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## 1. Background

Disinfection of drinking water supplies is one of the greatest public health accomplishments of the last century for the prevention of waterborne diseases. However, disinfection processes used in drinking water treatment (chlorination, chloramination, chlorine dioxide, ozonation, ultra-violet (UV), and UV/H<sub>2</sub>O<sub>2</sub>) can lead to the formation of potentially toxic disinfection by-products (DBPs) (Ijpelaar et al., 2007; Richardson et al., 2007). Since their discovery, several hundred individual DBPs compounds have been identified, many of which are halogenated (Richardson et al., 2007; von Gunten, 2003). The presence of bromide (Br<sup>-</sup>) and iodide (I<sup>-</sup>) in source waters can result in the formation of brominated and/or iodinated DBPs upon exposure to natural organic matter (NOM) and disinfectant, which are often more toxic than their chlorinated analogues (Magazinovic et al., 2004; Plewa et al., 2004; Richardson, 2003; Richardson et al., 2007; von Gunten, 2003). Both natural processes, including seawater intrusion and dissolution of geologic sources, and anthropogenic activities, such as seawater desalination, generation of mining tailings, chemical production, production of sewage and industrial effluents, may contribute to bromide concentrations in drinking water sources (Magazinovic et al., 2004; Richardson et al., 2007; Valero and Arbós, 2010; von Gunten, 2003). Similarly, seawater intrusion, seawater desalination and dissolution of geologic sources contribute to iodide concentrations in drinking water sources (Agus et al., 2009; Hua et al., 2006; von Gunten, 2003), although biological activity of microorganisms and marine algae can contribute to iodide removal from water sources through specific metabolic processes (Suzuki et al., 2012). Table 1 shows typical bromide and iodide concentration in different source waters.

Current drinking water treatment schemes are challenged to effectively remove ambient bromide and iodide before final disinfection, in order to produce acceptable levels of the suspected carcinogen bromate (Kurokawa et al., 1990), when using ozone or advanced oxidation processes (von Gunten et al., 1995), and brominated/iodinated DBPs when disinfecting with chlorine or

chloramines (Bichsel and von Gunten, 2000; Hua and Reckhow, 2007; Hua et al., 2006).

It is well known that bromide and iodide present in water may react differently with different disinfectants (Kumar et al., 1986; Kumar and Margerum, 1987; Nagy et al., 1988; Trofe et al., 1980). The kinetic rate constants of bromide and iodide with chlorine and chloramine in the formation of HOBr and HOI, respectively, are shown (Table 2).

The reaction of bromide with free chlorine is five orders of magnitude faster than with chloramine (Trofe et al., 1980). On the other hand both disinfectants react relatively quickly with iodide ion (Kumar et al., 1986; Nagy et al., 1988). HOBr, formed from bromide, may then react with NOM and generate bromine-containing DBPs. In the presence of excess free chlorine, HOI is largely oxidized to iodate (IO<sub>3</sub><sup>-</sup>), the desired sink for iodide, but in the presence of chloramines it is relatively stable, as shown by the relevant rate constants (Table 3) (Bichsel and von Gunten, 1999). Therefore, in the presence of chloramines, HOI will react with certain organic precursors producing iodine substitution and the generation of iodinated analogues of many of the chlorine- and bromine-containing DBPs.

Although some brominated DBPs are regulated in the Australian Drinking Water Guidelines (NHMRC, 2011) (in particular; bromate, bromodichloromethane, dibromochloromethane and bromoform) the highly variable nature of NOM and its reactivity with different disinfectants means that there may be many other brominated and/or iodinated DBPs species formed in any given treated water in which these halides are present. Strategies for DBP minimisation vary, but can be broadly classified into three categories; DBPs precursor removal (halides and NOM), optimising disinfection to minimise DBPs formation, and DBPs removal prior to water distribution (for example, air-stripping of volatile DBPs such as trihalomethanes (THMs)) (Wu and Wu, 2009). One advantage that DBPs precursor removal has over other DBPs minimisation strategies is that it is not specific to removing/lowering a particular suite of DBPs, it can broadly minimise all DBPs, both known and unknown, potentially creating greater trust in the quality of the water produced. All disinfection methods produce their own suite of DBPs, however, minimising the precursors available for this to occur is applicable regardless of disinfection method employed. As

**Table 1**  
Examples of levels of bromide and iodide in different source waters.

	Bromide (µg/L)	Iodide (µg/L)
Seawater	65000 (Stumm and Morgan, 1996)	35.8–51.1 (Duranceau, 2010)
Desalinated seawater	650 (Magara et al., 1996; Obolensky and Singer, 2005)	<4 (Duranceau, 2010)
US rivers (median)	35 (Amy and Siddiqui, 1998)	0.5–212 (Moran et al., 2002)
US ground water	16 (Davis et al., 2004)	30 (Land et al., 2004)

**Table 2**  
Rate constants for bromide and iodide oxidation by common disinfectants.

	Chlorine	Monochloramine
Br <sup>-</sup> ⇌ HOBr	1.5 × 10 <sup>3</sup> M <sup>-1</sup> s <sup>-1</sup> (Kumar and Margerum, 1987)	0.014 M <sup>-1</sup> s <sup>-1</sup> (Trofe et al., 1980)
I <sup>-</sup> ⇌ HOI	4.3 × 10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup> (Nagy et al., 1988)	2.4 × 10 <sup>10</sup> × [H <sup>+</sup> ] M <sup>-2</sup> s <sup>-1</sup> (Kumar et al., 1986)













































