

Disinfection by-products in desalinated and blend water: formation and control strategy

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ABSTRACT

Desalinated seawater is the major source of drinking water in many countries. During desalination, several activities including pretreatment, desalination, stabilization, mixing, storage and distribution are performed. Few disinfectants are used during these activities to control the biofouling agents and microbiological regrowth. The reactions between the disinfectants and natural organic matter (NOM), bromide and iodide form disinfection by-products (DBPs) in product water. The product water is stabilized and mixed with treated freshwater (e.g., groundwater) to meet the domestic water demands. The DBPs in desalinated and blend water are an issue due to their possible cancer and non-cancer risks to humans. In this paper, formation and distribution of DBPs in different steps of desalination and water distribution systems prior to reaching the consumer tap were reviewed. The variability of DBPs among different sources and desalination processes was explained. The toxicities of DBPs were compared and the strategies to control DBPs in desalinated water were proposed. Several research directions were identified to achieve comprehensive control on DBPs in desalinated water, which are likely to protect humans from the adverse consequences of DBPs.

Key words | control of DBPs, desalinated and blend water, desalination, disinfection by-products, human exposure and risk, toxicity of DBPs

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INTRODUCTION

Coastal regions are home to approximately two billion people. At least 14 mega cities with populations of more than ten million each and two-fifths of the major cities with populations between one and ten million are located in coastal areas (Tibbetts 2002). Seawater desalination has become the most common method to satisfy domestic water demands in coastal regions and in regions with a water crisis. Desalination of seawater is practised in many countries in the Middle East, the Mediterranean Basin, as well as in Australia and the USA (Reuther 2000; Dawoud 2005; De Munari *et al.* 2009; Greenlee *et al.* 2009) with the Middle East countries producing the most (Lattemann & Höpner 2008). For desalination, two main processes – thermal (MSF: multi-stage flash; MED: multi-effect distillation) and

membrane (RO: reverse osmosis) – are used. In the Arabian Gulf and Red Sea, the dominant processes are MSF and MED while in the Mediterranean Sea, the dominant process is RO (Lattemann & Höpner 2008). The MSF processes produce approximately 63.3% of desalinated water in the Arabian Gulf while RO and MED contribute 23.4% and 13.3%, respectively (Lattemann & Höpner 2008). Higher levels of seawater pollution and low energy costs are probably the main causes for the abundance of MSF processes.

During desalination, feed water is collected through different intakes while open collection systems are widely used. Chlorine (Cl₂) in the form of HOCl or OCl⁻ is typically applied during pretreatment to prevent bacterial growth and biofouling, and to enhance the performance of

filters. Pretreatment is performed using continuous or intermittent chlorination with initial doses of 0.5–2.0 mg/L to achieve the target residuals of 0.25–0.5 mg/L (Kim *et al.* 2015). Chlorine is also applied in different stages of desalination and in final disinfection to inactivate microorganisms (MWH 2005). Some other disinfectants, such as chloramines (e.g., NH_2Cl), ozone (O_3) and chlorine dioxide (ClO_2) are also used (MWH 2005). The disinfectants react with natural organic matter (NOM) and inorganic compounds (e.g., ammonia, chloramine, Fe^{2+} , Mn^{2+} , S^{2-} , bromide, iodide, etc.) to form disinfection by-products (DBPs), many of which have cancer and non-cancer risks to humans (USEPA 2016). Past studies reported that seawater could contain bromide and iodide in the ranges of 50,000–80,000 and 21–60 $\mu\text{g/L}$, respectively (Ali-Mohamed & Jamali (1989); Kristiansen *et al.* 1996; Agus *et al.* 2009; Duranceau 2010). The thermal desalination processes remove bromide and iodide to non-detectable levels. Although RO processes remove >99% bromide, RO permeate contains considerable amounts of bromide (250–600 $\mu\text{g/L}$) and iodide (<4–16 $\mu\text{g/L}$), which can increase brominated (Br-DBPs) and iodinated (I-DBPs) DBPs in desalinated and blend water (Kutty *et al.* 1995; Magara *et al.* 1996; Kim *et al.* 2015; Le Roux *et al.* 2015; Postigo *et al.* 2017). The Br-DBPs and I-DBPs are more cytotoxic and/or genotoxic than chlorinated DBPs (Cl-DBPs) (Richardson *et al.* 2007; Agus & Sedlak 2010; Wahab *et al.* 2010; Shi *et al.* 2013; Kim *et al.* 2015).

In the Middle East, desalinated water is often mixed with treated brackish groundwater, pH adjusted and chlorinated prior to distribution (Duranceau 2010). The chlorinated blend water remains in water distribution systems (WDS) or storage tanks for a few hours to several days during transportation from the coasts to inland cities, which can increase concentrations of DBPs (Tawabini *et al.* 2011; Kim *et al.* 2015). The RO permeate, which is rich in bromide, is mixed with treated brackish groundwater, rich in NOM, leading to the increased formation of Br-DBPs and I-DBPs. Past studies reported higher fractions of Br-DBPs in desalinated and blend water (Kutty *et al.* 1995). To date, over 100 DBPs have been reported in drinking water while approximately 600 DBPs are likely to be present (Richardson *et al.* 2007). The most investigated DBPs in desalinated and blend water are trihalomethanes (THMs)

and haloacetic acids (HAAs) (Kim *et al.* 2015). Several emerging DBPs, including iodo-THMs (I-THMs), halonitromethanes (HNMs), haloacetonitriles (HANs), bromate, haloamides, nitrosamines, 3-chloro-4-(dichloromethyl)-5-hydroxyl-2(5H)-furanone (MX) and MX homologues, aromatic halogenated DBPs, halo- and nitro phenols can also be present (Richardson 2003; Richardson *et al.* 2008, 2010; Agus *et al.* 2009; Agus & Sedlak 2010; Richardson & Postigo 2012; Kim *et al.* 2015; Le Roux *et al.* 2015; Postigo *et al.* 2017). Many DBPs are of concern due to their possible cancer and non-cancer risks (King & Marrett 1996; Cantor *et al.* 1998, 1999; Hildesheim *et al.* 1998; Savitz *et al.* 2006). Some of the effects associated with DBP exposure include increased rates of bladder and colorectal cancers, pre-term deliveries, neural tube defects, miscarriages, cardiac irregularities and low birth weights (King & Marrett 1996; Cantor *et al.* 1998, 1999; Hildesheim *et al.* 1998; Savitz *et al.* 2006). Regulatory agencies, such as the United States Environmental Protection Agency (USEPA), Health Canada, World Health Organization (WHO) and the European Union (EU) have set the guideline limits for DBPs. USEPA has limits of 80 and 60 $\mu\text{g/L}$ for THMs and HAA₅, respectively (USEPA 2016). Health Canada has limits of 100 and 80 $\mu\text{g/L}$ for THMs and HAA₅, respectively (Health Canada 2017). The limits for bromate and chlorite in Canada are 10 and 1,000 $\mu\text{g/L}$, respectively (Health Canada 2017). The WHO guidelines for chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (TBM) are 300, 60, 100 and 100 $\mu\text{g/L}$, respectively (WHO 2011). The WHO limits bromate and chlorite to 10 and 700 $\mu\text{g/L}$, respectively (WHO 2011).

To date, many studies have focused on DBPs in freshwater sourced supply water. Despite the public health relevance, not much is known about DBPs in desalinated and blend water, and the consequent exposure and risk. Formation of DBPs in desalinated water can vary depending on sources and type of desalination processes. Further, DBPs in different stages of desalination require better understanding to control DBPs in desalinated and blend water. In this study, research on DBPs in desalinated and blend water was reviewed. Formation of DBPs in different stages of desalination was investigated. Variability of DBPs depending on desalination and sources was characterized. The effects of

bromide on the formation and distribution of DBPs in desalinated water was investigated. The cytotoxicity and genotoxicity of DBPs on mammalian cells were compared. Strategies were identified to better control DBPs in tap water. Finally, future research needs to control DBPs in desalinated and blend water were outlined.

DESALINATION PROCESS

Desalination processes are classified into two categories: thermal and membrane separation. Thermal process is the oldest method, in which steam is collected by boiling seawater. Thermal process is divided into three types: MSF, vapour compression (VC) and MED with MSF being dominant in the Middle East region. Among the membrane separation techniques, RO processes are

mainly used (Kim *et al.* 2015). In MSF processes, seawater is heated while passing through multiple heating stages. Through different heating stages, the brine recirculation system contains heat recovery and heat denial units. Figure 1(a) illustrates a schematic of the MSF process where pressure decreases from the beginning to the end. The first chamber receives seawater, which is heated by a brine heater. The pressure around the first chamber is lower than the brine heater, leading to the formation of steam of a fraction of the seawater. The remaining water is passed through a series of supplementary stages with increased vacuum pressure. The vapour is condensed into fresh water and collected as potable water. The heat produced through condensation of vapour is generally recycled and reused to pre-heat the seawater.

RO processes are also used in Saudi Arabia, Bahrain, Jordan, Australia, UAE, Egypt and the USA (Patel &

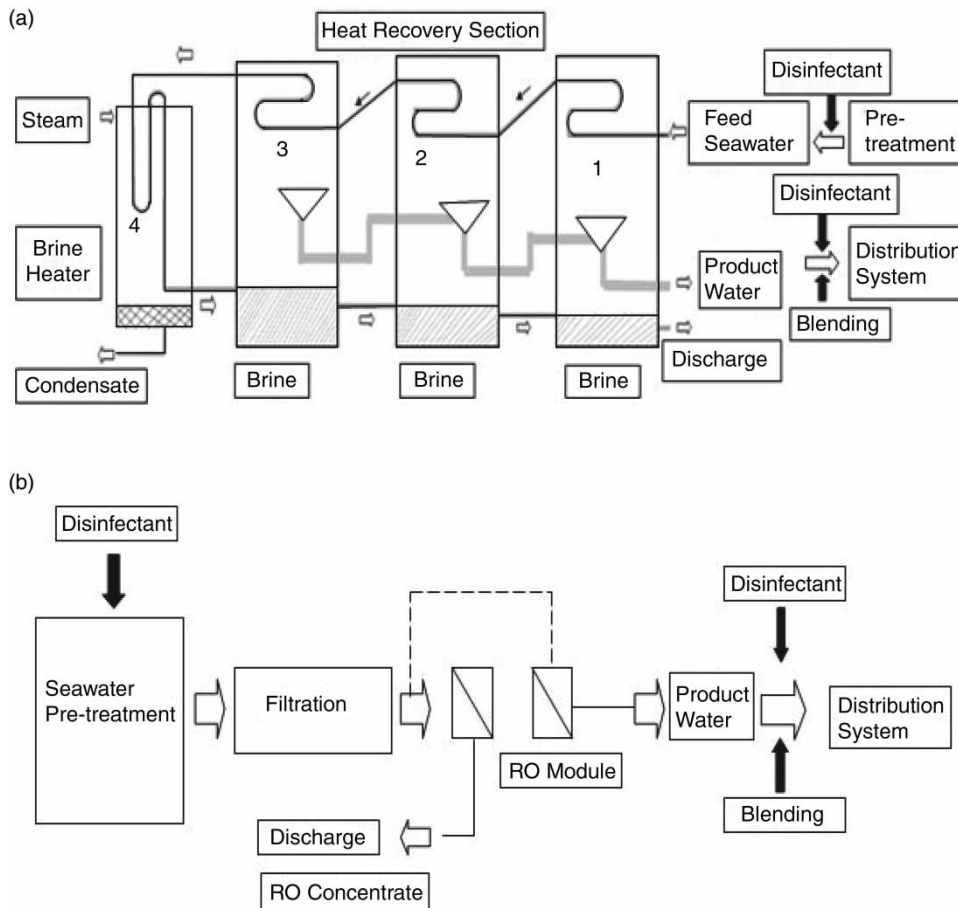


Figure 1 | Schematic of the main desalination processes in Saudi Arabia: (a) multistage flash (MSF) process and (b) reverse osmosis (RO) process.

Oakland 1976; Al Arrayedh *et al.* 1987; Ahmed *et al.* 2001; Djebedjian *et al.* 2007; Greenlee *et al.* 2009). RO processes work with one, two or four RO passes depending on source water quality, product water standards, and regulation and design constraints. Figure 1(b) shows a schematic of the RO process. In RO processes, water is separated from a pressurized saline solution using the water-permeable membrane. The seawater is pretreated to remove large particles using screening, and disinfectant (typically chlorine) is used to inactivate the bio-fouling agents before passing through the RO process. A dechlorinating reagent, such as sodium bisulfate, is often used to control the damage of membrane materials. In this stage, anti-foaming and anti-scaling chemicals are used to increase membrane efficiency. Concentrations of DBPs in RO permeate depend on the rejection efficiency of membranes. Past studies reported higher DBPs in RO effluent than the thermal processes (Al-Otoum *et al.* 2016; Kim *et al.* 2015; Le Roux *et al.* 2015).

DBP FORMATION

Pretreatment of feed water

Brackish water or seawater is used as feed water for desalination. The estuaries and aquifers in coastal areas generally contain brackish water with lower salinity than seawater. Feed water is collected from open or sub-surface intakes, beach wells and infiltration galleries (Jones & Campbell 2005; WRA 2011). The intake water is screened, followed by pretreatment using continuous or intermittent chlorination with initial doses in the range of 0.5–2.0 mg/L. The chlorination assists in coagulation, controls algae in sedimentation basins and reduces mud-ball formation (Kim *et al.* 2015). The unintended reactions between NOM and chlorine form DBPs, many of which are mutagenic and can pose risk to humans (Richardson *et al.* 2007). Formation of DBPs depends on several factors including the type and dose of disinfectants, concentration and distribution of NOM, pH, temperature, contact time, and bromide and iodide concentrations (Kutty *et al.* 1995; Yang *et al.* 2015; Kim *et al.* 2015; Gong *et al.* 2016; Ioannou *et al.* 2016; Jiang *et al.* 2017, 2018). Bromide and iodide ions in feed water

can increase Br-DBPs and I-DBPs during pretreatment (Gong *et al.* 2016; Ioannou *et al.* 2016; Jiang *et al.* 2017, 2018).

Table 1 summarizes DBPs in pretreated seawater for desalination, seawater under controlled laboratory studies and saline waste effluents treated with different disinfectants. In chlorinated seawater (pretreated seawater) collected from desalination plants, THMs and HAAs were in the ranges of 0–680 and 0–175 µg/L, respectively (Ali & Riley 1989; El Din *et al.* 1991; Kojima *et al.* 1995; Kutty *et al.* 1995; Magara *et al.* 1996; Allonier *et al.* 1999; Dalvi *et al.* 2000; El-Hassan & Al-Sulami 2005; Agus & Sedlak 2010; Le Roux *et al.* 2015). Several emerging DBPs including HANs, I-THMs and brominated phenols (Br-phenols) were also reported in pretreated seawater (Table 1). The DBPs in different sources showed wide ranges, possibly due to feed water quality, pretreatment, and type and doses of disinfectants (Table 1). In Saudi Arabia, concentrations of THMs, HAAs, HANs and I-THMs in chlorinated seawater were in the ranges of 3.1–27.9, ND–7.0, 0.4–0.8 and 1.9–2.6 µg/L, respectively (Table 1). In UAE, THMs and HAAs were <25–95 and ND–< 14.5 µg/L, respectively (Table 1) while in Qatar, THMs were in the range of 21.7–61.4 µg/L. The highest concentrations of THMs (490–680 µg/L) and HAAs (69–175 µg/L) were reported for a pilot plant in Tampa Bay, Florida, USA (Table 1). The total organic carbon (TOC) and chlorine doses were in the ranges of 4.3–10.9 and 2.5–5.0 mg/L, respectively (Agus *et al.* 2009). Sudden pollution near the desalination plants (e.g., oil spill) could also increase DBPs (El Din *et al.* 1991). In UAE, THMs and HAAs were below 100 µg/L in most cases (Table 1); however, THMs rose to 200 µg/L following an oil spill near the intake (El Din *et al.* 1991).

Laboratory studies on seawater showed different DBPs when Cl₂, NH₂Cl, ClO₂ and O₃ were used (Table 1). In chlorinated seawater in the laboratory, THMs, HAAs, HANs and haloacetamides (HAcAms) were in the ranges of ND–206, 0–122, 4.0–155 and 110–240 µg/L, respectively. In NH₂Cl and ClO₂ treated samples, total DBPs were much lower (Table 1) while O₃ treated samples showed higher Br-THMs, Br-HAAs, bromate and HNMs. Overall, THMs in laboratory studies from Saudi Arabia, Qatar, Spain, the USA and Canada were in the ranges of 35–180, 60–165, 0.34–154, 43–206 and 22–33 µg/L, respectively (Table 1). In a laboratory study from Halifax, Canada, bromate was

Table 1 | DBPs during pretreatment of seawater (DBPs in µg/L; dose: mg/L, unless specified)

Location	Disinfectant	THMs	HAAs	HANs	Other DBPs	Dose; contact time	Reference
Feed water of desalination plants							
Red Sea coast, Saudi Arabia	Chlorine	6.2–18.4	5.4–6.9	0.4–0.8 DBAN	1.9–2.6 (I-THMs)	0.7–1.0 (continuous); 0.25–0.5 (residual)	Le Roux <i>et al.</i> (2015)
Al-Jubail, Saudi Arabia		ND	7.0			1.0 (residual); 24 h	Dalvi <i>et al.</i> (2000)
Jeddah, Saudi Arabia		3.3–24.0	ND				Kojima <i>et al.</i> (1995)
East coast, Saudi Arabia		3.1–27.9	ND			2.0 (residual)	Kutty <i>et al.</i> (1995)
Umm Al-Nur, UAE		78–95	ND			0.5–2.0 (residual)	El Din <i>et al.</i> (1991)
Ruwais, UAE		<25	<14.5			0.2–0.25; 10–15 min	Elshorbagy & Abdulkarim (2006)
Okinawa, Japan		35	ND			0.3	Magara <i>et al.</i> (1996)
Ebara Corp., Japan		15–25	ND			0.2–0.3 (residual)	Kutty <i>et al.</i> (1995)
Carlsbad, USA		3.0–52	9.5–19	0.5–1.9	0.3–0.6 (Br-phenols)	0.5–2.0 (initial); 2 h	Agus & Sedlak (2010)
Tampa Bay, USA		490–680	69–175			2.5–5.0	Agus <i>et al.</i> (2009)
Laboratory studies with seawater							
Al-Jubail, Saudi Arabia	Chlorine	80	ND			10.0; 72 h	Kutty <i>et al.</i> (1995)
Thuwail, Saudi Arabia				18–155	110–240; Halo-acetamides	5; 72 h	Nihemaiti <i>et al.</i> (2015)
Doha, Qatar		60–165	ND			1.0–4.0; 168 h	Wahab <i>et al.</i> (2010)
Barcelona, Spain		154	ND			1	Simon <i>et al.</i> (2014)
Aquaria, undisclosed		ND	≤122			1.0–3.0; 30 min	Shi <i>et al.</i> (2013)
North Sea coast, Norway		ND	3.2–6.3			0.7–3.5 (Cl ₂ /DOC); 24 h	Kristiansen <i>et al.</i> (1996)
Seattle, USA		107	99	4.0 B/DCAN		1.0; 8 h	Fabbricino & Korshin (2005)
Florida, USA		43–206	39–75			2.0 (Cl ₂ /DOC); 24 h	Ged & Boyer (2014)
Al-Jubail, Saudi Arabia	Chloramine	35	ND			10.0; 72 h	Dalvi <i>et al.</i> (2000)
Thuwail, Saudi Arabia	Chlorine			10–45	25–76; Halo – acetamides	5; 72 h	Fabbricino & Korshin (2005)
Busan, Korea	Chlorine dioxide	ND	0.4–2.5			0.2–10.0; 72 h	Yu <i>et al.</i> (2014)
Barcelona, Spain		0.34	ND			0.2–0.4	Simon <i>et al.</i> (2014)
Al-Jubail, Saudi Arabia	Ozone	180 (TBM)	ND	ND		5.0; 72 h	Dalvi <i>et al.</i> (2000)
Halifax, Canada		22–33	ND		500–4,500; bromate	0.4–3.9	Brookman <i>et al.</i> (2011)

(continued)

Table 1 | continued

Location	Disinfectant	THMs	HAAs	HANs	Other DBPs	Dose; contact time	Reference
Aquaria, undisclosed		ND	61 (TBAA)		16.5–34.8(HNMs)	1.0–3.0; 15 min	Shi <i>et al.</i> (2013)
Cooling effluent of power plants							
North Sea coast, France	Chlorine	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	Jenner <i>et al.</i> (1997); Allonier <i>et al.</i> (1999)
Power stations, UK	Chlorine	3.50–53.5		<0.1–6.74 DBAN			Jenner <i>et al.</i> (1997); Allonier <i>et al.</i> (1999)

in the range of 500–4,500 µg/L (Table 1) while the guideline limit was 10 µg/L (USEPA 2006; WHO 2011). In other ozone treated samples, TBM, TBAA and HNMs were 180, 61 and 16.5–34.8 µg/L, respectively (Table 1). Higher concentrations of Br-THMs, bromate and total DBPs in O₃ treated water could be a health concern (USEPA 2018). However, O₃ is not commonly used in desalination due to higher levels of bromide. In addition, the power plant cooling effluents reported higher levels of TBM while HAAs, HANs and Br-phenols were also detected (Table 1).

In recent years, several laboratory studies on simulated water demonstrated the formation of emerging DBPs, many of which are yet to be identified, quantified and assessed for human risks. In simulated drinking water containing bromide and disinfected with NH₂Cl, as many as 29 aliphatic, aromatic or nitrogenous polar Br-DBPs were detected, and five of them were tentatively identified (Zhai *et al.* 2014). Application of NH₂Cl favoured the formation of aromatic and nitrogenous polar Br-DBPs. In another study, Postigo *et al.* (2017) compared the formation of emerging DBPs in simulated drinking water containing bromide and iodide. This study reported preferential formation of I-DBPs (I-THMs, I-HAAs) and haloacetaldehydes (HALs) in chloraminated water rather than chlorinated water. In this study, Cl₂ rapidly oxidized hypiodous acid (HOI) to iodate, which served as a sink for iodide. In the presence of NH₂Cl, HOI reacted with NOM to form I-DBPs, which acted as a sink for iodide (Bichsel & Von Gunten 2000). The total concentrations of I-THMs in NH₂Cl treated water were 1.5–18 times higher than chlorinated water (Postigo *et al.* 2017). Gong *et al.* (2016) investigated the effects of linear alkylbenzene sulfonates (LAS), an important group of organic pollutants in urban wastewater effluents, on the formation of DBPs in the presence of bromide ions. This study reported the formation of Cl-DBPs during chlorination of LAS without bromide while Br-DBPs were formed during chlorination of LAS with bromide. The major polar Cl-DBPs and Br-DBPs from LAS were proposed to be 2,6-dichloro-3,5-dihydroxy-4-dodecylbenzenesulfonic acid and 2,6-dibromo-3,5-dihydroxy-4-dodecylbenzenesulfonic acid, respectively. In another study, Gong & Zhang (2015) reported formation of polar I-DBPs in chlorinated saline wastewater effluents containing iodide. As an example, a new group of polar I-DBPs, iodo-trihydroxybenzenesulfonic

acids, was identified and quantified. Concentrations of bromide and iodide in seawater are high, and may form several emerging Br-DBPs and I-DBPs upon chlorination and/or chloramination.

Overall, THMs were higher than HAAs in feed water and laboratory studies using real seawater samples (Table 1). In chlorinated seawater, TCM was not detected while BDCM, DBCM and TBM were 0.9%, 4.3% and 94.7%, respectively (Br-THMs = 99.9%). In this study, MCAA, DCAA, TCAA, MBAA, DBAA, TBAA and CDBAA were 9.3%, 4.5%, 2.4%, 3.4%, 38.3%, 22.4% and 19.6%, respectively (Br-HAAs = 83.7%) while BCAA and BDCAA were not detected (Le Roux *et al.* 2015). The DBAA and TBAA contributed approximately 60.7% of total HAAs. In contrast, for chlorinated surface water, the major THMs were TCM (71.4%) and BDCM (28.6%) while DBCM and TBM were not detected. The major HAAs were MCAA (23.7%), DCAA (36.7%) and TCAA (13.0%), respectively (Cl-HAAs = 73.4%) (Kim *et al.* 2002; Sorlini & Collivignarelli 2005).

Seawater contains high levels of bromide ions, which are more reactive to hydrophilic NOM containing a larger proportion of aliphatic structure, and favours the formation of THMs over HAAs (Singer *et al.* 2002). In addition, higher pH ($\cong 8.0$) in feed water could form more THMs than HAAs while the reverse is true at lower pH ($\cong 6.0$). In general, HOCl reacts with bromide ions to form HOBr, which is almost 15 times as reactive as HOCl, resulting in faster replacement of lighter Cl⁻ atoms by heavier Br⁻ atoms, leading to the formation of chloro-bromo and other Br-DBPs (Liang & Singer 2003).

Desalination plants prior to distribution

The pretreated feed water is passed through thermal or membrane processes. In thermal plants, the heating chambers produce vapour, which is collected following condensation (Figure 1(a)), and thus many non-volatile DBPs (e.g., HAAs) are removed to trace levels in the product water. However, volatile DBPs (e.g., THMs) are partitioned into vapour phase (USEPA 1995; Chowdhury 2014) and can be present in desalinated water at relatively low concentrations (Table 2). For an example, THMs in MSF processes were reduced by 94% during distillation (Ali & Riley 1989; El Din *et al.* 1991; Dalvi *et al.* 2000; Le Roux

et al. 2015). On the east coast of Saudi Arabia, concentrations of THMs in feed water were in the range of 3.1–27.9 µg/L, which were reduced to 0.1–3.5 µg/L in thermal distillate (Kutty *et al.* 1989). In thermal distillate, BDCM, DBCM and TBM were 39.5%, 31.6% and 28.9%, respectively (Table 2). However, TBM was 94.7% in the feed water, indicating a higher fraction of TBM removal during this process (Kutty *et al.* 1989). Concentrations of THMs in product water were affected by THMs in pretreated water, heat generation, partition of THMs into vapour phase and condensation during cooling. HAAs are not volatile and the product water had negligible concentrations of HAAs (Table 2). In the feed water from the Red Sea (Saudi Arabia), HAAs were in the range of 5.4–6.9 µg/L, which were not detected in thermal distillate (Le Roux *et al.* 2015). The DBPs with low initial concentrations and/or low partition coefficients are likely to be negligible in thermal distillate.

In RO processes, desalinated water is collected after passing through RO membranes. Depending on the rejection performance of the membranes, concentrations of DBPs vary in RO permeate (Kristiansen *et al.* 1996). RO plants often function with one, two or four RO passes based on the initial and final water quality and design parameters (Leenheer 1981; Peuravuori & Pihlaja 1998; Peuravuori *et al.* 2001; Kim *et al.* 2015). In the pretreated feed water of Tampa Bay RO plant, THMs and HAAs were in the ranges of 490–680 µg/L and 69–175 µg/L, respectively (Agus *et al.* 2009). In the RO permeate, these were in the ranges of 2.3–6.4 µg/L and 1.0–2.5 µg/L, respectively, indicating more than 99% removal of THMs and HAAs from feed water. The plant used hydranautics seawater composite membranes (Agus *et al.* 2009).

Higher levels of THMs and HAAs were reported in RO permeate in Saudi Arabia (Table 2). Le Roux *et al.* (2015) reported THMs in an RO plant with cellulose triacetate membranes in the range of 39–67 µg/L while in feed water, THMs were in the range of 14.5–18.4 µg/L (Table 2). THMs in RO permeate were higher due to the reaction of residual chlorine with the adsorbed and accumulated reactive organic matter in the fouling layer (Le Roux *et al.* 2015). In some RO plants, chloramines are used to limit biofouling and to reduce membrane damage (Kim *et al.* 2015). However, chloraminated RO permeate had

Table 2 | DBPs in desalination plants (µg/L)

Location	Thermal distillate				Pretreated feed water				Reference
	THMs	HAAs	HANs	Other	THMs	HAAs	HANs	Other	
Thermal plant on Red Sea coast, Saudi Arabia	0.4	ND	0.5 (DBAN)		6.2–18.4	5.4–6.9	0.4–0.8 DBAN	1.9–2.6 (I-THMs)	Le Roux <i>et al.</i> (2015)
Al-Jubail, Saudi Arabia	ND	1.6			ND	7.0			Dalvi <i>et al.</i> (2000)
Jeddah, Saudi Arabia	0.2–0.6				3.3–24.0	ND			Kutty <i>et al.</i> (1995)
East Coast, Saudi Arabia	0.1–3.5				3.1–27.9	ND			Kutty <i>et al.</i> (1989)
Jazan, Saudi Arabia	2.3–2.7								Ozair <i>et al.</i> (2013)
Location	RO permeate				Pretreated feed water				Reference
RO plant on Red Sea coast, Saudi Arabia	39–66.7	ND–0.71	ND–2.0 (DBAN)	1.7–2.6 (I-THMs)	14.5–18.4				
Jeddah, Saudi Arabia	12.2–39.0								Kutty <i>et al.</i> (1995)
Qatar	4.0–73.0								Al-Otoum <i>et al.</i> (2016)
Jazan, Saudi Arabia	14.2								Ozair <i>et al.</i> (2013)
Makkah, Saudi Arabia	8.5								Ozair <i>et al.</i> (2013)
Carlsbad, USA	ND–6.7	2.1–6.1	0.6–0.8		3.0–52.0	9.5–19.0	0.5–1.9	0.3–0.6 (Br-phenols)	Agus & Sedlak (2010)
Tampa Bay, USA	2.3–6.4	1.0–2.5			490–680	69–175			Agus <i>et al.</i> (2009)
Okinawa, Japan	2.7				35.0	ND			Magara <i>et al.</i> (1996)
Ebara Corp., Japan	2.0–3.0				15.0–25.0	ND			Kojima <i>et al.</i> (1995)

I-THMs in the range of 1.7–2.6 µg/L (Table 2). In addition to regulated DBPs, several emerging DBPs were reported in desalinated water. Le Roux *et al.* (2015) reported I-THMs in desalinated water from two plants in Jeddah, Saudi Arabia. The averages of DCIM, BCIM, DBIM, CDIM, BDIM and IF were ND, ND, 1.73, ND, 0.6 and ND, respectively. It is to be noted that I-THMs have also been reported in surface and groundwater sourced supply water (Ioannou *et al.* 2016). Overall, DBPs in thermal distillate were much lower than the RO permeate (Table 2). Thermal distillation needs higher energy, which primarily uses fossil fuels leading to higher costs of desalinated water. In addition, thermal plants release higher levels of CO₂ into the environment (Darwish 2007; ESCWA 2009).

Distribution systems within desalination plants

The dissolved organic carbon (DOC) in RO permeates were in the range of <0.1–0.6 mg/L (Agus *et al.* 2009; Agus & Sedlak 2010), which were lower than the typical freshwater (Chowdhury *et al.* 2008). However, bromide and iodide were in the ranges of 250–600 µg/L and <4–16 µg/L, respectively, which were much higher than freshwater sources. Higher levels of bromide and iodide increased the Br-DBPs and I-DBPs (Magara *et al.* 1996; Agus *et al.* 2009; Agus & Sedlak 2010; Duranceau 2010; Ioannou *et al.* 2016). Recent studies have demonstrated the formation of emerging polar Br-DBPs and I-DBPs in the presence of bromide and iodide in source water (Zhai *et al.* 2014; Gong & Zhang 2015; Gong *et al.* 2016). Further, NH₂Cl treatment showed preferential formation of I-DBPs (Postigo *et al.* 2017). In chlorine treatment, iodide reacts with HOCl and HOBr to form hypiodous (HOI) acid, which can form I-THMs in the distribution systems of desalination plants. In addition, bromide can form Br-DBPs and bromo-iodo-DBPs (Br-I-DBPs). The Br-DBPs, I-DBPs and Br-I-DBPs are more cytotoxic and genotoxic to mammalian cells than the Cl-DBPs. The toxicity follows the order of Cl-THMs < Br-THMs < I-THMs (Richardson *et al.* 2007).

In an RO plant in Jeddah, Saudi Arabia, THMs in the distribution systems were in the range of 13.5–25.7 µg/L (Table 3). In this plant, averages of TCM, BDCM, DBCM and TBM were 0.5%, 1.0%, 2.6% and 93.4%, respectively (Table 3). In a MSF plant on the east coast of Saudi

Table 3 | DBPs in distribution systems of desalination plants (µg/L)

Location	DBPs	Mean	Range	Reference
Jeddah RO water line, Saudi Arabia	TCM	0.1	0.03–0.1	Tawabini <i>et al.</i> (1987)
	CCl ₄	0.01	0–0.01	
	BDCM	0.2	0.6–0.5	
	DBCM	0.5	0.3–0.8	
	TBM	18.3	13.1–24.7	
Al-Khobar MSF plant, Saudi Arabia	THMs	19.5	13.5–25.7	Chowdhury (2013, 2016)
	TCM	3.2	1.2–6.1	
	BDCM	2.0	0.5–3.4	
	DBCM	0.5	0–1.2	
	TBM	0.5	0–0.7	
Distillate received in Doha blending plant, Qatar	THMs	6.7	2.4–12.1	Latif (1991)
	TCM	0.1	0.00–0.5	
	BDCM	0.4	0.0–2.0	
	DBCM	0.2	0.0–0.9	
	TBM	1.8	0.2–5.9	
	THMs	2.3	0.4–8.2	

Arabia, averages of TCM, BDCM, DBCM and TBM were 47.8%, 29.9%, 7.5% and 7.5%, respectively, while in a MSF plant in Doha, these were 3.8%, 15.4%, 7.7% and 69.2%, respectively (Table 3) (Latif 1991; Chowdhury 2013, 2016). In Al-Khobar (east coast), THMs in the distribution system of an MSF plant were in the range of 2.4–12.1 µg/L (Chowdhury 2013, 2016). Several other MSF plants showed low concentrations of THMs (Chowdhury *et al.* 2018) in distribution systems. In all plants, Br-THMs were dominant (Latif 1991; Chowdhury 2013, 2016). Higher concentrations of THMs in distribution systems of RO plants might be due to higher initial concentrations and higher levels of bromide in RO effluents than the thermal effluents.

Blend water

Desalinated water generally has lower pH than the neutral range, which is adjusted through stabilization by blending with treated brackish/groundwater or untreated seawater prior to supplying to the WDS. The RO permeates with low DOC are mixed with treated groundwater with high DOC resulting in higher DOC in the blend water. High concentrations of DOC, and bromide and iodide in blend water, are likely to increase Br-DBPs, I-DBPs and total DBPs upon chlorination.

In a Jeddah plant, THMs in blend water were in the range of 9.3–30.1 µg/L, of which TBM contributed 42–96% (Table 4). In Al-Khobar, THMs were in the range of 2.1–52.4 µg/L, of which Br-THMs were 60–86% (Chowdhury *et al.* 2018). In Doha (Qatar), THMs in blend water were in the range of 10.5–36.3 µg/L (Table 4). On the east coast, Saudi Arabia, THMs in blend water were in the range of 3.1–12.8 µg/L (Table 4) while TBM contributed 61–86% (Chowdhury *et al.* 2018). In a laboratory study, averages of THMs were 29.0, 40.5 and 42.6 µg/L for desalinated and treated groundwater blending ratios of 1:10, 1:5 and 1:2, respectively (Tawabini *et al.* 2011). Overall, THMs in blend water were higher than the THMs in desalinated water (Chowdhury *et al.* 2018).

Water distribution system

Blend water with residual chlorine is pumped into the WDS to supply to cities. The water is transported to inland cities through inter-city pipe networks. In Saudi Arabia, desalinated water is transported from Jubail plant to Riyadh, which is a distance of almost 450 km. The water is transported further to Buraidah (Qassim), which is 350 km from Riyadh. The cities generally mix treated groundwater with desalinated water to augment water supplies. Depending on the distance and service areas, water can stay in the WDS for a few hours to several days, which can lead to the formation of additional DBPs. In particular, the summer temperature is very high, exceeding 40 °C on

Table 4 | DBPs in blended water (µg/L)

Location	DBPs	Mean	Range	Data location	Reference
Jeddah SWRO/MSF plant, Saudi Arabia	TCM	0.1	0.0–0.2	Field	Kutty <i>et al.</i> (1991)
	CCl ₄	0.01	0–0.01		
	BDCM	0.1	0–0.3		
	DBCM	0.4	0.2–0.7		
	TBM	8.9	3.9–29.4		
	THMs	9.5	9.3–30.1		
Al-Khobar plant	THMs	19.2	2.1–52.4	Field	Chowdhury <i>et al.</i> (2018)
East coast, Saudi Arabia	THMs		3.1–12.8	Field	
Jeddah Red Sea coast	TCM	0.3	0.2–0.5	Field	Kutty <i>et al.</i> (1989)
	BDCM	1.1	ND–8.4		
	DBCM	1.8	0.2–2.3		
	TBM	8.9	3.9–49.4		
	THMs		0.4–66.7		
Doha blending plant, Qatar	TCM	0.9	0–3.8	Field	Latif (1991)
	BDCM	2.3	1.2–3.8		
	DBCM	6.3	2.7–11.3		
	TBM	11.0	5.0–19.6		
	THMs	20.4	10.5–36.3		
Kuwait	TCM	0.8	ND–5.9	Field	Latif (1991)
	BDCM	2.4	1.0–7.9		
	DBCM	6.6	2.7–13.7		
	TBM	30.2	3.4–77.4		
Bahrain	TCM			Field	Al-Saleh & Al-Haddad (1994)
	BDCM	0.6			
	DBCM	0.6			
	TBM	5.9			
Al-Khobar: BR = 1:2	THMs	42.6		Laboratory	Tawabini <i>et al.</i> (2011)
Al-Khobar: BR = 1:5	THMs	40.5			
Al-Khobar: BR = 1:10	THMs	29.0			

BR: blending ratio of desalinated and treated groundwater.

many summer days (Tarawneh & Chowdhury 2018), which can accelerate the formation of Br-DBPs and I-DBPs in bromide- and iodide-rich water (Zhai *et al.* 2014; Kim *et al.* 2015; Postigo *et al.* 2017). The province-wide survey of 162 water supply systems in Ontario, Canada showed the ranges of THMs in water treatment plants (WTP) and WDS of 0.5–273 and 0.5–289 µg/L, respectively, with averages of 31.6 and 40.2 µg/L, respectively, indicating an increase of average THMs by 27.2% in the WDS (Chowdhury *et al.* 2008). The data from the Drinking Water Surveillance Program (DWSP) in Ontario, Canada showed a significant increase of THMs in WDS than the WTP (MOE 2018). Further, due to the prolonged stay in WDS during intercity transportation and storage in the inland reservoirs, residual disinfectant may be exhausted, resulting in microbiological regrowth in WDS (Chowdhury 2012).

In Saudi Arabia, Fayad (1993) reported THMs in WDS from eight major cities (Dammam, Riyadh, Makkah, Madinah, Jeddah, Abha, Hail, Buraidah) in the range of 0.03–41.7 µg/L with averages of 0.8–18.2 µg/L (Table 5). In a few smaller areas including Dhahran, Jubail, Qatif, Rahima and Khafji, the average of THMs was in the range of 4.1–12.3 µg/L. In these areas, TCM, BDCM, DBCM and TBM were in the ranges of ND–9.3, ND–3.4, ND–1.5 and 1.6–12.0 µg/L, respectively, and the averages were 0.1–5.5, 0.3–2.0, 0.2–1.8 and 0.5–10.7 µg/L, respectively (Table 5). In all locations, Br-THMs were in the range of 70–95% of THMs (Table 5). In addition, Alsohaimi *et al.* (2012) reported bromate concentrations in a few locations in Saudi Arabia in the range of 3.4–75.0 µg/L (Table 5).

In Kuwait, THMs were reported to be in the ranges of 8.4–92.4 µg/L (Latif 1991). In four locations, averages of TCM, BDCM, DBCM and TBM were in the ranges of ND–5.9, 1.3–7.9, 2.8–13.7 and 3.4–77.4 µg/L, respectively, with averages of 0.8–1.0, 2.2–2.9, 5.6–9.2 and 24.3–47.3 µg/L, respectively (Table 5). In Qatar, THMs were in the range of 1.5–89.3 µg/L (Al-Otoum *et al.* 2016). Concentrations of TCM, BDCM, DBCM and TBM were in the ranges of ND–4.6, 0.1–26.2, 0.1–7.2 and 1.4–56.0 µg/L, respectively, with averages of 0.5–0.8, 2.0–2.6, 1.0–4.6 and 9.6–14.6 µg/L, respectively (Table 5). In Egypt, THMs were in the range of 7.5–87.4 µg/L (Basiouny *et al.* 2008). In Bahrain, averages of TCM, BDCM, DBCM and TBM were in the ranges of 0.5–1.2, 0.3–0.7, 0.3–2.9 and 1.3–6.4 µg/L, respectively

(Al-Saleh & Al-Haddad 1994). In most locations, Br-DBPs were higher than the Cl-DBPs while many Br-DBPs are considered probable or possible human carcinogens (USEPA 2018).

Plumbing premise within the house

Past studies have reported an increase of DBPs in plumbing pipes (PP) and hot water tanks (HWT) (Weisel & Chen 1994; Wu *et al.* 2001; Baribeau *et al.* 2004; Weinberg *et al.* 2006; Dion-Fortier *et al.* 2009; Chowdhury 2016). In three locations in Quebec, Canada, THMs in PP were 136–181% times the THMs in WDS. In HWT, THMs were 191–269% times the THMs in WDS and 132–159% of THMs in PP. HAAs in PP and HWT were 23–224% and 53–261% of HAAs in WDS, respectively. The reduction of HAAs from WDS to PP and HWT might be due to increased microbiological activities in PP because of the consumption of free chlorine residuals and destruction of HAAs within the PP by microorganisms (Wu *et al.* 2001; Baribeau *et al.* 2004; Weinberg *et al.* 2006). In blend water in Dhahran, THMs in PP and HWT were 1.1–2.4 and 1.6–3.0 times the THMs in WDS, respectively. Concentrations of HAAs were 0.9–1.8 and 1.2–1.9 times the HAAs in WDS, respectively (Chowdhury 2016).

The populations are exposed to water from taps in houses, while the regulatory and monitoring agencies recommend measuring DBPs at various points within the WDS. Depending on the size of PP, water may stay in PP and HWT for a considerable time before it reaches taps (Wu *et al.* 2001; Baribeau *et al.* 2004; Weinberg *et al.* 2006; Dion-Fortier *et al.* 2009). This stagnation may be even longer during off-peak hours (e.g., midnight to morning; late morning to early evening), which allows extended reactions between the residual organics and free residual chlorine and increases DBPs in the PP and HWT.

HUMAN HEALTH RISK AND TOXICITY

Several DBPs can pose cancer and non-cancer risks to humans (Table 6). The effects include higher rates of colorectal and bladder cancers, neural tube defects, miscarriages, cardiac irregularities and low birth weight babies

Table 5 | DBPs in water distribution system prior to entering the consumer's home ($\mu\text{g/L}$)

Location	Desalination plant	DBPs	Range	Mean	SD	Median	Reference
Dhahran, Saudi Arabia		TCM	1.2–6.1	3.2	1.3		Chowdhury (2013)
		BDCM	0.5–3.4	2	0.7		
		DBCM	0.0–1.2	0.5	0.3		
		TBM	0.0–0.7	0.5	0.3		
Dhahran, Saudi Arabia		TCM	1.3–9.3	5.5	2.2		Chowdhury (2016)
		BDCM	0.5–1.3	0.8	0.2		
		DBCM	0.1–0.4	0.2	0.07		
		TBM	0.1–0.2	0.1	0.03		
Red Sea community, Saudi Arabia	Yanbu MSF/RO	TCM	0.2–0.5	0.3			Ahmad & Bajahlan (2009)
		BDCM	0.7–1.4	1.1			
		DBCM	1.2–2.3	1.8			
		TBM	4.3–6.7	5.4			
Jubail	Al-Jubail SWRO plant	TCM	0.0–0.7	0.2			El-Hassan & Al-Sulami (2005)
		BDCM	0.0–0.5	0.4			
		DBCM	0.0–1.0	0.9			
		TBM	0.0–5.9	4.7			
Khobar	Al-Khobar MSF Plant	TCM	0.0–0.05	0.02			
		BDCM	0.2–0.3	0.3			
		DBCM	0.9–1.1	1.0			
		TBM	5.6–8.5	7.2			
Dammam		TCM	0.0–0.04	0.02			
		BDCM	0.3–0.5	0.4			
		DBCM	1.0–1.9	1.4			
		TBM	7.8–9.7	9.1			
Qatif		TCM	0.0–0.3	0.1			
		BDCM	0.2–0.3	0.25			
		DBCM	0.7–1.2	1.1			
		TBM	7.7–9.7	8.5			
Rahima		TCM					
		BDCM	0.25–0.3	0.29			
		DBCM	1.1–1.5	1.3			
		TBM	9.0–12.0	10.7			
Khafji	Al-Khafji SWRO Plant	TCM	0.0–0.9	0.5			
		BDCM	0.7–0.9	0.8			
		DBCM	0.7–0.9	0.8			
		TBM	1.6–2.0	1.8			
Riyadh		TCM	0.0–0.1	0.04			
		BDCM	0.3–0.5	0.4			
		DBCM	1.2–1.4	1.3			
		TBM	2.3–2.7	2.4			
Dammam (Summer)	Dammam	TTHMs	0.2–26.9			9.1	Fayad (1993)
Dammam (Winter)			0.1–28.9			18.2	
Riyadh (Summer)	Riyadh	TTHMs	1.0–8.4			5.6	
Riyadh (Winter)			1.3–8.1			4.9	
Buraydah (Summer)	Buraydah	TTHMs	0.5–5.0			0.8	
Buraidah (Winter)			0.8–3.9			1.0	

(continued)

Table 5 | continued

Location	Desalination plant	DBPs	Range	Mean	SD	Median	Reference
Hail (Summer)	Hail	TTHMs	1.1–2.5			1.4	
Hail (Winter)			1.1–6.3			1.4	
Madinah (Summer)	Madinah	TTHMs	5.4–11.0			4.6	
Madinah (Winter)			2.6–13.1			6.6	
Jeddah (Summer)	Jeddah	TTHMs	4.0–41.7			7.1	
Jeddah (Winter)			0.03–17.8			2.9	
Makkah (Summer)	Makkah	TTHMs	5.9–17.6			6.9	
Makkah (Winter)			1.4–19.3			3.2	
Abha (Summer)	Abha	TTHMs	1.4–1.0			1.5	
Abha (Winter)			1.1–1.3			1.3	
Al-Andalus	Doha Water Blending Complex	TCM	0.0–2.0	0.5	0.7		Latif (1991)
		BDCM	1.0–2.8	2.0	0.4		
		DBCM	2.7–7.2	4.6	1.1		
		TBM	5.8–16.8	9.6	2.8		
Al-Jubail		TCM		0.02			Kutty <i>et al.</i> (1991)
		BDCM		0.4			
		DBCM		0.8			
		TBM		2.4			
Al-Jabriya, Kuwait	Doha Water Blending Complex	TCM	0.0–2.9	0.9	1.0		Kim <i>et al.</i> (2015)
		BDCM	2.0–3.8	2.8	0.5		
		DBCM	7.0–13.7	9.2	1.5		
		TBM	17.6–36.8	24.7	5.0		
Hawalli, Kuwait	Doha Water Blending Complex	TCM	0.0–4.0	0.8	1.2		
		BDCM	1.3–3.8	2.2	0.6		
		DBCM	3.2–9.1	7.0	1.6		
		TBM	12.9–33.3	24.3	5.0		
Keifan, Kuwait	Shuwaikh Water Blending Complex	TCM	0.0–3.1	0.9	1.1		
		BDCM	1.6–7.9	2.9	1.4		
		DBCM	2.8–9.1	5.6	1.4		
		TBM	3.4–71.5	47.4	20.9		
Al-Sharq, Kuwait	Shuwaikh Water Blending Complex	TCM	0.0–5.9	1.0	1.5		
		BDCM	1.6–3.3	2.4	0.5		
		DBCM	3.0–10.3	6.7	1.5		
		TBM	7.4–77.4	44.5	20.3		
Qatar	Ras Laffan, Ras Abu-Fontas, Ras-Girtas	TCM	0.0–4.6	0.82			Al-Otoum <i>et al.</i> (2016)
		BDCM	0.01–26.2	2.6			
		DBCM	0.01–2.4	1.0			
		TBM	1.4–56.0	14.6			
Hoorah, Bahrain		TCM		0.5			
		BDCM		0.5	0.1		
		DBCM		0.3	0.1		
		TBM		1.3	0.1		
Salmania, Bahrain		TCM		0.6	0.1		
		BDCM		0.7			
		DBCM		2.3	0.3		
		TBM		3.6	0.3		

(continued)

Table 5 | continued

Location	Desalination plant	DBPs	Range	Mean	SD	Median	Reference
Mahooz, Bahrain		TCM		1.2			
		BDCM		0.5	0.1		
		DBC		0.9	0.1		
		TBM		2.6	0.1		
Musalla, Bahrain		TCM					
		BDCM		0.6	0.1		
		DBC		2.4	0.1		
		TBM		3.0	0.1		
Sanabis, Bahrain		TCM					
		BDCM		0.7			
		DBC		2.4	0.1		
		TBM		3.1	0.1		
Hammad Town, Bahrain		TCM					
		BDCM					
		DBC		2.9	0.1		
		TBM		2.9	0.1		
West Riffa, Bahrain		TCM					
		BDCM		0.5			
		DBC		5.9	0.2		
		TBM		6.4	0.2		
Sitra, Bahrain		TCM		0.1	0.2		
		BDCM		0.9	0.03		
		DBC		1.5	0.2		
		TBM		2.5	0.2		
Umm-al, Bahrain		TCM					
		BDCM					
		DBC		0.3	0.1		
		TBM		0.3	0.1		
Saudi Arabia	SWCC	Bromate	3.4–75.0				Alsohaimi <i>et al.</i> (2012)
Egypt		TTHMs	7.5–87.4				Basiouny <i>et al.</i> (2008)

(King & Marrett 1996; Cantor *et al.* 1998; Hildesheim *et al.* 1998). Exposure to DBPs can occur throughout a lifetime via multiple pathways, such as ingestion with drinking water, and inhalation and dermal absorption during showering, bathing, cooking, house cleaning and swimming (Cantor *et al.* 1998; Savitz *et al.* 2006). Past studies have reported increased cancer and non-cancer risks to humans from exposure to DBPs (Weisel & Chen 1994; Lee *et al.* 2004; Nuckols *et al.* 2005; Xu & Weisel 2005; Savitz *et al.* 2006; Semerjian & Dennis 2007; Chowdhury 2016; Chowdhury *et al.* 2018).

Among DBPs, Br-DBPs, N-DBPs and I-DBPs are more toxic than Cl-DBPs (Plewa *et al.* 2002, 2008; Muellner *et al.* 2007; Zhang *et al.* 2012; Wagner & Plewa 2017). A summary of some DBPs, their cytotoxicity, genotoxicity and risk

factors are presented in Table 6. Most of the DBPs were cytotoxic and/or genotoxic (Table 6). Among THMs, TIM induced cytotoxicity to the Chinese hamster ovary (CHO) cell at the lowest concentration of 3,937 µg/L while BDCM induced genotoxicity to human-derived hepatoma line (HepG2) cell at the lowest concentration of 164 µg/L (Table 6). For IAA, the lowest values for cytotoxicity and genotoxicity were 93 and 930 µg/L, respectively (Table 6). In HANs, IAN induced cytotoxicity to the CHO cell at the lowest concentration of 17 µg/L while BAN induced genotoxicity at the lowest concentration of 4,798 µg/L (Table 6). Among the cyanogen halides, CNBr induced cytotoxicity at the lowest concentration of 106 µg/L (Table 6). The I-DBPs, Br-DBPs and N-DBPs were more cytotoxic and genotoxic than Cl-DBPs (Table 6). In drinking water,

Table 6 | Health effects and toxicity data for some DBPs (Zhang et al. 2012; Wagner & Plewa 2017; USEPA 2018)

DBPs	Name	Symbol	Formula	CAS No.	MW	LCC (μM)	LGC (μM)	LCC [$\mu\text{g/L}$]	LGC [$\mu\text{g/L}$]	SF (mg/kg-day^{-1})	RfD (mg/kg-day)	DUR (per $\mu\text{g/L}$)
THMs	Chloroform	TCM	CHCl_3	67-66-3	119.4	NA	10,000	NA	1,193,690	RA	0.01	
	Bromodichloromethane	BDCM	CHBrCl_2	75-27-4	163.8		1		164	0.062	0.02	1.8×10^{-6}
	Dibromochloromethane	DBCM	CHBr_2Cl	124-48-1	208.3		10		2,083	0.084	0.02	2.4×10^{-6}
	Bromoform	TBM	CHBr_3	75-25-2	252.7	NA	1,000	NA	252,731	0.0079	0.02	2.3×10^{-7}
	Bromodiodomethane	BDIM	CHBrI_2	557-95-9	346.7	1,500	NS	520,098	NS			
	Chlorodiodomethane	CDIM	CHClI_2	638-73-3	302.3	100	2,000	30,228	604,556			
	Bromochloroiodomethane	BCIM	CHBrClI	34970-00-8	255.3	2,200	NS	561,609	NS			
	Dichloroiodomethane	DCIM	CHCl_2I	594-04-7	210.8	2,000	NS	421,658	NS			
	Iodoform	TIM	CHI_3	75-47-8	393.7	10	NS	3,937	NS			
HAAs	Bromochloroacetic acid	BCAA	$\text{C}_2\text{H}_2\text{BrClO}_2$	5589-96-3	173.4	300	3,000	52,017	520,170			
	Bromodichloroacetic acid	BDCAA	$\text{C}_2\text{HBr}_2\text{ClO}_2$	7113-314-7	207.8	500	NS	103,920	NS			
	Chlorodibromoacetic acid	CDBAA	$\text{C}_2\text{H}_2\text{Br}_2\text{O}_2$	5278-95-5	252.3	100	13,000	25,230	3,279,900			
	Dichloroacetic acid	DCAA	$\text{C}_2\text{H}_2\text{Cl}_2\text{O}_2$	79-43-6	128.9	2,000	NS	257,880	NS	0.05	0.004	1.4×10^{-6}
	Dibromoacetic acid	DBAA	$\text{C}_2\text{H}_2\text{Br}_2\text{O}_2$	631-64-1	217.9	200	750	43,572	163,395			
	Bromoacetic acid	BAA	$\text{C}_2\text{H}_3\text{BrO}_2$	79-08-3	139.0	2	13	278	1,806			
	Chloroacetic acid	CAA	$\text{C}_2\text{H}_3\text{ClO}_2$	79-11-8	94.5	250	300	23,625	28,350			
	Tribromoacetic acid	TBAA	$\text{C}_2\text{HBr}_3\text{O}_2$	75-96-7	296.8	5	3,000	1,484	890,280			
	Trichloroacetic acid	TCAA	$\text{C}_2\text{HCl}_3\text{O}_2$	76-03-9	163.4	400	NS	65,356	NS	0.07	0.02	2.0×10^{-6}
	Iodoacetic acid	IAA	$\text{C}_2\text{H}_3\text{IO}_2$	64-69-7	186.0	0.5	5	93.0	930			
	Diiodoacetic acids	DIAA	$\text{C}_2\text{H}_2\text{I}_2\text{O}_2$	598-89-0	311.8	100	1,000	31,184	311,840			
	Bromiodoacetic acids	BIAA	$\text{C}_2\text{H}_2\text{BrIO}_2$	71815-43-5	264.8	250	2,500	66,210	662,100			
	Chloriodoacetic acid	CIAA	$\text{C}_2\text{H}_2\text{ClIO}_2$	53715-09-6	220.4	170	NA	37,466.3	NA			
HANs	Bromochloroacetonitrile	BCAN	C_2HBrClN	83463-62-1	154.4	7	250	1,081	38,598			
	Dibromoacetonitrile	DBAN	$\text{C}_2\text{HBr}_2\text{N}$	3252-43-5	198.9	1	30	199	5,965			
	Dichloroacetonitrile	DCAN	$\text{C}_2\text{HCl}_2\text{N}$	3018-12-0	109.9	10	2,400	1,099	263,849			
	Trichloroacetonitrile	TCAN	$\text{C}_2\text{Cl}_3\text{N}$	545-06-2	144.4	25	1,000	3,609	144,379			
	Bromoacetonitrile	BAN	$\text{C}_2\text{H}_2\text{BrN}$	590-17-0	120.0	1	40	120	4,798			
	Chloroacetonitrile	CAN	$\text{C}_2\text{H}_2\text{ClN}$	107-14-2	75.5	50	250	3,775	18,874			
	Iodoacetonitrile	IAN	$\text{C}_2\text{H}_2\text{IN}$	624-75-9	167.0	0.1	30	17	5,008.5			
	Cyanogen halides	Cyanogen bromide	CNBr		506-68-3	105.9	1	500	106	52,961		0.09
Cyanogen chloride		CNCl		506-77-4	61.5	3,000	NS	184,404	NS			
Cyanogen iodide		CNI		506-78-5	152.9	1	200	153	30,584			
Nitrosamines	N-nitrosodimethylamine	NDMA	$\text{C}_2\text{H}_6\text{N}_2\text{O}$	62-75-9	74.1	NS	NA	NS	NA	51		1.4×10^{-3}
Haloacetamides	Bromoacetamide	BACAm	$\text{C}_2\text{H}_4\text{BrNO}$	683-57-8	138.0	0.5	25	69	3,449			
	Chloroacetamide	CACAm	$\text{C}_2\text{H}_4\text{ClNO}$	79-07-2	93.5	75	750	7,013	70,133			
	Iodoacetamide	IACAm	$\text{C}_2\text{H}_4\text{INO}$	144-48-9	185.0	0.5	30	92	5,549			
Haloaldehydes	Bromoacetaldehyde		$\text{C}_2\text{H}_3\text{BrO}$	17157-48-1	123.0	8	200	984	24,590			
	Chloroacetaldehyde		$\text{C}_2\text{H}_3\text{ClO}$	107-20-0	78.5	0.5	100	39	7,850			
	Iodoacetaldehyde		$\text{C}_2\text{H}_3\text{IO}$	55782-51-9	170.0	5	900	850	152,954			

(continued)

Table 6 | continued

DBPs	Name	Symbol	Formula	CAS No.	MW	LCC (nM)	LGC (µM)	LCC (µg/L)	LGC (µg/L)	SF (mg/kg-day) ⁻¹	RfD (mg/kg-day)	DUR (per µg/L)
Others	Bromate		BrO ₃	15541-45-4	127.9	NA	NA	NA	NA	0.7	0.004	2.0 × 10 ⁻⁵
	Chloral hydrate	CH	C ₂ H ₃ Cl ₃ O ₂	302-17-0	165.4	NA	20	NA	3,308		0.1	
	3-Chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone	MX	C ₃ H ₃ Cl ₃ O ₃	77439-76-0	217.4	NA	100	NA	217,430			

LCC: lowest concentration to induce cytotoxicity in the Chinese hamster ovary (CHO) cell; LGC: lowest concentration to induce genotoxicity in the CHO cell; SF: slope factor (the upper bound lifetime probability of an individual's developing cancer as a result of exposure to potential carcinogen (mg/kg-day)⁻¹); RfD: reference dose refers to non-carcinogenic effects (mg/kg-day); DUR: drinking water unit risk (per µg/L); NS: not significant; NA: not available. The genotoxicity data for TCM, BDCM, DBCM, TBM, CH and MX were obtained from Zhang *et al.* (2012), where the human-derived hepatoma line (HepG2) cell was investigated instead of CHO cell. The cytotoxicity and genotoxicity data for the other DBPs were obtained from Wagner & Plewa (2017). The SF, RfD and DUR were obtained from USEPA (2018).

concentrations of DBPs, to date, were much lower (e.g., USEPA 2012; NLDOE 2016; MOE 2018) than the lowest concentrations needed to induce cytotoxicity and genotoxicity to the CHO and/or HepG2 cells (Zhang *et al.* 2012, 2017; Wagner & Plewa 2017). However, the slope factor (SF) and drinking water unit risk (DUR) demonstrated the possibility of cancer risks from several DBPs through the oral pathway (USEPA 2018). Although the concentrations of individual DBPs in supply water were much lower than the lowest concentrations needed to induce cytotoxicity and genotoxicity to the CHO cells, the effects of the mixture of DBPs need better understanding. In general, DBPs in drinking water are present in the form of a mixture. Consequently, the synergistic effects might play an important role in inducing cytotoxic and genotoxic effects. Future research is needed to explain the effects of a mixture of DBPs.

CONTROLLING DBPS

The DBPs are formed in many stages from source to the consumer's tap (Figure 2). In producing and supplying the desalinated and blend water, desalination plants rarely adopt any approach to reduce DBPs throughout the stages of desalination and supply. In thermal plants, steam is mostly free from non-volatile DBPs (Stage II in Figure 2). However, volatile DBPs can be present at low concentrations. In product water from thermal plants, precursor concentrations for DBPs (e.g., NOM, bromide and iodide) are very low. In contrast, effluents from RO plants have higher DBPs and higher concentrations of precursors (Kutty *et al.* 1995; Magara *et al.* 1996; Kim *et al.* 2015; Le Roux *et al.* 2015), which are carried over through the next stages (Figure 2). Thermal plants are likely to reduce many DBPs in the distillate. However, these plants are energy intensive, leading to higher costs and greenhouse gas emissions. The cost of 1.0 m³ of desalinated water was reported to be in the range of US\$1.31–2.37, which could be increased further depending on the cost of energy (e.g., fossil fuel) and partial/full withdrawal of subsidized oil supplies for desalination. In producing 1.0 m³ of desalinated water, MSF plants typically emit 13.9–25.0 kg of CO₂ into the environment (Darwish 2007; ESCWA 2009). There is a need to perform a risk–cost trade-off analysis in selecting the desalination process.

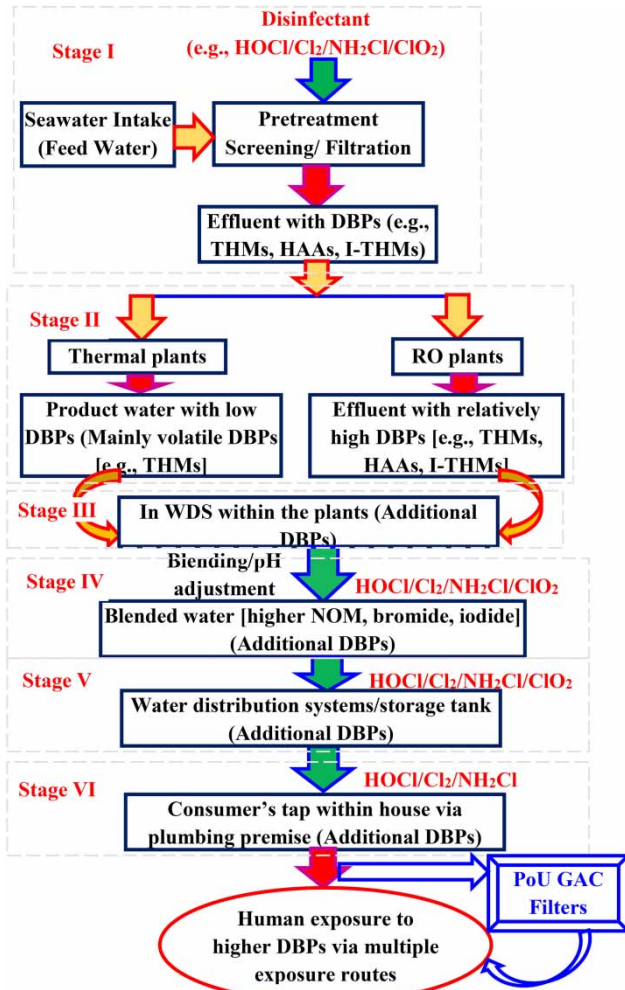


Figure 2 | Formation of DBPs in different stages of supplying desalinated water (from feed water at sea to tap water within the house).

In Stages III–V, many plants in Saudi Arabia apply HOCl or Cl₂ (Kim *et al.* 2015). In these stages, desalinated seawater is mixed with treated groundwater containing higher levels of NOM, bromide and iodide. The higher levels of bromide and iodide can increase the formation of Br-DBPs, I-DBPs and Br-I-DBPs (Gong & Zhang 2015; Gong *et al.* 2016; Ioannou *et al.* 2016). Past studies reported increased formation of Br-DBPs and I-DBPs in the presence of bromide and iodide, respectively (Zhai *et al.* 2014; Gong & Zhang 2015; Gong *et al.* 2016; Ioannou *et al.* 2016; Postigo *et al.* 2017). In these stages, DBPs are seldom controlled. In Stage VI, water enters the plumbing premise of a house or building where water can be stagnant for several hours leading to the formation of additional DBPs (Chowdhury *et al.*

2010; Chowdhury 2016). Although DBPs in product water from thermal plants are low (Stage II), concentrations at consumers' taps can be significantly high due to the implications of the subsequent stages (Stages III–VI).

The efficient control of DBPs can be achieved through multiple steps. In Stage II, solar or low-energy distillation may be the first step, which can exclude the non-volatile DBPs while a small fraction of volatile DBPs can be present in water. In desalinated and blend water, concentrations of Br-DBPs were much higher than the Cl-DBPs while I-DBPs were occasionally reported (Ioannou *et al.* 2016; Postigo *et al.* 2017). Removal of bromide and iodide prior to Stage V may be the second step (Figure 2). The third and final step prior to water consumption (post-Stage VI) may include filtration of water through granular activated carbon (GAC) filters. Past studies reported the decrease of THMs and HAAs using GAC filters in the ranges of 84–89% and 58–71%, respectively (Chowdhury *et al.* 2010). Weinberg *et al.* (2006) reported removal of 93–99% of THMs and 68–95% of HAAs using different types of activated carbon filters. Very recently, Jiang *et al.* (2017, 2018) have applied GAC adsorption to remove intermediate aromatic halogenated DBPs, which formed during chlorination and acted as intermediate DBPs to form the commonly known DBPs (e.g., THMs, HAAs, etc.). Through increasing the initial bromide level from 0.0 to 2.0 mg/L, removal of total organic halides (TOX) was increased from 52% to 74% (Jiang *et al.* 2018). In addition, an increase of chlorine contact time from 0.5 to 3.0 h increased TOX removal from 61% to 75%. Levesque *et al.* (2006) reported reductions of THMs by 30%, 87% and 92%, respectively, through storage in a refrigerator and boiling and filtering followed by storage in a refrigerator. However, boiling was found to increase DCAA by 35% and decrease TCAA by 42% while no change to the total HAAs was observed (Levesque *et al.* 2006). Filtration through the GAC point-of-use (PoU) filters can be an option while the cost of filters and handling of contaminated GAC laden waste can be other issues which need better attention.

Application of alternative disinfectants might reduce formation of DBPs. ClO₂ and NH₂Cl have been reported to produce low amounts of DBPs (Dalvi *et al.* 2000), which can be an option for Stage I (Figure 2). Laboratory studies on seawater with ClO₂ have reported very low concentrations of THMs and HAAs in Korea and Spain (Simon

et al. 2014; Yu *et al.* 2014). However, ClO_2 is to be generated on-site, requiring transportation and storage of chemicals, which can increase the operational costs. In addition, ClO_2 forms chlorite, which is critical and limited to 0.7 mg/L (WHO 2011). Following production of desalinated water, application of NH_2Cl in Stages III–V is likely to produce lower amounts of DBPs. However, the weak performance of NH_2Cl may need additional contact times and higher costs (Figure 2). In addition, past studies reported relatively higher levels of NDMA and I-THMs in NH_2Cl treated supply water (USEPA 2012; Chowdhury 2014; Ioannou *et al.* 2016; Postigo *et al.* 2017) while these DBPs were more toxic than the regulated DBPs (USEPA 2018). In desalinated water, the product water is unlikely to have precursors for NDMA (e.g., liquid rocket fuel, dimethylamine (DMA), cationic polymers, ion-exchange resins with amine functional groups, etc.). The excellent disinfection capacity and low DBP formation potential of ClO_2 is attractive for the pretreatment of feed water at the intakes. The combined disinfection of ClO_2 (Stage I) and NH_2Cl (Stages III–V) can be evaluated in the context of performance, cost, types and amounts of different DBPs in desalinated and blend water, and human exposure and risk. Future study is warranted in this direction.

FUTURE RESEARCH NEEDS

Since 1974, studies have made significant progress on the occurrences and distributions of DBPs in supply water. In the past two decades, DBPs in desalinated and blend water have attracted the attention of many researchers. The advanced analytical capacities of the recent instruments have assisted in detecting many emerging DBPs in desalinated and blend water while their comprehensive effects upon humans are yet to be investigated. In addition, many DBPs are yet to be discovered, thus their effects upon humans are also unknown. Several issues need further attention to improve desalinated and blend water quality. The following research directions can assist in achieving better control on DBPs and their risks to humans:

- During pretreatment (Stage I), use of Cl_2 is likely to form higher levels of Br-DBPs and I-DBPs in feed water.

Thermal distillation removes most of the non-volatile DBPs and precursors to trace levels while volatile DBPs are likely to be present in the product water at relatively low concentrations. The RO process (Stage II) removes more than 99% of bromide and iodide from feed water while RO effluents contain considerable amounts of bromide (250–600 $\mu\text{g/L}$) and iodide (<4–16 $\mu\text{g/L}$), which are higher than most freshwater systems (Kutty *et al.* 1995; Magara *et al.* 1996; Kim *et al.* 2015; Le Roux *et al.* 2015). Concentrations of DBPs in RO effluents were higher (Table 2). Application of ClO_2 during pretreatment (Stage I) is likely to reduce DBPs while disinfection in the other stages (Stages II–VI) can be ensured using NH_2Cl . However, past studies reported relatively higher levels of NDMA and I-THMs in NH_2Cl treated supply water while these DBPs are more cytotoxic and genotoxic than the regulated DBPs (Table 6). Further, such a combined disinfection is likely to increase the cost and induce other health effects, thus needs better understanding. Future study is needed to investigate the feasibility of using the combined disinfection (ClO_2 and NH_2Cl) in different stages of desalination.

- Dechlorination of pretreated water prior to feeding RO processes is likely to reduce DBPs formation. Chloramines (NH_2Cl , NHCl_2) are often used to control biofouling agents in desalination intake structures and RO membranes, which also minimizes the damage of the membranes. However, it may form bromamine (BrH_2N) due to the high concentrations of bromide in feed water, leading to the loss of disinfectant residual. In addition, BrH_2N can also increase brominated DBPs (Zhai *et al.* 2014; Zhu & Zhang 2016). Recent studies have reported the formation of several emerging DBPs following chloramination of bromide and iodide containing water (Zhai *et al.* 2014; Gong & Zhang 2015; Gong *et al.* 2016; Postigo *et al.* 2017). Formation of DBPs in chloraminated seawater needs better understanding. Future study is warranted on dechlorination of pretreated water prior to feeding RO processes.
- In Stages III–V (Figure 2), desalinated water is stabilized, mixed, stored and transported through the WDS. During these stages, NOM, bromide, iodide and DBPs are increased, which leads to increased demand for disinfectants. There is a need for the removal of residual bromide

and iodide, which can be performed in Stages III and IV. However, removal of bromide and iodide is a challenge. Advanced technologies can be applied for the removal of bromide and iodide. Future study is warranted for the cost-effective removal of bromide and iodide from the supply water.

- Filtration through PoU filters equipped with an activated carbon filtration unit has been reported to reduce the exposure concentrations of THMs and HAAs significantly (Levesque *et al.* 2006; Weinberg *et al.* 2006; Chowdhury *et al.* 2010; Jiang *et al.* 2017, 2018). The performance of these filters can be evaluated in the context of emerging DBPs. In addition, the cost of activated carbon filters is typically higher, which can be an additional financial burden (Chowdhury *et al.* 2010). Future research is needed to produce low-cost activated carbon PoU GAC filters.
- Thermal plants remove non-volatile DBPs, bromide and iodide to trace levels. In the context of DBPs, these plants are attractive. In contrast, these plants consume more energy and they emit higher levels of CO₂ into the environment. The overall cost is likely to be higher. Development of hybrid or solar technology for seawater distillation is likely to produce better quality water at low cost. Future research is needed to develop low-cost distillation technology for seawater desalination.
- There are almost 600 types of DBPs (Richardson *et al.* 2007) in supply water whereas approximately 100 have been characterized with respect to cytotoxicity and genotoxicity (Wagner & Plewa 2017). Most of the DBPs reported, to date, are cytotoxic and/or genotoxic to the CHO cell while few studies have reported their genotoxicity on the human HepG2 cells (Zhang *et al.* 2012; Wagner & Plewa 2017). Although the lowest concentrations for such effects from DBPs were much higher than the environmentally available concentrations in supply water, the synergistic effects of various DBPs need better understanding. Future study is needed to explain the effects of a mixture of DBPs to humans.
- The seasonal and geographic variability of seawater quality affects the formation of DBPs. Temporal events (e.g., storms, algal blooms, oil spills) can increase DBPs formation. As an example, algal blooms are higher during summer, which increases the demand for Cl₂ doses,

leading to the formation of higher DBPs. Further research is needed to characterize the effects of seasonal, geographic variability and temporal events on the formation and speciation of DBPs.

- The contributions of THMs and HAAs to the total organic halide (TOX) are around 50% (Le Roux *et al.* 2015) and many DBPs are yet to be identified. The relation between TOX and DBPs should be assessed. Further study is needed to understand the characteristics of emerging DBPs. The feasibility of using TOX as the indicator of toxicity may be investigated in future.
- To date, no model has been reported to predict DBPs in different stages of desalination (Figure 2). Availability of models is likely to assist in predicting and controlling DBPs in different stages of desalination. Future study is needed to identify the factors affecting formation of DBPs, and develop and validate models using these factors.
- Use of ozone (O₃) as a disinfectant during pretreatment and post-treatment of desalination processes may result in the formation of bromate and bromate is one of the highly undesirable DBPs in water. The methods of removing bromide prior to disinfection and bromate following disinfection need to be investigated prior to application of O₃ for seawater desalination.

CONCLUSIONS

This study presented a review on the formation of DBPs in different stages of desalinated and blend water production and supplies from source to tap, and their toxic effects to mammalian cells. The high concentrations of bromide in seawater result in higher fractions of Br-DBPs while the presence of iodide and I-DBPs have been reported in recent years. Br-DBPs and I-DBPs are more cytotoxic and genotoxic than the regulated DBPs. In addition, new-generation DBPs are being identified in supply water. There is a need to better characterize DBPs, their formation kinetics, effects upon humans and control strategies. Coastal regions are the homes of around 2 billion people and groundwater aquifers in these regions might be polluted due to seawater intrusion. These populations, as well as

the populations supplied with desalinated and blend water, are likely to be affected by the high concentrations of bromide and iodide in seawater. There is no single approach to providing the solution for the entire spectrum of problems. A multi-barrier approach for different stages of desalinated and blend water supplies might assist in controlling DBPs at the exposure points, and thus better protect humans.

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