefore, when bromine reactive species are present in solution, they will be stable and a high formation of organic Br-DBPs is expected[26,33]. Similarly, chlorine will oxidise iodine at a slow rate and therefore high concentration of I-DBPs are expected[34]. During ozonation, iodine will be quickly oxidised to iodate, and low formation of I-DBPs is expected. However, during chloramination, NH₂Cl is not able to oxidise iodine and high formation of I-DBPs is expected.

Bromide is ubiquitous in natural waters, and depending on its concentrations, the contact time and the physico-chemical characteristics of the water, HOBr rather than HOCl may become the dominant oxidant/disinfectant and halogenating agent during chlorination. In many cases, the reactivity of HOBr in oxidation and halogenation reactions far outweighs the reactivity of HOCl[35–39]. It has been shown that second order rate constants for reactions with phenolic compounds are on average 3000 times higher for HOBr compared to HOCl[26]. Hence, the formation of Br-DBPs is kinetically favoured compared to the formation of Cl-DBPs.

HOBr reacts through two different pathways, electrophilic substitution and addition reactions which leads to the formation of Br-DBPs or electron transfer which leads to the oxidation of the DOM components and the release of bromide. It was shown using DOM extracts that around 20% of the reaction leads to halogenation and the major part of the oxidants reacts with DOM through electron transfer and leads to the release of bromide in solution[35]. The partition between halogenation and

electron transfer reaction strongly depends on the nature of the organics, for example the relative position of hydroxyl moieties on the benzene ring. The *ortho* and *para* position of the dihydroxybenzenes (*e.g.* catechol and hydroquinone) lead to the quantitative formation of quinones and do not exhibit substantial halogenation; in contrast to the *meta* position which undergoes full halogenation[35] (*e.g.* resorcinol, which is known to have a high yield of THM formation[40]). In real systems, chlorine is always in excess to provide a disinfectant residual. Even though, 80% of the bromide is released in the water after electron transfer reaction it can then be re-oxidized by HOCl, resulting in a bromide-catalysis and additional formation of Br-DBPs. As long as there is a disinfectant residual as well as organic precursors, such as DOM present, bromide will enhance the disinfectant demand and eventually 100% of the initial bromide will be transferred to Br-DBPs[33].

Iodine is also generally more reactive towards organic compounds than reactive chlorine. HOI generally exhibits an intermediate reactivity between HOBr and HOCl[41]. There is no comprehensive study to date on the mechanism of iodine reaction with DOM. A similar behaviour as chlorine and bromine is expected, *i.e.* electrophilic substitution/addition reactions and electron transfer reactions. However, in presence of excess chlorine, while iodide will be recycled, both I-DBPs and iodate will be formed. If chloramination is used for disinfection, as NH_2Cl is not able to oxidise HOI to iodate, 100% of the initial iodide is expected to be transferred to I-DBPs as iodide will be recycled and re-oxidised to HOI by NH_2Cl .

Figure 2

3. Role of bromide during monochloramination

Monochloramine (NH_2Cl) has increasingly been used over the last decade as an alternative disinfectant to chlorine for drinking water distribution systems due to its greater stability and lower potential to form regulated DBPs [42–44]. However, although NH_2Cl is more stable than HOCl, it can still decompose or react with the water matrix to form other haloamines, which may be more reactive than NH_2Cl and form more potent DBPs. Therefore, not only the concentration, but also the speciation, is an important

parameter, which needs to be considered. NH_2Cl can react with bromide, albeit slowly, and therefore the chemistry of the system becomes even more complex.

Various haloamines may form from reactions between chlorine, bromide and ammonia (*e.g.* chloramines, bromamines and bromochloramines) (Figure 2). Monobromamine (NH_2Br) can be formed from the reaction of HOBr and NH_3 or NH_3Cl^+ and Br^- ; bromochloramine (NHBrCl) may be formed from the reaction of HOBr with NH_2Cl [45–47]. A major concern related to the formation of bromamines is that they can accelerate the decay of NH_2Cl [48] and react with DOM. There is a paucity of reported information on the reactivity of bromamines, but as for HOBr , it has been shown that the reactivity of bromamines was higher than that of its chlorine analogues for the reaction with acetic acid[49], which confirms earlier studies showing that NHBrCl was more reactive than NH_2Cl [50]. It has been shown that brominated amines form halogenated phenols via electrophilic aromatic substitution[43]. The presence of bromide in a chloraminated system was also found to catalyze DOM oxidation[48]. It is thus hypothesized that the reaction of bromamines with DOM in raw and treated waters may enhance the formation of undesired Br-DBPs, as well as accelerate the decay of chloramine[51]. In addition to inorganic halamines, organic halamines may form from the reaction of inorganic halamines or chlorine/bromine with dissolved organic nitrogen (*i.e.*, DON, nitrogenous moieties in DOM) and participate to the formation of Br-DBPs[26,52]. Therefore, not only is the concentration of the primary oxidant important, but secondary oxidants which are formed from reaction with bromide may also be important during chloramination.

4. The detrimental effects of halide

4.1. Br-DBPs and/or I-DBPs induce a highest toxicity

Br-DBPs and I-DBPs are of particular concern since they have been reported to be more cytotoxic and genotoxic than their chlorinated and brominated analogues[4,53,54]. Within a class of DBPs, the toxicity increases in the order $\text{Cl} < \text{Br} < \text{I-DBPs}$ [4]. Yang et al.[5] demonstrated that the cytotoxicity and genotoxicity of waters treated by chlorine or chloramines was correlated to the total formation of

iodinated and brominated organic compounds named TOI and TOBr (total organic halides). As expected, the toxicity increased with increasing concentration of bromide and iodide. It is interesting to note that the toxicity was inversely correlated to the formation of chlorinated organic compounds (TOCl), since the formation of Cl-DBPs decreased with increasing concentration of bromide and iodide. This is due to the competition between HOCl, HOBr and HOI for DOM reactive sites. As HOBr and HOI react faster with DOM, this induced a shift from Cl-DBPs to Br- and I-DBPs formation.

Another approach to estimate the DBP-mediated toxicity is to use the sum of the measured concentrations of individual disinfection by-products (DBPs) divided by their respective Chinese hamster ovary (CHO) cell cytotoxicity LC_{50} (lethal concentration for 50% of a population) values to estimate the DBP associated cytotoxicity of disinfected waters. This gives the contribution of each DBP to the overall calculated toxicity and allows the prioritization of DBPs not only based on their concentrations but also their toxicity. It has recently been showed that the additivity of individual toxicities was representative of the CHO cell cytotoxicity associated with known DBPs in real disinfected waters[55]. Several studies reported the importance of Br-and/or I- DBPs over Cl-DBPs using this approach[55–60]. I-DBPs exhibiting particularly high toxicity, despite their usually much lower concentration in treated waters may be important toxicity drivers. I-THMs using this approach showed a similar or up to 2.1 fold higher toxicity than regulated THMs[2,61]. Bromoacetic acid, despite its relatively low concentration, was responsible for more than 60% of the relative toxicity related to the formation of 17 different HAAs and THMs[59]. In addition to toxicity, brominated by-products from different antibiotics have been shown to accumulate in aquatic organism more easily than their chlorinated analogues[62].

4.2. Bromide enhanced NDMA formation

N-Nitrosamines have long been recognised as extremely potent carcinogens, and their significance in drinking water and wastewaters has been recognised in numerous studies[63–65]. The most common and most extensively studied N-Nitrosamines being N-nitrosodimethylamine (NDMA). Even though NDMA does not contain any halogen, its formation may be influenced by the presence of bromide. It

has been found that not only chloramines but also NH_2Br and NHBrCl were precursors in the formation of the NDMA during chloramination[43,66–69]. Another study reported that the formation of NDMA was catalysed by bromide during ozonation[70]. These studies highlight the fact that the presence of halogens may affect the formation of toxic DBPs which are not necessarily halogenated DBPs.

5. The beneficial effects of halide on DBP formation

5.1. Bromide-catalysed iodate formation and mitigation of I-DBPs

As shown in Table 2, HOBr/BrO^- oxidises iodine at a much higher rate than chlorine. In natural waters, high concentrations of iodide are usually accompanied by the presence of a substantial amount of bromide. During chlorination, chlorine is always in large excess compared to bromide and iodide. As discussed previously, the rate of iodate formation is relatively low during chlorination. Therefore, iodine is stable in solution and may react with DOM to form I-DBPs. In presence of bromide the formation of non-toxic iodate increases and the formation of I-DBPs decreases. During this process, bromide is released in solution and can react with chlorine to re-form bromine. Therefore, small quantities of bromide are able to greatly enhance the formation of iodate. It has been shown that increasing the bromide concentration from 40 to 200 $\mu\text{g/l}$ increased the conversion of iodide to iodate from 45 to 90% while the I-incorporation into I-THMs decreased from 10 to 2%[30].

5.2. Enhanced micropollutant degradation in presence of Br^-

One consequence of the generally higher reactivity of HOBr compared to HOCl is the enhanced micropollutant degradation in presence of bromide during chlorination. As stated earlier, HOBr reacts in average 3000 times faster with aromatic compounds than HOCl . A large number of micropollutants contain phenolic groups in their structure. This phenomenon has been demonstrated for 17 α -ethinylestradiol[39], in addition to the faster degradation, the bromination process is also able to destroy the estrogenic properties of this compound[71]. Examples with different reactive moieties are discussed in details in Heeb et al.[26]. Lately, numerous studies confirmed the increased degradation of

micropollutants in presence of bromide such as benzophenone[72], bromacil[73] ephedrine[74], ciprofloxacin and lomefloxacin[62], methylparaben and halogenated by-products[75] and polycyclic aromatic hydrocarbons[76].

The enhanced degradation of micropollutants is not clear during advanced oxidation processes (AOPs). The presence of bromide results in both an increased rate of micropollutant degradation[78,79] and no or detrimental effects depending on the micropollutant and the experimental conditions[80]. However, Hua et al. [81] showed that the presence of bromide during UV/chlorination of wastewater effluents induced a decrease of the acute toxicity and genotoxicity of the treated effluents despite the increase of toxic brominated DBPs.

6. Mitigation of brominated and iodinated DBPs

Different mitigation strategies have been proposed in recent years to mitigate the formation of DBPs. There are different options for removing the precursors, *i.e.* halogens and/or DOM or removing the DBPs once formed. These processes based either on specific halide removal, combination of oxidants, and physical removal such as adsorption or stripping are at different stages between development and application. Common water treatments trains (*e.g.* coagulation, activated carbon adsorption, membrane filtration and ion exchange) are designed to remove DOM and could be efficient to meet the DOC quality standards where they exist. However, these concentrations (*e.g.* recommendation of 2 mgC/L in France) could be sufficient to induce the formation of toxic and/or odorous DBPs especially in presence of bromide and iodide. In addition, the removal of DOM generally promotes the formation of brominated compounds favouring the reaction of chlorine with Br⁻ instead of DOM. This could induce a greater toxicity, despite an overall decrease of DBP concentrations[82–86]. There is currently no economically feasible method to remove the halogens precursors of DBP, bromide and iodide.

6.1. Removal of halides

Some research has concentrated on the selective adsorption of bromide and iodide on synthetic silver-doped materials[87–89]. This process is based on the high affinity of halide ions towards silver ions. The solubility product for AgX (for X = Cl⁻, Br⁻, I⁻) decreases in the order Cl⁻ ($K_{so} = 2.8 \times 10^{-10}$) > Br⁻ ($K_{so} = 5.2 \times 10^{-13}$) > I⁻ ($K_{so} = 8.5 \times 10^{-17}$), in the reverse order of their occurrence in natural waters and in the order of increasing toxicity for their corresponding DBPs. Even in excess of chloride, which is typical for natural waters, bromide and iodide can be selectively removed from solution using silver ions. Silver may be immobilised in carbon aerogels[87,88], polymeric beads or on activated carbon surface (silver impregnated activated carbon)[90,91] or directly used as nanoparticles[92]. AgCl has also been tested to remove iodide by ion exchange[93]. This has not been implemented to full-scale treatment plant to date. More work is needed to confirm the impact of competing anions and to better understand the extent of silver leaching from these materials.

The different strategies for the removal of halides, including membrane filtration or ion exchange have been reviewed by Watson et al.[94]. Recently Br-selective anion exchange resins showed good performances for an efficient control of Br-DBPs, including in presence of competing anions and/or DOM[95].

6.2. Mitigation of I-DBPs

6.2.1. The chlorine ammonia process

During chloramination HOI is formed and is stable in solution inducing a high formation of I-DBPs. A process based on free chlorine followed by ammonia addition to form chloramine has been proposed in several studies[30,31,56,96]. This process intends, in a first step, to mitigate the formation of I-DBPs by converting most of iodide to iodate during pre-chlorination. In a second step, to quench the chlorine by addition of ammonia to form chloramine which is less reactive with DOM and control the formation of regulated chlorinated and brominated DBPs. The presence of bromide enhances the formation of iodate[30] and can reduce the pre-chlorination contact time but it may also increase the formation of

more toxic Br-I-DBPs such as CHBr_2I (compared to CHCl_2I)[56]. For low bromide concentrations, a long contact time is needed to allow the full conversion of iodide to iodate and to mitigate the formation of I-DBPs. For high concentrations of bromide, a short chlorination contact time could be sufficient to limit the formation of I-DBPs. Furthermore, for highly reactive DOM, a pre-chlorination step is not beneficial compared to preformed monochloramine[56]. Overall, the process efficiency is highly depended on the DOM concentration and reactivity, the bromide concentration and the pre-chlorination contact time.

6.2.2. Selective oxidation of iodide to iodate by ozone for I-DBP mitigation

Ozone readily reacts with iodide and HOI to form iodate and is an attractive option to mitigate the formation of I-DBPs. However, the downside of using ozone is the formation of bromate since in most natural waters containing iodide, bromide is present at significant concentration. It was shown that it is possible to fully oxidised iodide to iodate while keeping the bromate concentration below the guideline value by using ozone[97]. This is based on the difference between the kinetic of bromide/bromine and iodide/iodine reactivity with ozone. Table 1 and 2 shows that iodide will be fully oxidised to iodate in less than 1 ms (at pH 7 and 1 mg L^{-1} Ozone) while the formation of bromate will take several minutes. Therefore, it is possible by applying an appropriate ozone dose to mitigate the formation of I-DBPs while controlling the bromate formation. In addition, the oxidation of the different hypohalous acids and hypohalite ions by ozone are dramatically different (Table 2). HOI and IO^- are both rapidly oxidised ($k = 3.6 \times 10^4$ and $1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ respectively) while only BrO^- is reacting with ozone ($k = 110 \text{ M}^{-1} \text{ s}^{-1}$). Therefore, lowering the pH to below 8.3 (pK_a of HOBr/BrO^- [23]) to shift the equilibrium of the reactive bromine to HOBr further decreased the formation of bromate while the iodate formation is not significantly affected. Allard et al.[97] demonstrated that it was possible to fully oxidised iodide to iodate while keeping the bromate concentration below $10 \text{ } \mu\text{g L}^{-1}$ for a wide range of bromide concentrations up to $940 \text{ } \mu\text{g L}^{-1}$.

6.3. Strategies to mitigate the formation of bromate during ozonation

While HOBr is formed during ozonation, the formation of organic Br-DBPs is usually low [28]. The main halogenated by-product of concern during ozonation is bromate due to its potential human carcinogen classification. Therefore, different mitigation strategies to control the bromate concentration below the drinking water quality standard ($10 \mu\text{g L}^{-1}$) have been proposed. Among the mitigation processes, pH depression and ammonia addition are the most suitable at industrial scale[28].

As previously mentioned, lowering the pH favours the presence of HOBr which is less reactive towards ozone compared to BrO^- and mitigates the formation of bromate (Table 2). In addition, a lower pH increases the ozone stability which in turn reduces the formation of OH radicals that are a main contributor to the formation of bromate[98].

In order to quench HOBr, a key intermediate in the formation of bromate, ammonia may be added to the water. Bromamines are then formed and hinder the formation of bromate[98]. This mitigation strategy quench HOBr, but does not limit the radical pathway and is limited by the amount of ammonia addition inducing a reduction of the bromate formation[98].

Similar to the mitigation of iodide, the chlorine ammonia process may be used prior to ozonation[99]. In this process, chlorine will oxidise bromide to HOBr. HOBr is then quenched with ammonia to form bromamines and the formation of bromate mitigated. Buffle et al.[99] reduced the bromate formation by a factor of 4 using this process. The addition of hydrogen peroxide has also been proposed to reduce the formation of bromate. An optimal dosage of H_2O_2 is needed because an increasing concentration of peroxide may induce an increase in bromate formation. However, this AOP may induce a decrease of the disinfection efficiency by favouring the radical pathway and is then unsuitable for industrial processes.

6.4. Pre-oxidation for Br-DBPs mitigation

Oxidants such as HOCl, O₃, KMnO₄, ClO₂ and Fe(VI) (the latter only in research) have been widely used as pre-treatment options. These oxidants have been applied successfully to reduce the formation of regulated DBPs during post-chlorination by reducing the reactivity of the DOM. However, in some cases, an increase or a similar formation of Br-DBPs has been observed[60,100,101]. Applying O₃, KMnO₄, ClO₂ or Fe(VI) as a pre-treatment oxidizes reactive moieties in the DOM, which renders them typically less reactive towards chlorine or bromine in post-disinfection, thereby affecting the subsequent formation of Br-DBPs. The reactivity of the above oxidants toward DOM varies significantly[102] in the order O₃ >> ClO₂, Fe(VI) > MnO₄⁻. Since the bromide oxidation by ozone is a relatively slow process, a selective oxidation of fast reacting DOM-moieties is possible, with negligible formation of HOBr/Br-DBPs or bromate. A good correlation was observed between the abatement of DOM reactivity characterized by the UV absorbance at 254 nm (UV₂₅₄) and the electron donating capacity (EDC) and the total halogenated organic compounds formation[103]. However, in many cases the concentration of Br-DBPs increased after pre-oxidation. The pre-oxidant dose should be optimized to decrease the reactivity of the matrix while controlling the toxicity induced by the formation of brominated DBPs, notably brominated HANs[60].

6.5. Removal of preformed DBPs by activated carbon adsorption

Activated carbon may be used to remove halogenated disinfection by-products after a pre-chlorination step to some extents. According to the Freundlich adsorption constants, the adsorption of regulated THMs increased with increasing bromine content[104]. This is in agreement with results obtained from a full scale drinking water treatment plant where the removal efficiency of Cl-Br-THM by Granular Activated Carbon (GAC) ranged from 15 to 58% with 15% for CHCl₃, 18% for CHBrCl₂, 43% for CHBr₂Cl and 58% for CHBr₃[59]. A similar trend has been observed for I-THMs, with much higher removal rates: 77 % for CHCl₂I, 88% for CHBrClI, 94% for CHBr₂I and 96% for CHClI₂, increasing with the molecular weight and hydrophobicity[59]. No clear trend could be obtained for HAAs, rising

questions around the mechanisms of HAAs removal and the partition between adsorption and biodegradation[59,105,106].

Recently several studies showed the benefit to perform a pre- or intermediate chlorination followed by GAC adsorption to lower the DBPs and total organic halogens formed during final disinfection[59,107–110]. While a concomitant reduction of toxicity has been suggested[108,109], the reduction of calculated cytotoxicity could be rather low due to the formation of brominated and nitrogenous compounds (*e.g.* tribromonitromethane)[109]. Erdem et al.[111] showed that the adsorption of halogenated DBPs precursors mainly occurs in the mesoporous areas of the GAC and suggested that basic GAC would be more favourable as the oxidant residual increases the surface acidity, which impairs the adsorption of halogenated precursors.

6.6. Air Stripping for removal of volatile DBPs

Air stripping for DBPs mitigation has been implemented mainly in the US for the control of regulated THMs in small utilities. While efficient for chloroform, which exhibit the highest Henry's constant ($2.99 \times 10^{-3} \text{ atm m}^3 \text{ mol}^{-1}$), this process is less efficient for brominated THMs (*e.g.* Henry's constant for bromoform= $5.35 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$)[112] and not useful for non-volatile and more toxic DBPs like HAN or HAA for example.

7. Conclusion

Reactive bromine and iodine species may be formed during different oxidative processes. The propensity of disinfectants to form hypohalous acids and the lifespan of these species are key factors in the formation of halogenated DBPs. Chloramination has been shown to be at high risk for organic I-DBP formation as chloramine rapidly forms HOI but cannot further oxidise it to the non-toxic iodate, in contrast to ozone and chlorine. High concentrations of bromide and iodide are usually associated with a higher formation of Br- and I-DBPs that are more toxic than their chlorinated analogues and consequently induced a higher toxicity risk. However, some beneficial effects of the presence of halides

are found such as the enhancement of micropollutant and estrogenicity removal during oxidative treatment. Due to the high risk related to the Br- and I-DBPs, the removal of their precursors is an attractive option to limit their formation. So far, no industrial processes are available to specifically remove iodide and bromide, however the new designed Br-specific-ion exchange resins look promising. Enhanced DOM removal could therefore be beneficial, but very low DOC concentrations are necessary in order to minimise the formation of such DBPs. Therefore, sustainable processes are needed to treat halide-impacted waters, especially considering the recurring droughts and increasing water scarcity that many urban metropolises are experiencing.

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Tables

Table 1. Second order rate constants of bromide and iodide oxidation by principal oxidants used in drinking water treatment and half - life ($t_{1/2}$) of halides for 1 mg/L of oxidant at pH 7.

Oxidant	Br ⁻			I ⁻				
	Second order rate constant k (M ⁻¹ s ⁻¹)	t _{1/2} at pH 7 (s)	References	Second order rate constant k (M ⁻¹ s ⁻¹)	t _{1/2} at pH 7 (s)	References		
HOX producing processes								
HOCl	1550	33	[18]	4.3 × 10 ⁸	10 ⁻⁴	[20,21]		
ClO [•]	9 × 10 ⁻⁴			< 30				
HOBr				5 × 10 ⁹	10 ⁻⁵	[22]		
BrO [•]				6.8 × 10 ⁵				
O ₃	160	208	[23]	2 × 10 ⁹	10 ⁻⁵	[24]		
NH ₂ Cl				2.4 × 10 ³ at pH 7	15	[25]		
Non-HOX producing processes								
NH ₂ Cl	0.14 at pH 7	2.6 × 10 ⁵	[26]					
ClO ₂	<10 ⁻⁴	high	[27]	1870	25	[19]		

ND: not determined

Table 2. Second order rate constants of hypohalous and hypohalite oxidation by principal oxidants used in drinking water treatment and half time life ($t_{1/2}$) of these species for 1 mg/L of oxidant at pH 7.

Oxidant	HOBr/BrO ⁻				HOI/IO ⁻			
	k (HOBr) (M ⁻¹ s ⁻¹)	k (BrO ⁻) (M ⁻¹ s ⁻¹)	$t_{1/2}$	References	k (HOI) (M ⁻¹ s ⁻¹)	k (IO ⁻) (M ⁻¹ s ⁻¹)	$t_{1/2}$ (s)	References
HOCl					8.2	-		
ClO ⁻					52	-	1760	[31]
HOBr	2×10^{-3}		One year	[32]	Not significant	1.9×10^6	90	[30]
BrO ⁻					-	1.8×10^3		
O ₃	<0.01	110	5.4 h	[23]	3.6×10^4	1.6×10^6	0.9	[31]
ClO ₂					ND			
NH ₂ Cl					$< 2 \times 10^{-3}$	<3	Several months	[31]

Figure Captions

Figure 1: General scheme of disinfection by-product formation in presence of bromide and iodide and relation to increasing toxicity of halogenated analogues in order Cl-<Br-<I-DBPs. Inset figure: Toxicity expressed as inhibition of GAPDH (glyceraldehyde-3-phosphate dehydrogenase) in CHO cells (Chinese Ovary Cells) treated with iodo-, bromo and chloro-acetic acids; reprinted with permission from [113]. Copyright (2011) American Chemical Society.

Figure 2: Formation pathway of halogenated DBPs during chlorination. The direct oxidation of DOM leads to the recycling of halides.