



Review

Disinfection by-product formation during seawater desalination: A review



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ABSTRACT

Due to increased freshwater demand across the globe, seawater desalination has become the technology of choice in augmenting water supplies in many parts of the world. The use of chemical disinfection is necessary in desalination plants for pre-treatment to control both biofouling as well as the post-disinfection of desalinated water. Although chlorine is the most commonly used disinfectant in desalination plants, its reaction with organic matter produces various disinfection by-products (DBPs) (e.g., trihalomethanes [THMs], haloacetic acids [HAAs], and haloacetonitriles [HANs]), and some DBPs are regulated in many countries due to their potential risks to public health. To reduce the formation of chlorinated DBPs, alternative oxidants (disinfectants) such as chloramines, chlorine dioxide, and ozone can be considered, but they also produce other types of DBPs. In addition, due to high levels of bromide and iodide concentrations in seawater, highly cytotoxic and genotoxic DBP species (i.e., brominated and iodinated DBPs) may form in distribution systems, especially when desalinated water is blended with other source waters having higher levels of organic matter. This article reviews the knowledge accumulated in the last few decades on DBP formation during seawater desalination, and summarizes in detail, the occurrence of DBPs in various thermal and membrane plants involving different desalination processes. The review also identifies the current challenges and future research needs for controlling DBP formation in seawater desalination plants and to reduce the potential toxicity of desalinated water.

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1. Introduction

Rapid population growth and frequent droughts have accelerated the demand for fresh water supply around the world. Fourteen of the world's largest cities (with populations in excess of 10 million) and two-fifths of cities with populations between 1 million and 10 million are located in coastal areas (Tibbetts, 2002). Since 96.5% of the earth's water is located in seas and oceans, seawater desalination is a useful technology for addressing water scarcity problems in coastal regions. For decades, desalination operations in many countries in the Middle East, the Mediterranean Basin, as well as Australia, and the United States (US) have provided drinking water to their populations (De Munari et al., 2009; Greenlee et al., 2009; Dawoud, 2005; Reuter, 2000). The largest number of desalination plants is found in the Arabian Gulf with a total seawater desalination capacity of approximately 11 million m³/day (Lattemann and Höpner, 2008). Due to low costs of energy in the

Middle East area, thermal desalination processes (MSF: multi-stage flash; MED: multi effect distillation) have been predominant, accounting for almost 90% of the production, whereas other parts of the world deploy more membrane-based desalination plants (e.g., the main process in Spain is reverse osmosis [RO], accounting for 95% of all plants) (Lattemann and Höpner, 2008). In addition, more large-scale desalination projects are being proposed in many countries, spurred by the development of novel desalination technologies combined with the increasing demands for freshwater in those regions.

Although seawater desalination plants receive feed water via different intakes and coastal locations, open seawater intakes are the most common option. To prevent bacterial growth and biofouling in the intake structures and to improve the performance of filters, chemical disinfectants are used as a pre-treatment before multi-media filtration. Free chlorine (i.e., HOCl/OCl⁻) is the most commonly used disinfectant for pre-treatment as well as final disinfection. Chloramines, ozone, and chlorine dioxide are alternative disinfectants used frequently in water treatment to inactivate any residual pathogenic microorganisms (MWH, 2005). An

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Nomenclature			
CTA	cellulose triacetate	I-THM	iodinated THM
DBP	disinfection by-product	Log K _{OW}	octanol-water partition coefficient
DOC	dissolved organic carbon	MCL	maximum contaminant limit
DWTP	drinking water treatment plant	MED	multi effect distillation
HAA	haloacetic acid	MSF	multi stage flash
HAN	haloacetonitrile	NOM	natural organic matter
HK	haloketone	PA	polyamide
HNM	halonitromethane	RO	reverse osmosis
HOBr	hypobromous acid	SUVA ₂₅₄	specific UV absorbance
HOCl	hypochlorous acid	THM	trihalomethane
HOI	hypoiodous acid	TOC	total organic carbon
I-HAA	iodinated HAA	TOX	total organic halide
		UV	ultraviolet

unintended consequence of the use of chemical disinfectants is the production of disinfection by-products (DBPs) that pose adverse public health effects and environmental risks. Most studies on the formation and control of DBPs have focused on drinking water treatment utilities using surface water sources, wastewater treatment systems, and power plants, while limited research has focused on DBPs in seawater desalination systems. Since desalinated waters are low in total organic carbon (TOC) levels, it is expected that the disinfection demand and DBP formation would be relatively low. However, high bromide and iodide levels in seawater at concentrations from 50,000 to 80,000 µg/L and from 21 to 60 µg/L, respectively (Le Roux et al., 2015; Shi et al., 2013; Abdel-Wahab et al., 2010; Duranceau, 2010; Agus et al., 2009; Martinelango et al., 2006; Magara et al., 1996; Kristiansen et al., 1996; Mayankutty et al., 1995), may enhance the formation of brominated and iodinated DBPs that are known to be much more cytotoxic and genotoxic than their chlorinated analogues (Richardson et al., 2008; Plewa and Wagner, 2009). Typical concentrations of bromide in freshwater are orders of magnitude lower than those in seawater. Bromide levels in the US natural waters ranged from non-detectable to 2200 µg/L with an average of 100 µg/L, according to a survey conducted by Amy et al. (1995) and 70 µg/L based on an American Water Works Association Committee Report (2000). Recently reported bromide values are also consistent with these values. Weinberg et al. (2002) and Uzun et al. (2015) reported bromide concentrations ranging 22–400 µg/L and 7–237 µg/L, respectively, in different surface waters used by water utilities in the US. In another survey of 23 source waters of drinking water treatment plants (DWTPs), iodide concentrations varied between <0.13 and 104 µg/L with a median of 10 µg/L, while bromide concentrations varied from 24 to 1120 µg/L with a median of 109 µg/L (Richardson et al., 2008). Although bromide and iodide concentrations are substantially reduced down to non-detectable levels along with other components such as chloride and minerals present in feed water after thermal desalination processes, considerable amounts of bromide (i.e., 250–600 µg/L) and iodide (<4–16 µg/L) can still remain in seawater RO permeate and increase the formation of DBP in distribution systems (Duranceau, 2010; Agus et al., 2009; Magara et al., 1996; Ali-Mohamed and Jamali, 1989).

Blending desalinated water with conventionally treated single or multiple fresh waters drawn from other sources is a preferred method to meet the demands of drinking water and to increase the concentration of some desired ions (i.e., water conditioning). Indeed, desalinated product waters are often blended with brackish ground waters prior to distribution in many Middle East countries with inherently limited fresh water resources (Al-Mudhaf and Abu-Shady, 2008; Al-Mudhaf et al., 2009, 2011; Tawabini et al., 2011;

Fayad, 1993; Ali and Riley, 1989). According to an international survey, 64% of desalination plant operators surveyed indicated blending desalinated water with treated surface/ground water during post-treatment processes (Duranceau et al., 2011). When RO permeate rich in bromide (Agus et al., 2009; Magara et al., 1996) is mixed with treated surface water, more brominated DBP species will form in the distribution system since hydrophilic organic matter remaining after coagulation/flocculation/sedimentation incorporate bromide even at low dissolved organic carbon (DOC) levels such as 1–2 mg C/L (Kitis et al., 2002).

In the past decades, extensive research has been conducted to understand the stabilization of desalinated water by adjusting the pH and alkalinity, adding corrosion inhibitors, or through blending with pre-treated water for remineralization. However, little research has been undertaken to elucidate the formation and potential toxicity of DBPs in desalinated and blended waters. The purpose of this review is to document DBP formation in both thermal and membrane desalination systems and to suggest research requirements for the assessment of potential risks of DBPs which can form in distribution systems.

2. DBP formation during pre-treatment

2.1. DBPs of interest in disinfected water and DBP regulations

Disinfection of seawater and product water is essential in desalination plants to prevent biofouling and pathogen contamination, respectively. The types and concentrations of DBPs depend on several factors, but most specifically the type and amount of disinfectant used, the contact time, the organic and inorganic contents, the temperature, and the pH (Yu et al., 2015; Yang et al., 2013; Brookman et al., 2011; Agus and Sedlak, 2010; Abdel-Wahab et al., 2010; Kampioti and Stephanou, 2002; Mayankutty et al., 1995). To date, several classes of DBPs have been identified in drinking waters, specifically trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), and halonitromethanes (HNMs), iodinated THMs (I-THMs), iodinated HAAs (I-HAAs), haloketones (HKs), *N*-nitrosamines, bromate, and chlorite. Table S1 summarizes the physicochemical properties of the most prevalent DBPs and some emerging DBPs that are now the subject of research because of their potential toxicity. Enhanced brominated and iodinated DBP species have been observed in bromide/iodide rich waters (Ged and Boyer, 2014; Richardson et al., 2003; Kampioti and Stephanou, 2002). Among more than 600 DBPs identified and reported in the literature (Richardson, 1998), THMs and HAAs are the most abundant and commonly detected DBPs in chlorinated waters. Because of the potential health risks, many countries have established maximum contaminant limits (MCLs) of total THMs for

drinking water (Table 1). In the US, Stage 2 of the D/DBP Rule requires water utilities to comply with an MCL of 80 µg/L of THMs (i.e., chloroform [TCM], bromodichloromethane [BDCM], dibromochloromethane [DBCM], and bromoform [TBM]) (USEPA, 2006), and an MCL of 60 µg/L for five HAAs (i.e., monochloroacetic acid [MCAA], dichloroacetic acid [DCAA], trichloroacetic acid [TCAA], monobromoacetic acid [MBAA], and dibromoacetic acid [DBAA]) (USEPA, 2006) as the running annual average at individual locations in a distribution system. Although the standard for THMs in a few Asian nations and the European Union is 100 µg/L, some European countries have adopted a more stringent standard for THMs as shown in Table 1 (Karanfil et al., 2008; Yoon et al., 2003; Premazzi et al., 1997). Currently, there is no regulatory limit for HAAs in Europe. Unlike US policy, which emphasizes the running of annual averages, the compliance with European Union regulations is based on absolute maximums. The MCLs for bromate and chlorite in the US are 10 µg/L and 1.0 mg/L, respectively. Health guidelines for *N*-nitrosodimethylamine (NDMA), an emerging DBP, adopted by agencies around the world range from 9 to 100 ng/L (Table 1) (FPTCDW/FPTCHE, 2014; NHMRC/NRMMC, 2011; WHO, 2011; CDPH, 2011; GovOnt, 2006; MassDEP, 2004). World Health Organization (WHO) guidelines for dichloroacetonitrile (DCAN) and dibromoacetonitrile (DBAN) are 20 µg/L and 70 µg/L, respectively (WHO, 2011).

2.2. DBP formation in chlorinated seawater

Continuous or intermittent chlorination is generally used as pre-treatment of seawater prior to desalination processes to control biofouling problems associated with heat exchangers in thermal processes and membranes in the RO process. DBP formation is strongly dependent on two factors: chlorine dosage and contact time. Organic carbon content (i.e., TOC or DOC), temperature, and pH also play important roles in DBP formation. During seawater desalination, chlorine is the most commonly used disinfectant at intakes to control biofouling in the intake structures, equipment and on RO membranes. Chlorine is typically applied for an initial dose at 0.5–2.0 mg/L or for a target residual at 0.25–0.5 mg/L. To

maintain pre-determined residual chlorine concentrations, continuous chlorination is often used on an intermittent shock basis, with chlorine contact times ranging from 10 to 15 min to a few hours, depending on the seawater characteristics at intakes. Only a limited number of studies on DBP formation in chlorinated seawater used as feed water of desalination plants have been conducted because most DBPs do not remain in distillate during the thermal desalination process (i.e., MSF and MED) or in RO permeate. Table 2 shows DBP formation in chlorinated seawater samples collected from various locations worldwide and their related operational conditions. THM and HAA concentrations reported in most chlorinated feed water and cooling effluents of coastal power plants were well below 100 µg/L (Table 2) (Le Roux et al., 2015; Agus and Sedlak, 2010; Elshorbagy and Abdulkarim, 2006; Dalvi et al., 2000; Magara et al., 1996; Kojima et al., 1995; El Din et al., 1991; Mayankutty et al., 1989, 1991; Ali and Riley, 1989; Allonier et al., 1999). However, the occurrence of oil spills near intakes greatly increased THMs (mostly TBM) to more than 200 µg/L (El Din et al., 1991). Exceptionally high THM and HAA levels were reported in a pilot desalination plant, which was probably due to high chlorine doses and abundant precursors present in urban coastal areas characterized by high TOC (Agus et al., 2009). Relatively low levels of HANs (mostly DBAN, DCAN, and bromochloroacetonitrile [BCAN] among nine HAN species) and other DBPs such as bromophenols and I-THMs were also detected in chlorinated seawater (Le Roux et al., 2015; Agus and Sedlak, 2010). Under artificial lab conditions (e.g., longer contact times and higher chlorine dose conditions instead of typical desalination pre-treatment processes), chlorinated seawater of varying water qualities exhibited a wide-ranging amount of THM (60–165 µg/L) and HAA (3–122 µg/L) formation as well as HANs (4 µg/L) and HNMs (15–17 µg/L) (Simon et al., 2014; Shi et al., 2013; Abdel-Wahab et al., 2010; Fabbicino and Korshin, 2005; Kristiansen et al., 1996; Mayankutty et al., 1995).

The high bromide and iodide concentrations in seawater cause a difference in the formation and speciation in DBP as compared to disinfected fresh waters. The THM and HAA speciation patterns in typical chlorinated seawater and surface water are shown in Fig. 1

Table 1
Regulatory DBP limits and health guidelines (µg/L) for drinking water.

Country	THM	HAA	HAN	Bromate	Chlorite	Chlorate	NDMA
Switzerland ^a	25*						
Austria, Belgium, Italy ^b	30*						
Germany, Luxembourg, Sweden ^b	50*						
USA ^c	80*	60* (HAA5)		10*	1000*		0.01 (California) ^d 0.01 (Massachusetts) ^e 0.04 0.009 (Ontario) ^g
Canada ^f	100	80 (HAA5)		10	1000	1000	
China, Czech Republic, Ireland, Korea, Norway, Spain, Scotland, UK, Japan ^{b,h}	100*						
Australia ⁱ	250	150 (MCAA) 100 (DCAA) 100 (TCAA)		20	800		0.1
WHO ^j	100 (TCM) 60 (DCBM) 100 (DBCM) 100 (TBM)		20 (DCAN) 70 (DBAN)	10	700	700	0.1

*Maximum contaminant limit (MCL).

^a Goufopoulos and Nikolaou, 2005.

^b Karanfil et al., 2008.

^c USEPA, 2006.

^d CDPH, 2011.

^e MassDEP, 2004.

^f FPTCDW/FPTCHE, 2014.

^g GovOnt, 2006.

^h Yoon et al., 2003.

ⁱ NHMRC/NRMMC, 2011.

^j WHO, 2011.

Table 2
DBP formation in chlorinated seawater.

Source and location	DOC, mg/L	Br ⁻ , mg/L	THMs, µg/L	HAAs, µg/L	HANs, µg/L	Other DBPs, µg/L	Dose (mg/L) and contact time
Feed water of desalination plants							
Red Sea coast, Saudi Arabia ^a	0.98–1.62	60 (0.05: 1 ⁻)	6.18–18.41	5.35–6.86 (HAA9)	0.43–0.76 (DBAN)	1.90–2.57 (I-THMs)	0.25–0.5 (residual) or 0.7–1.0 (continuous)
Carlsbad, USA ^b	2.8		3.0–52	9.5–19 (HAA9)	0.5–1.9	0.3–0.6 (Br-phenols)	0.5–2.0 (initial), 2 h
Tampa Bay, USA ^c	4.3–10.9*	49–56	490–860	69–175 (HAA5)			2.5–5.0
Ruwais, UAE ^d	5.3–9.0*		<25	<14.5 (HAA5)			
Al-Jubnail, Saudi Arabia ^e			N/A	7.0 (HAA6)			0.2–0.25, 10–15 min
Okinawa, Japan ^f		68	35 (55: FP**)	N/A			1.0 (residual), 24 h
Ebara Corp, Japan ^g			15–25	N/A			0.3
Umm Al Nar, UAE ^h			78–95	N/A			0.2–0.3 (residual)
Jeddah, Saudi Arabia ⁱ	3.7*		3.3–24.0	N/A			0.5–2.0 (residual)
Eastern Coast, Saudi Arabia ^j	1.4–2.0*		3.1–27.9	N/A			
Shuwaikh, Shuaiba, Doha, Kuwait ^k	4.2–4.7		21.7–61.4	N/A			2.0 (residual)
Cooling effluents of power plants							
North Sea coast, France ^l			7.7–26.8 (TBM)	7.3–10.2 (DBAA)	0.9–3.6 (DBAN)	0.1–0.4 (Br-phenols)	0.2–0.77
Lab studies with seawater							
Barcelona, Spain ^m	0.93		154	N/A			1.0
Aquaria, undisclosed ⁿ		64.9 (0.06: 1 ⁻)	N/A	<122 (HAA9)		14.6–16.5 (HNMs)	1.0–3.0, 30 min
Doha, Qatar ^o	5.8	64	60–165	N/A			1.0–4.0, 168 h***
Seattle, USA ^p	0.5		107	99 (HAA9)	4.0 (DCAN, BCAN)		1.0, 8 h***
North Sea coast, Norway ^q	1.5	65	N/A	3.2–6.3 (HAA4)			0.7–3.5 (Cl ₂ /DOC), 24 h
Al-Jubnail, Saudi Arabia ^r	2.5*	79	80	N/A			10.0, 72 h***

*TOC, **Formation potential, ***Kinetic study, N/A not available.

- ^a Le Roux et al., 2015.
^b Agus and Sedlak, 2010.
^c Agus et al., 2009.
^d Elshorbagy and Abdulkarim, 2006.
^e Dalvi et al., 2000.
^f Magara et al., 1996.
^g Kojima et al., 1995.
^h El Din et al., 1991.
ⁱ Mayankutty et al., 1991.
^j Mayankutty et al., 1989.
^k Ali and Riley, 1989.
^l Allonier et al., 1999.
^m Simon et al., 2014.
ⁿ Shi et al., 2013.
^o Abdel-Wahab et al., 2010.
^p Fabbicino and Korshin, 2005.
^q Kristiansen et al., 1996.
^r Mayankutty et al., 1995.

(Le Roux et al., 2015; Sorlini and Collivignarelli, 2005; Kim et al., 2002). Here, TBM is the most abundant THM species present in chlorinated seawater with TCM barely observed, while TCM predominates followed by DCBM in chlorinated surface water. As for HAAs, chlorinated acetic acids (i.e., MCAA, DCAA, and TCAA) account for 16% and 73% of total measured HAAs in seawater and surface water, respectively. In both THMs and HAAs, brominated species are predominant in chlorinated seawater. In the US, only five HAAs (HAA5) are currently regulated. TBAA and DBCAA which are not included in HAA5 contributed over 40% of 9 HAA compounds that were measured in chlorinated seawater (Fig. 1c). Therefore, the compliance with MCL (e.g., 60 µg/L in the US) for the regulated HAA compounds is not representative for desalinated waters in which the majority of DBPs are highly brominated. All nine HAA species (HAA9) should be monitored and considered to assess the adverse impacts of DBPs formed in desalination systems.

2.3. DBP formation in seawater oxidized with alternative disinfectants; chloramines, chlorine dioxide, and ozone

Chloramines are widely used by drinking water utilities, particularly in the US, as an alternative to chlorine to comply with stringent regulations for THMs and HAAs since chloramines form lesser amounts of regulated THMs and HAAs (Seidel et al., 2005;

Hong et al., 2007). In the presence of high bromide, however, bromamines which are more reactive oxidants and decay rapidly can be produced from chloramines. Furthermore, chloramines form other types of DBPs including *N*-nitrosamines, HANs, HNMs, I-THMs, and I-HAAs as well as other unidentified compounds (Krasner et al., 1989; Bichsel and von Gunten, 2000; Richardson et al., 2000; Choi and Valentine, 2002; Mitch et al., 2003). Despite increasing attention on *N*-nitrosamines in chloraminated drinking waters, seawater is not likely a significant source of their precursors (Agus et al., 2009). Especially, the formation of I-THMs can be enhanced during chloramination compared to chlorination (Jones et al., 2011, 2012b), because the oxidation of hypiodous acid (HOI), the principal oxidant involved in I-THM formation, to iodate (IO₃⁻) is much slower for monochloramine (NH₂Cl) than for HOCl (Bichsel and von Gunten, 1999, 2000; Hua and Reckhow, 2007). I-THMs have been known to be much more cytotoxic and genotoxic than the regular four THM species (Richardson et al., 2008). Although chloramines are used to control biofouling in desalination intake structures and RO membrane systems and to minimize the membrane damage associated with free chlorine, the DBP formation in chloraminated seawater at intakes of desalination plants has not been extensively studied.

Chlorine dioxide (ClO₂) does not form appreciable levels of chlorinated DBPs such as THMs and HAAs under typical water

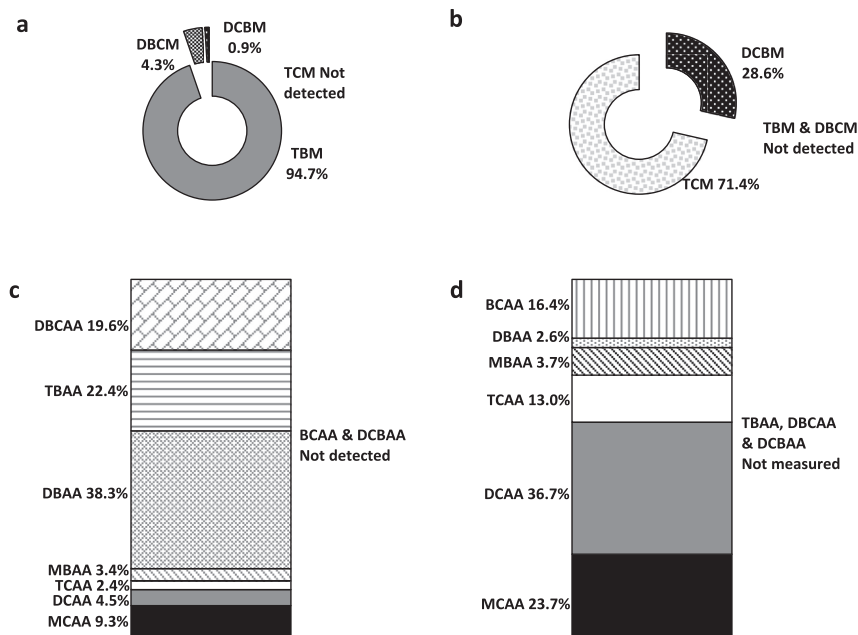


Fig. 1. Typical patterns of THM and HAA speciation in chlorinated seawater (a and c, Le Roux et al., 2015) and surface water (b and d, Sorlini and Collivignarelli, 2005; Kim et al., 2002).

treatment conditions (Aieta and Berg, 1986; Hua and Reckhow, 2007). Many drinking water utilities have been using ClO_2 as an alternative disinfectant to chlorine for pre-oxidation and post-oxidation to reduce the formation of THMs and total organic halide (TOX) due to its strong oxidizing capacity (Lykins and Griese, 1986; Linder et al., 2006). Even in the presence of high bromide, ClO_2 is a good disinfectant. However, the use of ClO_2 for disinfection produces inorganic DBPs such as chlorite (ClO_2^-) and chlorate (ClO_3^-). The average conversion of ClO_2 consumed to chlorite and chlorate in a surface water matrix during disinfection was estimated as approximated 68% and 9%, respectively (Korn et al., 2002). Although some RO desalination plants in the US and Spain use ClO_2 for pre-treatment and the UAE employs increasingly ClO_2 in thermal desalination plants as an alternative disinfectant (Agus et al., 2009), the DBP formation in seawater from ClO_2 or during pre-treatment for desalination has also not been the subject of study.

Due to the formation of elevated bromate (BrO_3^-), a probable human carcinogen, in the presence of high bromide, ozonation is generally not considered as a pre-treatment method at intakes of seawater desalination plants even though ozone (O_3), a strong oxidant, can effectively remove a variety of microorganisms resistant to other disinfectants (Westerhoff et al., 2005). Furthermore, the reaction between ozone and bromide produces either hypobromous acid (HOBr) or hypobromite ion (OBr^-). HOBr can react with organic matter to produce brominated DBPs. The use of ozone may change the reactivity of organic matter and consequently reduce the formation of THM and HAA during subsequent chlorination of many water supplies. However, HOBr formed in bromide-rich water such as seawater may lead to elevated TBM formation (Mayankutty et al., 1995; Brookman et al., 2011).

Ultraviolet (UV) irradiation and the use of potassium permanganate (KMnO_4) are also viable alternative water treatment techniques. Unlike chemical disinfection, UV light does not affect the biological stability of the water (Hijnen et al., 2006). Coupled with photocatalysts (e.g., H_2O_2 , TiO_2), the UV process either oxidized or completely removed the model organic compounds (Kang et al., 2003; Al-Bastaki, 2003). Although UV disinfection of seawater is not as common as drinking water and wastewater treatment, UV/

TiO_2 had faster disinfection kinetics than only UV_{254} light irradiation in a lab-scale experiment with synthetic seawater showing the effectiveness of photocatalytic treatment on seawater disinfection (Rubio et al., 2013). However, it has been shown that the presence of nitrate can lead to nitrogen incorporation into organic matter through nitrate photolysis (Kolkman et al., 2015; Thorn and Cox, 2012; Vione et al., 2001; Suzuki et al., 1987).

KMnO_4 has been widely used to control taste and odor problems, to eliminate iron and manganese, and to remove algae in raw water (Ma et al., 1997). However, KMnO_4 may produce manganese dioxide (MnO_2) by which I-DBP formation can be catalyzed in iodide-rich waters (Petruševski et al., 1996; Gallard et al., 2009). It has been reported that I-DBPs formed during the oxidation of I^- -containing waters by KMnO_4 and ClO_2 (Richardson et al., 2003; Hua and Reckhow, 2007; Jones et al., 2012b; Ye et al., 2012, 2013). Recently, Zhang et al. (2015) reported that iodoform (TIM) was the major I-THM species formed in I^- (20–800 $\mu\text{g/L}$) spiked surface water during oxidation using chlorine, KMnO_4 and ClO_2 . There is currently no available data in the peer-reviewed literature regarding DBP formation in seawater samples or in feed water of desalination plants disinfected with UV or KMnO_4 .

Some previous studies have examined DBP formation in seawater samples treated with alternative disinfectants and the results are summarized in Table 3. The formation of THMs in chloraminated seawater decreased by approximately 55% compared to chlorination, while ozonation increased THM formation (only TBM was observed with no trace of TCM) (Mayankutty et al., 1995). In addition, ozonation and chlorination of seawater produced more THMs as pH increased, whereas pH effects were not apparent on THM formation in chloraminated seawater. On the contrary, ClO_2 produced negligible amounts of THMs and HAAs at <10 mg/L of application (Simon et al., 2014; Yu et al., 2015). Longer contact times (i.e., >10 h) with a very high dose of 20–30 mg/L ClO_2 increased HAA formation by two orders of magnitude (Yu et al., 2015). On the other hand, 27% of DCAA and 73% of MCAA were observed at 0.5 mg/L of ClO_2 dose for 30 min of contact time. The speciation pattern shifted to brominated HAAs (i.e., mostly DBAA among measured HAA5) as ClO_2 dose and contact time increased

Table 3
DBP formation in seawater oxidized with alternative disinfectants.

Disinfectant	Source and location	DOC, mg/L	Br ⁻ , mg/L	THMs, µg/L	HAAs, µg/L	Other DBPs, µg/L	Dose (mg/L) and contact time
Chloramine	Al-Jubnail, Saudi Arabia ^a	2.5*	79	35	N/A		10.0, 72 h**
Chlorine dioxide	Barcelona, Spain ^b	0.93		0.34	N/A		0.2–0.4
	Busan, Korea ^c	4.6	60	N/A	0.4–2.5 (HAA5)		0.2–10, 72 h**
Ozone	Aquaria, undisclosed ^d		64.9 (0.06: 1 ⁻)	N/A	61 (TBAA)	16.5–34.8 HNMs	1.0–3.0, 15 min
	Halifax, Canada ^e	2.5	75***	22–33	N/A	0.5–4.5 mg/L (Bromate)	0.4–3.9
	Al-Jubnail, Saudi Arabia ^a	2.5*	79	180 (TBM)	N/A		5.0, 72 h**

*TOC, **Kinetic study, ***Seawater samples (44 mg/L Br⁻) were spiked with NaBr to achieve 75 mg/L Br⁻, N/A not available.

^a Mayankutty et al., 1995.

^b Simon et al., 2014.

^c Yu et al., 2015.

^d Shi et al., 2013.

^e Brookman et al., 2011.

(Yu et al., 2015). During ozonation of seawater only TBM and TBAA were predominant species (Shi et al., 2013; Brookman et al., 2011; Mayankutty et al., 1995). 17–35 µg/L of HNMs (dibromonitromethane [DBNM]) is the most abundant and 0.5–4.5 mg/L of bromate which is far above the US MCL of 10 µg/L were also reported in ozonated seawater samples (Shi et al., 2013; Brookman et al., 2011).

3. DBP formation in desalination plants prior to distribution

3.1. DBP occurrences in distillate and RO permeate

Thermal (i.e., MSF, MED) and membrane processes (i.e., RO) are two main categories of seawater desalination processes, with MSF being the dominant thermal process. Thermal desalination has been the major technology of choice for many years in the Middle East countries because of easily accessible fossil fuel resources and the poor water quality of the local feed water, which is characterized by extremely high salinity, high temperature, and high fouling potential for membrane systems, while membrane processes have been rapidly developed in the past decades and new RO desalination plants have been built outside of the Middle East (Greenlee et al., 2009). Typical desalination process schemes of MSF and RO plants are illustrated in Fig. 2. The feed water is separated into distillate and brine while passing through multiple stages at

different operating temperatures in MSF plants. A brine recirculation system consists of heat recovery stages and heat rejection stages. Regardless of the amount of DBPs formed in disinfected seawater, the chance of DBPs that carry over into distillate is very low in thermal desalination plants. Seawater RO plants often operate with either one or two RO passes, or even four passes depending on the design parameters and fresh water standards (Petry et al., 2007; Sauvet-Goichon, 2007; Wilf and Klinko, 2001). Before disinfected seawater is fed to the desalination process, dechlorination (reducing) reagents such as sodium bisulfite are often added to quench residual chlorine which may damage membrane materials. Anti-foaming and anti-scaling chemicals are also used. Due to the differences in desalination processes between thermal and membrane systems, higher DBP concentrations are typically observed in RO permeate than in thermal distillate, depending on the rejection performance of RO membranes.

Several studies have reported DBP occurrences in thermal distillate and RO permeate of full-scale seawater desalination plants or pilot plants where chlorine was used for the pre-treatment of seawater, and mostly THM levels have been measured and reported (Table 4). Compared to chlorinated intake water or feed water, 94% of THMs and ~100% of HAAs were removed during distillation in a MSF plant, while only DBAN was detected among four measured HAN species (i.e., DCAN, trichloroacetonitrile [TCAN], BCAN, and DBAN) both in thermal distillate and RO

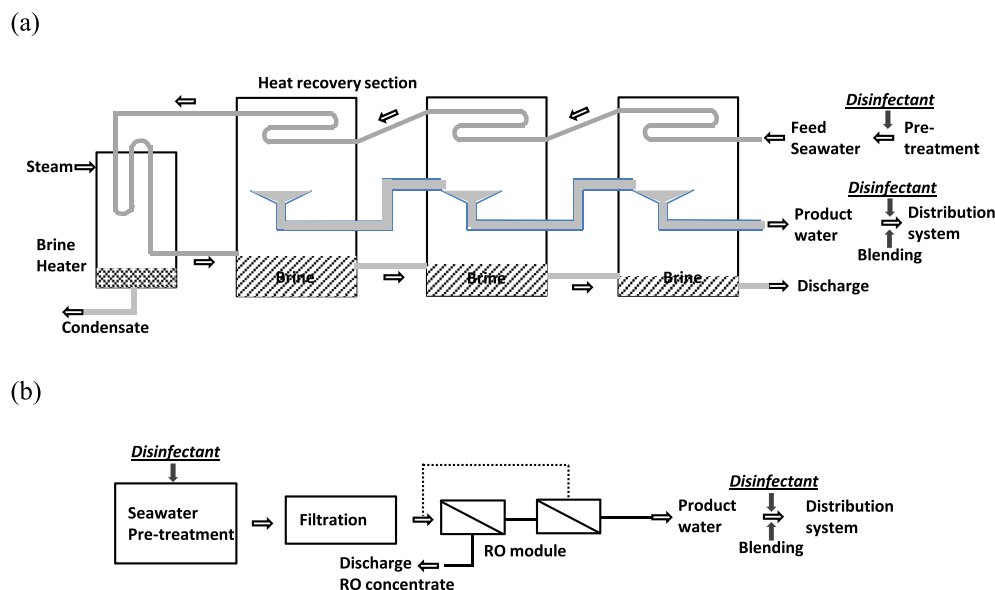


Fig. 2. Flow diagrams of MSF (a) and RO (b) desalination plants.

Table 4
DBP occurrences in thermal distillate and RO permeate of desalination plants.

Source and location	THMs, µg/L	HAAs, µg/L	HANs, µg/L	Other DBPs, µg/L	Reference
Thermal distillate					
Red Sea coast, Saudi Arabia	0.38	ND	0.45 (DBAN)		Le Roux et al., 2015
Al-Jubnail, Saudi Arabia		1.6 (HAA6)			Dalvi et al., 2000
Jeddah, Saudi Arabia	0.17–0.55				Mayankutty et al., 1991
Umm Al Nar, UAE	7–15 ^a				El Din et al., 1991
Eastern Coast, S. Arabia	0.09–3.48				Mayankutty et al., 1989
Shuwaikh, Shuaiba, Doha, Kuwait	2.7–22.8				Ali and Riley, 1989
RO permeate					
Red Sea coast, Saudi Arabia	0.36–66.7	ND–0.71	ND–1.98 (DBAN)	1.74–2.64 (I-THMs)	Le Roux et al., 2015
Carlsbad, USA	ND–6.7	2.1–6.1	0.58–0.79		Agus and Sedlak, 2010
Tampa Bay, USA	2.3–6.4	1.0–2.5			Agus et al., 2009
Okinawa, Japan	2.7				Magara et al., 1996
Ebara Corp, Japan	2.0–3.0				Kojima et al., 1995
Jeddah, Saudi Arabia	12.2–39.0				Mayankutty et al., 1991

^a Measured in tap water.

permeate (Le Roux et al., 2015). TBM was the dominant species (94.7% of THMs) in chlorinated feed water, while DCBM (39.5%) was the most abundant followed by DBCM (31.6%) and TBM (28.9%) in distillate, indicating that most of the TBM formed during pre-treatment with chlorine is removed during thermal processes. Either TCM, chloropicrin (TCNM), or haloketone (HK) was not detected in any processes (e.g., feed water and brine) of this MSF plant. In one study conducted by Dalvi et al. (2000), they detected 1.6 µg/L of HAAs in thermal distillate: TCAA (51%), DCAA (38%), and BCAA (10%), and no MCAA or DBAA. Other earlier studies showed various levels of THM occurrences in distillate (Mayankutty et al., 1989, 1991; Ali and Riliy, 1989), but there is no more information available on other DBP formation and speciation in seawater distillate.

THMs have been monitored in RO permeate fed with chlorinated seawater at different desalination plants worldwide (Table 4). Le Roux et al. (2015) reported DBP occurrences in two RO desalination plants as well as one MSF plant. One RO plant was equipped with polyamide (PA) membranes that can offer high permeate flux and adequate salt rejection (Fujioka et al., 2012) and the other with cellulose triacetate (CTA) membranes that are chlorine-resistant (Konagaya et al., 2001). Very low level of THMs (0.36 µg/L) were detected in the 1st pass permeate of the former RO plant with no detectable level of HAA and HANs, while THM levels in the latter RO plant increased from the chlorinated intake (14.5–18.4 µg/L) to the 1st pass permeate (39–67 µg/L). The observed difference in the THM occurrences is likely due to a combination of both different formation before and rejection by the membrane. In addition, reactive organic matter may adsorb and accumulate on the fouling layer of CTA RO membranes and then react with residual chlorine to cause possible THM and HAA formation in the permeate (Le Roux et al., 2015). Therefore, dechlorination before the membranes is recommended to avoid DBP formation during the desalination processes using RO membranes (especially, CTA). Interestingly, I-THMs were also detected in CTA RO permeate ranging 1.7–2.6 µg/L. Dibromiodomethane (DBIM) and bromodiodomethane (BDIM), which are the most cytotoxic I-THMs after iodoform (TIM) (Richardson et al., 2008), were detected in all samples collected at different processes (i.e., after dual media filters, after micron cartridge filters, RO permeate and concentrate) of RO plant after chlorination and even in the product water (0.92 and 0.58 µg/L, respectively). In general, concentrations of THMs and HAAs observed in RO permeate were lower than those in chlorinated seawater intakes (Agus and Sedlak, 2010; Agus et al., 2009; Magara et al., 1996; Kojima et al., 1995; Mayankutty et al., 1991). Although extremely high levels of THMs and HAAs (i.e., 490–860 and 69–175 µg/L, respectively) were observed in a chlorinated intake

due to high TOC and high chlorine dose and contact time, >99% of DBP removals during pilot-scale testing using Hydranautics SWC membranes at the Tampa Bay desalination plants were reported (Agus et al., 2009). It has been known that the rejection rates of charged compounds such as HAAs are higher than those of THMs or other uncharged low-molecular weight compounds which can pass through RO membranes (Xu et al., 2005; Bellona et al., 2004).

3.2. Rejection of DBPs by RO membranes

Membrane fouling by inorganic, organic, and biological foulants is a major inhibitor of RO membrane performance. Adsorption, size exclusion, and electrostatic repulsion may affect the rejection rates of trace organic compounds (Yangali-Quintanilla et al., 2009; Van der Bruggen et al., 1999; Berg et al., 1997). In terms of DBP rejection by RO membranes, it has been reported that removal efficiencies of THMs and HAAs were >60% and >90%, respectively (Xu et al., 2005; Chalati et al., 2009; Kimura et al., 2003; Van der Bruggen and Vandecasteele, 2003; Waniek et al., 2002). A relatively high rejection of HAAs is attributed to their pKa values that are lower than the typical operating pH of RO processes. HAAs are likely to be negatively charged and consequently electrostatically repulsed from the negatively charged membranes (Verliefde et al., 2008). However, lower rejection rates were reported for HANs (>50%) and NDMA (10–50%) (Linge et al., 2013; Agus and Sedlak, 2010; Fujioka et al., 2013, 2015; Farré et al., 2011; Steinle-Darling et al., 2007). Such low rejection rates of nitrogenous DBPs may significantly affect the water quality of RO permeate and blended waters, especially when wastewater impacted source water is disinfected with chloramines. Compound-specific properties (e.g., molecular size, charge, hydrophobicity, solubility, and diffusivity) and membrane properties (e.g., pore size, charge, permeability, and hydrophobicity) as well as operational conditions such as temperature, pH, and ionic strength can be critical factors governing the permeation of DBPs through membranes. Linge et al. (2013) investigated several chemical properties of DBPs with respect to RO rejection. Rejection of HAAs were consistently high (>90%) and did not vary with log K_{OW} (octanol–water partition coefficient), while for all other DBPs, present as neutral molecules, rejection was variable and decreased with decreasing log K_{OW}. Doederer et al. (2014) observed that increasing transmembrane flux led to increased rejection of DBPs due to hydrophobic interactions between DBPs and the membrane, and there was no discernible impact on rejection by RO with change in crossflow velocity. They also observed that increasing temperature led to a considerable decrease in DBP rejection, and increasing pH and ionic strength did not have discernible impact on DBP rejection during low pressure

RO filtration. Using multiple linear regression, the following equation was proposed to predict the passage of neutral DBPs through an RO membrane;

$$\text{Rejection (\%)} = -38.7 + 0.6 \text{ PSA} + 1.5 \text{ MV} - 5.9 \text{ DM} - 1.3 \text{ T} + 0.3 \text{ F} \quad (R^2 = 0.901)$$

where, PSA, MV, DM, T, and F denote polar surface area, molecular volume, dipole moment, temperature, and flux, respectively. For the normalized model conducted to compare the regression coefficients, the impact of these parameters follows the order: PSA > MV > DM > Temperature > Flux.

3.3. DBP occurrences in brine and RO concentrate

Either brine or RO concentrate discharges may significantly affect the marine environment, especially in the vicinity of outfalls if not diluted sufficiently, because discharges may contain residues of pre-treatment and cleaning chemicals (e.g., disinfectants, coagulants and coagulant aids, anti-scalants, and anti-foaming agents), DBPs, and even heavy metals released due to corrosion. Salinity and temperature altered by constant discharges can also influence the marine ecosystem (Miri and Chouikhi, 2005; Lattemann and Höpfer, 2008). However, the impact of brine discharges from seawater desalination plants on aquatic organisms has not been well studied. Therefore, occurrences of DBPs and their potential impact on both the water quality and aquatic community in impacted ocean areas should be investigated. The high temperatures created in thermal desalination processes cause the rejection of most volatile DBPs through the venting systems; which greatly reduces the presence of DBPs in the brine blowdown of MSF plants (Le Roux et al., 2015; Saeed et al., 1999; Mayankutty et al., 1991). However, very high THMs (2900 µg/L) were reported in the condensed steam of a MSF plant in Kuwait (Ali and Riley, 1989). DBP occurrences in brine and RO concentrate of seawater desalination plants from several previous reports are listed in Table 5. In addition to THMs, HAAs, and HANs, low levels of I-THMs and brominated phenols were also reported in a few RO concentrates (Le Roux et al., 2015; Agus and Sedlak, 2010).

4. DBP formation in distribution systems of desalination plants

4.1. DBP occurrences in the finished water

Due to relatively low DBP levels observed and very low levels of natural organic matter expected in distillate, further DBP formation in the finished water is not likely to occur in the distribution systems of thermal desalinated waters. However, thermal desalinated waters are often blended with treated brackish well water or untreated seawater for stabilization prior to the distribution network. According to a survey along the eastern coast of Saudi Arabia, THMs in blended potable water (i.e., desalinated water + chlorinated well water) ranged from 3.1 to 12.8 µg/L with TBM > CDBM > DCBM > TCM (Mayankutty et al., 1989) where TBM constituted 61–86% of the total THMs in the 13 distribution points. In terms of seasonal variations, samples collected from the distribution systems of eight major cities in Saudi Arabia showed that THMs occurred in all the water supplies ranging from 0.03 to 41.7 µg/L, and the median total THM concentrations in several cities were higher during the summer than during the winter (Fayad, 1993). In addition, THM concentrations were low in cities that did not mix groundwater and desalinated water. In another study, 10–40% higher THMs during summer months than winter months

were also reported in Dhahran, Saudi Arabia (Chowdhury, 2013), indicating that temperature is an important factor governing the formation kinetics of THMs. However, Al-Mudhaf et al. (2009) reported contrasting results in that higher THMs in winter were observed in Kuwait, where drinking water is processed by blending desalinated seawater with 5–10% brackish water. THMs in drinking water ranged from 5.0 to 91.0 µg/L with average 30.1 µg/L (Al-Mudhaf et al., 2009) and HAAs ranged from 5.1 to 52.0 µg/L (Al-Mudhaf and Abu-Shady, 2008). For an analysis of water samples (desalinated or desalinated + groundwater disinfected with HOCl) collected from different places in Saudi Arabia, 3.4–75.0 µg/L of bromate was observed and 10 out of 12 samples exceeded regulatory threshold (Alsohaimi et al., 2012). These elevated bromate levels may be attributed to catalytic disproportionation of HOBr generated from the reaction between bromide and HOCl in the presence of CuO which accumulate on the surface of the pipes during chlorination of bromide-containing waters (Liu et al., 2012).

4.2. DBP formation in blended waters

Reported DOC levels in seawater RO permeates are very low, ranging from <0.1 to 0.6 mg C/L (Farré et al., 2013; Agus et al., 2009; Agus and Sedlak, 2010), while Br⁻ (i.e., 250–600 µg/L) and I⁻ (i.e., <4–16 µg/L) concentrations are high enough to affect brominated/iodinated DBP formation in distribution systems (Duranceau, 2010; Agus et al., 2009; Magara et al., 1996; Ali-Mohamed and Jamali, 1989). Upon chlorination for post-disinfection, bromide reacts with chlorine to form hypobromous acid (HOCl + Br⁻ → HOBr + Cl⁻; HOBr, pK_a 8.7) which is a better substitution agent than hypochlorous acid (HOCl, pK_a 7.5) (Eigen and Kustin, 1962). Iodide reacts with chlorine and bromine to form hypoiodous acid (HOCl + I⁻ → HOI + Cl⁻ or HOBr + I⁻ → HOI + Br⁻; HOI, pK_a 10.6), and HOI is further oxidized to iodate (IO₃⁻) at longer chlorine contact time, thus decreasing its potential reactivity to form iodinated DBPs. However, chloramines do not further oxidize HOI to iodate, and the presence of HOI can cause the formation of highly toxic iodinated or bromo/iodo-DBPs. In addition, the presence of high bromide in desalinated waters produces more reactive substitution agents (e.g., bromamines) (Lei et al., 2004) which produce brominated DBPs and can cause instability of the residual disinfectant in the distribution system.

DOC levels in treated surface and ground waters are generally higher than those in seawater RO permeate, since conventional water treatment processes are marginally effective in removing the hydrophilic and neutral NOM (natural organic matter) fractions. These fractions are responsible for the DBP formation upon post-disinfection with chlorine or chloramine (Kitis et al., 2002). Bromine is also more effectively incorporated into low SUVA₂₅₄ (specific UV absorbance at 254 nm, an index of aromaticity), low molecular weight, and hydrophilic NOM fractions than high SUVA₂₅₄, high molecular weight, and hydrophobic fractions (Kitis et al., 2002; Liang and Singer, 2003; Hua et al., 2006). As a result, blending RO permeate with treated surface waters prior to the application of post-disinfectants can create circumstances favoring the formation of significantly more toxic DBPs, even though their total mass concentration may be low, and the final water quality may be in compliance with DBP regulations.

Previous DBP studies show that pH and temperature are important variables influencing the bromine and iodine incorporation (Jones et al., 2012a; Plewa et al., 2004). Generally, I-THM formation from preformed chloramines decreased as pH increased for a Br⁻/I⁻ mass ratio of approximately 10 (Jones et al., 2011, 2012a, 2012b). Greater formation at lower pH was due to monochloramine decomposition and the formation of additional oxidants and substituting agents, most notably chlorine. For pH ≥ 7.5, I-THM

Table 5
DBP occurrences in thermal brines and RO concentrates.

Source and location	THMs, µg/L	HAA5, µg/L	HANs, µg/L	Other DBPs, µg/L
Thermal brine				
Red Sea coast, Saudi Arabia ^a	9.53 (brine recycle)	5.49 (brine recycle)	1.46 (brine recycle)	
	0.53 (brine blowdown)	4.50 (brine blowdown)	0.50 (brine blowdown)	
Doha west and Al-Zor, Kuwait ^b	1.0–2.0			
Jeddah, Saudi Arabia ^c	12.7–17.8			
Shuwaikh, Kuwait ^d	2900 (condensed steam)			
RO concentrate				
Red Sea coast, Saudi Arabia ^a	6.19 (1st pass conc. in plant 1)	0.78 (1st pass conc. in plant 1)	ND (1st pass conc. in plant 1)	1.6–2.0
	22.6–52.9 (1st pass conc. in plant 2)	5.7–7.2 (1st pass conc. in plant 2)	0.6–1.2 (1st pass conc. in plant 2)	(I-THMs in plant 2)
Carlsbad, USA ^e	5.0–61.0	17.0–27.0	0.78–3.1	0.53–0.96 (Br-phenol)
Ebara Corp, Japan ^f	24.0–39.0			

^a Le Roux et al., 2015.

^b Saeed et al., 1999.

^c Mayankutty et al., 1991.

^d Ali and Riley, 1989.

^e Agus and Sedlak, 2010.

^f Kojima et al., 1995.

formation depended on I^-/DOC ratio and the NOM characteristics of the source water. I-THM yield increased with increasing I^-/DOC ratio and decreasing $SUVA_{254}$ of the water. At pH 6, dichloroiodomethane and bromochloroiodomethane were the dominant species at the common Br^- and I^- levels. For $pH \geq 7.5$ and for elevated Br^- and I^- levels, iodoform was the dominant species regardless of the Br^-/I^- ratio. These results indicate the importance of examining the effects of pH and temperature on DBP formation in desalinated waters and/or blended waters.

4.3. Toxicity of desalinated waters

In a study with coagulated surface water collected from three different DWTPs and RO permeate from a desalination plant, the assessment of DBP formation potential and toxicity has shown that all reactive modes (i.e., cytotoxicity, genotoxicity, DNA damage, and oxidative stress) of action were induced to a greater degree after chlorination than chloramination, and the effect was higher if the source water had a higher organic matter content (Farré et al., 2013). On the contrary, Yang and co-workers found that while water disinfected with chlorine was less cytotoxic, it was more genotoxic than water disinfected with chloramines (Yang et al., 2014). Treated water samples collected from a DWTP were disinfected with free chlorine (2 mg/L) or preformed chloramine (2 mg/L as total Cl_2) for 48 h at pH 8 and then extracted using XAD resins (XAD-2 and XAD-8). Chinese hamster ovary (CHO) cell was used for the mammalian toxicity studies with concentrated water samples. Adding Br^- and I^- to both disinfectants increased cytotoxicity and genotoxicity, with a greater response observed with monochloramine (NH_2Cl) disinfection. Both cytotoxicity and genotoxicity were highly correlated with total organic bromide (TOBr) and total organic iodide (TOI), while toxicity was weakly and inversely correlated with total organic chloride (TOCl). Therefore, disinfection should be taken with great care, especially when using source waters with elevated Br^- and I^- levels. Increasing evidence shows that brominated and iodinated DBPs are more toxic than their chlorinated analogues (Plewa and Wagner, 2009; Plewa et al., 2004; Richardson et al., 2007; Komaki et al., 2014). According to a comprehensive genotoxicity/cytotoxicity database of the DNA damage and cytotoxicity study with CHO cell assays, halogenated DBPs follow a toxicity order of $I^- > Br^- > Cl^-$ as shown in Fig. 3 (Yang et al., 2014). The origins of the data in Fig. 3 are from Plewa and Wagner (2009) and Richardson et al. (2008). Iodinated DBPs are more toxic than brominated DBPs, which in turn are much more toxic than

chlorinated DBPs (Muellner et al., 2007; Plewa et al., 2004, 2008). Iodoacetic acid (IAA) is twice as genotoxic as bromoacetic acid (BAA), and BAA is an order of magnitude more genotoxic than chloroacetic acid (CAA) (Plewa et al., 2010). Consequently, compounds with iodo-groups have enhanced mammalian cell cytotoxicity and genotoxicity, compared to their brominated and chlorinated analogues (Richardson et al., 2008). The same pattern was also observed in both *Salmonella*, and in new human cell data (Attene-Ramos et al., 2010; Escobar-Hoyos et al., 2013). This epidemiology and toxicology research suggest that adverse human health effects, particularly adverse pregnancy outcomes and bladder cancer, are associated with the presence and elevated concentration of brominated DBPs (Waller et al., 1998; Swan et al., 1998; Villanueva et al., 2004; Jeong et al., 2012; Rivera-Nunez and Wright, 2013). Despite these adverse health effects, no systematic investigation has been taken to elucidate the formation and speciation of DBPs and the toxicity of seawater desalinated waters and blended waters.

5. Future research needs

Many studies thus far have explained the basic understanding with respect to DBP formation and speciation during seawater desalination processes. However, a more systematic understanding

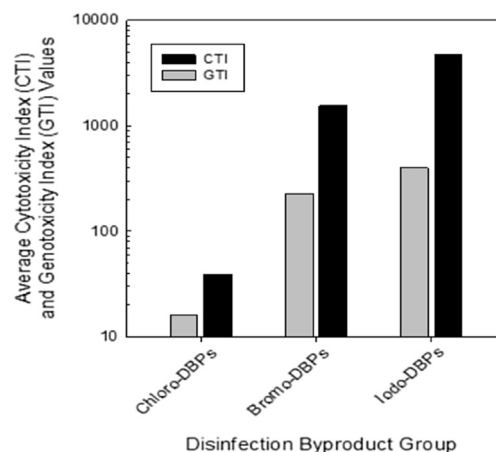


Fig. 3. Relative toxic potencies of chloro, bromo, and iodo-DBPs in inducing chronic cytotoxicity or acute genotoxicity in mammalian cells. Adopted with permission from Yang et al. (2014). Copyright (2015) American Chemical Society.

is needed to control DBP formation and to reduce the toxicity of desalinated water blended with different source waters.

- Systematic DBP studies in full-scale seawater desalination plants are required to provide profiles of non-regulated emerging DBPs (e.g., HANs, HNMs, *N*-nitrosamines, I-THMs) at each process and to articulate DBP formation and speciation during seawater disinfection with chlorine and alternative disinfectants.
- Additional research is needed to characterize the organic matter present in seawater, which contains DBP precursors, and to assess effects of organic matter developed during various temporal events (e.g., algal blooms and oil spills) on DBP formation and speciation.
- No data are available for the reactions of disinfectants with antiscalants (e.g., BaSO₄, CaSO₄, SrSO₄, CaCO₃, and silica) or anti-foaming agents (e.g., acylated polyglycols, fatty acids and fatty acid esters, silicon-based compounds). Although these chemicals are not expected to influence DBP formation during desalination, confirmation experiments will be beneficial; furthermore, their environmental fate and degradation products which may affect the marine ecosystem need to be studied.
- Because THMs and HAAs account for only about 50% of TOX, an analysis of TOX changes during desalination is needed to understand the behavior of unidentified DBPs and to explore the relationship between DBP speciation and measured TOX values in desalinated water.
- DBP formation and speciation in blended water of seawater RO desalinated water with other source waters, especially with different organic matter characteristics (e.g., wastewater impacted and algal impacted) must be studied to optimize mixing ratios and to determine appropriate types of fresh source water.
- DBP studies in desalinated waters produced from emerging and innovative membrane-based technologies (e.g., forward osmosis, membrane distillation, electrodialysis, and their potential hybrids with seawater RO) and blended waters are warranted.
- The change of toxicity caused by the formation of brominated DBPs should be investigated when RO desalinated water is blended with treated fresh water at different mixing ratios, pH, and temperatures.
- TOX (including TOCl, TOBr, and TOI) should be measured in desalinated water or blended water and assessed to see if they can be used as indicators of water toxicity.

6. Conclusions

Although many studies have been undertaken to elucidate the formation and speciation of DBPs in DWTPs using fresh surface water systems, very little data is available detailing the formation of DBPs in seawater desalination plants. Most of these have focused on THMs and HAAs in chlorinated feed water, thermal distillate, RO permeate, and the product water. Only a few studies have monitored HANs, I-THMs, and brominated phenols in desalination plants. Although seawater desalination is a well-established technology, very little information exists about the creation of DBP profiles during thermal and membrane desalination processes and the toxicity of the finished water blended with other source waters. The type and amount of disinfectants, elevated bromide/iodide, and NOM concentrations and characteristics affect DBP formation and speciation in desalinated water. Temperature and pH are also crucial factors governing bromide/iodide incorporation, which in turn increases water toxicity. However, controlling DBP formation in distribution networks and assessing the human exposure and

health risks require more effort and additional research due to limited information currently available. With increasing attention to water recycling and reuse technologies, seawater desalination is becoming an increasingly important source of drinking water. Further improvements in controlling harmful DBP formation will allow a wider application of seawater desalination to address the issue of global water scarcity.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2015.05.040>.

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