

BROMIDE CONCENTRATIONS IN SURFACE DRINKING WATER SOURCES

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SUMMARY

WHAT IS BROMIDE AND WHERE DO YOU FIND IT NATURALLY IN SURFACE WATERS?

Bromine (Br₂) is a chemical element (atomic number 35) belonging to the highly reactive halogen group, which also includes fluorine, chlorine, and iodine. Halogens are oxidizing agents that form anions by accepting an electron (their outer electron shell is one electron short of being full). Bromide (Br⁻) is the anion of the element Bromine. Since elemental bromine is highly reactive, it does not occur freely in nature, but instead exists as salts (e.g. NaBr, AgBr) or acids (e.g. HBr, HOBr; WHO 2018).

Bromide naturally occurs in the earth's crust, seawater, salt lakes, and underwater brines (VanBriesen 2014). Fossil fuels, such as coal, also contain varying concentrations of bromide (Kolker et al. 2006). The highest natural concentrations of bromide are found in seawater (66-68 mg/L), shale geologic formations (24 mg/kg), and coastal groundwater (2.3 mg/L) and soils (850 mg/kg). In the United States, inland groundwaters, fresh surface waters, and drinking water sources do not typically have naturally high bromide values (0.014-0.2 mg/L; VanBriesen 2014).

WHAT ARE THE RISKS ASSOCIATED WITH BROMIDE IN SOURCE WATER?

Bromide in itself is not a risk to human or ecosystem health when present in source water (WHO 2009). However, during drinking water decontamination, bromide reacts with natural organic matter (NOM) present in source water and chemical disinfectants to create brominated disinfection by-products (DBPs), which may pose a significant threat to human health (Richardson et al. 2007). During the drinking water treatment process, chemical disinfectants (chlorine, chloramine, ozone, chlorine dioxide, and ultraviolet radiation) are used to remove pathogenic microbes and nuisance metals. Hundreds of species of DBPs can be produced at various stages of the drinking water disinfection process depending on source water characteristics (NOM concentration, pH, temperature, and halide concentrations), disinfectant type, engineering practices, water distribution network characteristics, and climate (Krasner 2009).

Since the 1970's when DBPs were first discovered in finished drinking water (Rook 1974), many toxicological and epidemiological studies have examined the relationship between DBP exposure and potential human health consequences (Charrois and Hruddy 2012). Results from toxicological studies using a variety of *in vitro* (*Salmonella typhimurium* and Chinese hamster ovary assays) and *in vivo* (rodent and fish bioassays) methods, indicate that many classes of DBPs are cytotoxic, neurotoxic, mutagenic, genotoxic, carcinogenic, and even teratogenic (Richardson et al. 2007). Elevated bromide in source waters is particularly concerning because brominated DBPs have been shown to be more carcinogenic and cytotoxic than their chlorinated analogs (Richardson et al. 2007, Pan et al. 2014, Ersan et al. 2019). In epidemiological studies, long-term exposure to DBPs has been consistently associated with an increased risk of bladder cancer (Villanueva et al. 2003, 2004, Costet et al. 2011), while acute exposure to DBPs during pregnancy has been inconsistently associated with adverse effects on fertility, pregnancy, and fetal development (Hruddy 2009, Nieuwenhuijsen et al. 2009, 2010, Grellier et al. 2010, Villanueva et al. 2015). Importantly, even a relatively low increase in source water bromide concentration can shift the species and quantity of DBPs produced during drinking water disinfection to a greater number of brominated DBPs (Singer and Reckhow 2011, Mctigue et al. 2014) escalating the risk of adverse human health effects (Richardson et al. 2007, Ersan et al. 2019). Recently, Regli et al. (2015) estimated an increased risk of bladder cancer associated with elevated source water bromide at concentrations equivalent those frequently associated with anthropogenic contamination.

WHAT ARE ANTHROPOGENIC DRIVERS OF INCREASING BROMIDE CONCENTRATIONS?

Historical bromide uses include early photograph development (silver bromide) and sedatives in human medicine (potassium bromide) during the 18th and 19th centuries (Soltermann et al. 2016). The first significant anthropogenic releases of bromide into the environment occurred in the 1920s-1990s when brominated compounds were added to gasoline to prevent lead deposition in the engine (Thomas et al. 1997). Engine combustion of the added bromine released methyl bromide gas (also called bromomethane) into the environment. The use of methyl bromide as an agricultural fungicide also represented a significant anthropogenic release of bromide until its use was largely phased out by the 2000s (Taylor 1994). Finally, bromide has been released as a waste product of potassium (potash) mining activities and found to elevate surface water bromide concentrations in several European countries, particularly the River Rhine (Flury and Papritz 1993) and the Llobregat River (Ventura and Rivera 1985). Salt mining still a major industry in various parts of the world and continues to create water quality issues when brines pollute source waters (Valero and Arbós 2010).

Current anthropogenic sources of bromide include energy extraction and utilization, coal-fired power plants, water treatment, flame retardants, pre-planting and post-harvest biocides, agricultural herbicides, municipal waste incinerators, landfill leachate, road deicers, and pharmaceuticals (Vainikka and Hupa 2012, Mctigue et al. 2014, VanBriesen 2014, Winid 2015).

WHY IS IT IMPORTANT TO UNDERSTAND WHAT IS DRIVING INCREASING BROMIDE CONCENTRATIONS?

Elevated levels of bromide in source water leads to a higher production of brominated DBPs following drinking water disinfection (Cowman and Singer 1996). Brominated DBPs are more carcinogenic than their chlorinated analogs, meaning that there are greater human health risks associated with drinking, food preparation, and bathing with chemically-disinfected water (Richardson et al. 2007, Yang et al. 2014). Also, greater source water bromide levels can lead to increased formation of unregulated DBP classes, including halonitromethanes, haloamides, haloacetronitriles (Krasner et al. 2006, Pressman et al. 2010), which may be more harmful than regulated DBPs (Richardson et al. 2007). Source water bromide concentration is one of the most important DBP formation factors and elevated bromide can lead to as much as a two-fold increase in both regulated and unregulated DBPs (Hua et al. 2006, Sfyntia 2017).

Short-term exposure to high levels of DBPs has been weakly associated with restricted fetal growth (small for gestational age; Grellier et al. 2010), while long-term exposure to DBPs is consistently associated with an increased risk of urinary bladder cancer (Villanueva et al. 2003, 2004, Costet et al. 2011). Identifying drivers of increasing bromide concentrations in source water is essential because once bromide levels are elevated, there are no practical methods to remove the anion prior to disinfection (Rivera-Utrilla et al. 2019). Further, there are no practical methods available to reduce the number of brominated DPBs in finished water following drinking water treatment (Rivera-Utrilla et al. 2019). The best method to control bromide levels in source water and prevent the formation of brominated DBPs in finished drinking water is to regularly monitor bromide levels and if elevated levels are detected, then identify and stop anthropogenic inputs of bromide.

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BROMIDE: NATURAL SOURCES AND CHEMICAL INTERACTIONS

WHAT IS BROMIDE?

Bromine (Br₂) is a chemical element (atomic number 35) belonging to the highly reactive halogen group, which also includes fluorine, chlorine, and iodine. Halogens are oxidizing agents that form anions by accepting an electron (their outer electron shell is one electron short of being full). Bromide (Br⁻) is the anion of the element Bromine. Since elemental bromine is highly reactive, it does not occur freely in nature, but instead exists as salts (e.g. NaBr, AgBr) or acids (e.g. HBr, HOBr; WHO 2018).

WHAT ARE NATURAL SOURCES OF BROMIDE IN SURFACE AND GROUND WATER?

Bromide is a naturally occurring trace element of the earth's crust and seawater. Fossil fuels, such as coal, also contain varying concentrations of bromide. A recent report by (VanBriesen 2014) summarized available information regarding natural bromide concentrations in the US, which highlights the low natural bromide concentrations of inland waters:

Natural bromide source	Concentration
Seawater	66-68 mg/L
Earth's crust	6 mg/kg
Shale	24 mg/kg
Coastal groundwater	2.3 mg/L
Coastal soils	850 mg/kg
Inland groundwater	0.0032 to 0.058 mg/L
Inland fresh surface waters	0.014-0.2 mg/L
Rainfall	<0.01 mg/L
Drinking water sources	0.095±0.132

Compared to inland waters, natural bromide concentrations of coastal waters and soils can be quite high due to seawater deposition and intrusion. Saltwater intrusion is the process by which seawater moves into freshwater aquifers, increasing the mineral (bromide) concentration of coastal drinking water sources (Konikow and Reilly 1999). Human activities (groundwater extraction, canal construction, and the creation of drainage networks) and anthropogenic climate change (sea level rise and extreme weather events) can exacerbate saltwater intrusion (Rasmussen et al. 2013).

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WATER DISINFECTION BY-PRODUCTS AND INCREASING BROMIDE IN SOURCE WATER

WHAT ARE DISINFECTION BY-PRODUCTS?

Disinfection by-products (DBPs) are compounds created unintentionally when halides (bromide and iodine) and other pollutants react with natural organic matter present in source water and disinfectants (chlorine, chloramine, ozone, chlorine dioxide, and UV) during drinking water treatment processes (Charrois and Hrudey 2012). Around 700 DBPs have been discovered worldwide, but only a subset of these have been evaluated for risks to human health (Richardson et al. 2007). Along with bromate and chlorate, the 11 regulated species of DBPs include trihalomethanes (referred to as TTHMs or THM4) and haloacetic acids (HAAs or HAA5). There are 4 other bromine-containing haloacetic acids that are not regulated but are monitored as a part of HAA6Br and HAA9. The following table from Cortés and Marco (2018) summarizes the major classes of DBP and their occurrence values:

Table 1
Main groups of DBPs and their levels of occurrence.
Occurrence data taken from [4,38,77–81].

Disinfection by-products	Occurrence (µg/L)
HALONITROMETHANES Chloronitromethane, Dichloronitromethane, Trichloronitromethane (Chloropicrin), Bromonitromethane, Dibromonitromethane, Tribromonitromethane (Bromopicrin), Bromochloronitromethane, Bromodichloronitromethane, Dibromochloronitromethane	0.1–5
HALOACETIC ACIDS AND OTHER HALOACIDS Chloroacetic acid, Dichloroacetic acid, Trichloroacetic acid, Bromoacetic acid, Dibromoacetic acid, Tribromoacetic acid, Iodoacetic acid, Diiodoacetic acid, Triiodoacetic acid, Bromochloroacetic acid, Bromodichloroacetic acid, Bromoiodoacetic acid, Dibromochloroacetic acid, Chlorodibromoacetic acid	1–2600
TRIHALOMETHANES Chloroform, Bromoform, Dibromochloromethane, Bromodichloromethane, Dichloroiodomethane, Bromochloroiodomethane, Dibromoiodomethane, Chlorodiiodomethane, Bromodiiodomethane, Iodoform, Dichloromethane, Bromochloromethane, Chlorodibromomethane, Dibromomethane	0.05–380
OXYHALIDES Bromate (0.2 – 25.1), Chlorate (up to 190), Chlorite (up to 1100)	0.2–1100
HALOFURANONES MX, Red-MX, Ox-MX, EMX, ZMX, Mucochloric acid, BMX-1, BMX-2, BMX-3, BEMX-1, BEMX-2, BEMX-3	0.08–0.85 MX (0.08–0.85), 0.5–219
HALOACETONITRILES Chloroacetonitrile, Dichloroacetonitrile, Trichloroacetonitrile, Bromoacetonitrile, Dibromoacetonitrile, Tribromoacetonitrile, Bromochloroacetonitrile, Bromodichloroacetonitrile, Dibromochloroacetonitrile, Iodoacetonitrile	10–60
HALOKETONES Chloroacetones	Up to 9.4
HALOAMIDES Chloroacetamide, Dichloroacetamide, Trichloroacetamide, Bromoacetamide, Dibromoacetamide, Tribromoacetamide, Bromochloroacetamide, Bromoiodoacetamide, Bromodichloroacetamide, Dibromochloroacetamide, Iodoacetamide, Diiodoacetamide, Chloroiodoacetamide	1–1180
HALOAMINES & OTHER AMINES Chloramines, Nitrosamines (NDMA), Heterocyclic amines	0.4–497
ALDEHYDES Formaldehyde, Acetaldehyde, Chloroacetaldehyde, Dichloroacetaldehyde, Bromochloroacetaldehyde, Trichloroacetaldehyde (chloral hydrate), Tribromoacetaldehyde	Formaldehyde (up to 13.7)
Other DBPs Quinones, Cyanogen halides, Chlorophenols, Alkylketocarboxylic acids, Carboxylic acids, Haloacetates, Halopyrroles, Others	

WHAT ARE THE PROCESSES THAT CREATE BROMINATED COMPOUNDS?

During chlorination (disinfection with chlorine), bromide is oxidized to hypobromous acid (HOBr), which reacts with NOM to form brominated DBPs, including bromoform, trihalomethanes, and haloacetic acids (Heeb et al. 2014). Alternatively, during ozonation hypobromous reacts with ozone (O₃) to primarily form bromate (BrO₃⁻) (additional formation reactions discussed in von Gunten 2003). Thus, depending on which types of disinfectants are used and the characteristics of the natural organic matter present in the source water, there are several processes that can create brominated DBPs (Heeb et al. 2014). As summarized in Regli et al. (2015), elevated bromide in source waters leads to brominated DBP formation following chlorination (Krasner et al. 1989, Petri et al. 1997, Obolensky and Singer 2005), chloramination (Diehl et al. 2000), ozonation (Richardson et al. 1999), disinfection with chlorine dioxide

(Richardson et al. 2003), and combinations of these disinfectants through a variety of chemical reactions. Detailed descriptions of chemical reactions that create brominated DBPs can be found in von Gunten 2003, Heeb et al. 2014, Sharma et al. 2014.

WHAT ARE THE HUMAN HEALTH RISKS TO EXPOSURE?

Bromide in itself is not a risk to human or ecosystem health when present in source water (WHO 2009). The levels of bromide that are toxic to humans and other species are much higher than most natural environmental bromide concentrations. In fact, since natural background levels of bromide are so low in the environment (except in seawater, shales, and coastal groundwater and soils), bromide has been regularly used in environmental studies as a nonreactive tracer to study water and solute movement in soils (Flury and Papritz 1993).

In contrast, the brominated DBPs formed when bromide reacts with natural organic matter present in source water and chemical oxidants during drinking water decontamination processes may represent serious risks to human health (Rook 1974, Charrois and Hrudey 2012). Across all classes of DBPs, toxicological studies using a variety of *in vitro* (*Salmonella typhimurium* and Chinese hamster ovary assays) and *in vivo* (rodent and fish bioassays), indicate cytotoxic, neurotoxic, mutagenic, genotoxic, carcinogenic, and teratogenic consequences of DBP exposure (Reviewed in Richardson et al. 2007). The following table from Richardson et al. (2007) summarizes toxicological findings for the regulated DBPs:

Summary of occurrence, genotoxicity, and carcinogenicity of regulated DBPs

DBP	Occurrence ^a	Genotoxicity						Carcinogenicity			
		Gene mutation		Chrom. mutation		DNA damage		Rodent		Human ^b	
		Bacteria	MC ^c	<i>In vitro</i>	<i>In vivo</i>	<i>In vitro</i>	<i>In vivo</i>	Mouse	Rat	IARC	EPA
Bromodichloromethane	****	+	-	-	-	+	-	+, -, -	+, +, -	2B	B2
Bromoform	****	+	+	+	+	+	-	-	+	3	B2
Chlorodibromomethane	****	+	+	+	-	-	-	+	-	3	C
Chloroform	*****	-	-	-	-	+	-	+, -	+, +, +	2B	
Chloroacetic acid	***	-	+	-	-	-	-	-	-	-	
Bromoacetic acid	***	+	-	-	-	+	-	-	-	-	
Dibromoacetic acid	*****	+	-	-	-	+	-	+	+		
Dichloroacetic acid	*****	+	+	+	+	-	-	+	+	2B	B2
Trichloroacetic acid	*****	-	-	-	-	-	-	+	-	3	
Bromate	***	+	+	+	+	+	+	+	+	2B	B2
Chlorite	*****	-	-	-	-	-	-	-	-		

^a *Low-ng/L levels; **ng/L to sub-µg/L levels; ***sub- to low-µg/L levels; ****low-µg/L levels; *****low- to mid-µg/L levels; ***** high µg/L levels.

^b IARC: 1 2B, possibly carcinogenic to humans; 3, not classifiable as to its carcinogenicity in humans. EPA: B2, probably carcinogenic to humans as evaluated using the U.S. EPA's 1986 *Guidelines for Carcinogen Risk Assessment*; C, possibly carcinogenic to humans as evaluated using the U.S. EPA's 1986 *Guidelines for Carcinogen Risk Assessment*.

^c MC, mammalian cells.

Regulated and unregulated brominated DBPs are particularly concerning because they are more carcinogenic than their chlorinated analogs in animal studies (Wagner and Plewa 2017). It is important to note that a growing number of toxicological studies show that emerging DBPs containing iodine and nitrogen are even more carcinogenic and cytotoxic than brominated DBPs, although they are typically present in finished drinking water at much lower quantities (Wagner and Plewa 2017).

Since the 1980s, several epidemiological studies have investigated whether exposure to DBPs in chlorinated water is associated with negative human health consequences, including cancer and reproductive effects (Charrois and Hrudey 2012, Grellier et al. 2015, Villanueva et al. 2015). There is consistent evidence from individual studies and meta-analyses of an association between urinary bladder cancer and DBP exposure, typically measured as trihalomethane (THM) or haloacetic acid (HAA) concentration (Villanueva et al. 2003, 2004, Costet et al. 2011). It is important to note that a mechanism for THMs or HAAs to contribute to bladder cancer has not been identified and therefore support for a causal relationship between THMs or HAAs and bladder cancer is weak (Charrois and Hrudey 2012). Nevertheless, the consistent association of chlorinated water consumption with urinary bladder cancer is a cause for concern and more research is necessary to identify the classes or species of DBPs driving this relationship (Charrois and Hrudey 2012). Several studies have looked for associations between DBP exposure and colon (Doyle et al. 1997, King et al. 2000) and rectal (Hildesheim et al. 1998, Bove et al. 2007) cancer, but results between studies are inconsistent, so this relationship is considered inconclusive (Rahman et al. 2010). Further, recent critical reviews have highlighted methodological problems that limit confidence in the findings of these studies (Charrois and Hrudey 2012, Grellier et al. 2015).

Studies investigating the adverse effects of DBP exposure (again, typically measured as THM or HAA concentration) on fertility, pregnancy, and fetal development have yielded inconsistent and controversial results (Nieuwenhuijsen et al. 2009, 2010, Mitra et al. 2009, Grellier et al. 2010, Villanueva et al. 2015). Similar to the concerns regarding results that associate DBP exposure with colon and rectal cancer, the current links between DBP exposure and negative reproductive outcomes are inconclusive (Charrois and Hrudey 2012, Grellier et al. 2015, Villanueva et al. 2015). However, there is some evidence of an association between THM exposure and fetal growth, specifically weight according to gestational age (small for gestational age; Grellier et al. 2010). Fertility endpoints that have been studied in response to DBP exposure include sperm quality and menstruation cycle length, but findings have been inconsistent. One study found an association between tap water consumption (THM levels greater than 75 µg/L) during pregnancy and an increased risk of spontaneous abortion (Waller et al. 1998). However, this finding has not been confirmed in subsequent studies with improved DBP exposure estimates (Savitz et al. 2006).

WHAT IS THE RELATIONSHIP BETWEEN ORGANIC MATTER, BROMIDE, AND BROMINATED COMPOUNDS?

Brominated DBPs are created when bromide, natural organic matter (NOM), and chemical disinfectants react during drinking water decontamination. Specifically, bromide is oxidized to hypobromous acid and then bromine is substituted into organic structures present in NOM (Heeb et al. 2014). Although chlorine and bromine compete for organic reaction sites, bromine is more efficient at substitution and has faster reaction kinetics than chlorine (Westerhoff et al. 2004). Natural organic matter is composed of humic substances, hydrophilic acids, protein, lipids, carbohydrates, carboxylic acid, amino acid, and hydrocarbons, in quantities that vary geographically and seasonally (Westerhoff et al. 2004). Although groups of compounds commonly found in NOM have been investigated as indicators of potential DBP formation, the specific UV absorbance at 254 nm (SUVA₂₅₄) of a water sample (which depends on the nature of NOM present) has been established as a reliable predictor of DBP formation (Ersan et al. 2019). Recent experimental work has demonstrated increased trihalomethane and haloacetic acid formation with increasing SUVA₂₅₄ (Ersan et al. 2019). The removal of NOM prior to

disinfection can reduce overall DBP formation, but when the source water also contains high levels of bromide, increasing the bromide:NOM ratio can lead to proportionally greater brominated DBPs (Kristiana et al. 2011). Independent of NOM characteristics, several studies have confirmed that greater bromide concentrations in source water results in greater brominated DBP formation (Cowman and Singer 1996, States et al. 2013, Mctigue et al. 2014). Finally, cytotoxicity has been shown to significantly increase with greater bromide levels in source water and greater brominated DBP formation (Sawade et al. 2016, Ersan et al. 2019).

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REGULATIONS GOVERNING BROMINATED COMPOUNDS

WHAT ARE THE LAWS IN THE US ABOUT DISINFECTANTS/DISINFECTION BY-PRODUCTS AND HOW HAVE THEY CHANGED OVER THE PAST 10 YEARS?

As of 2019, only 11 of the ~700 disinfection by-product (DBP) species that have been identified are regulated by the US Environmental Protection Agency (US EPA; Singer 2006). Four of these DBPs belong to the trihalomethane group (THM4: bromodichloromethane, bromoform, dibromochloromethane, and chloroform), five are haloacetic acids (HAA5: dichloroacetic acid, trichloroacetic acid, chloroacetic acid, bromoacetic acid, and dibromoacetic acid), and the final two are bromate and chlorite (USEPA 1998, 2006).

The first regulation of DBPs in the US was established by the US EPA's Total Trihalomethane Rule in 1979, which set a maximum contaminant level (MCL) for trihalomethanes present in finished drinking water at 0.10 mg/L (USEPA 1979). This regulation was created to strike a balance between the risks of reduced efficiency in removing waterborne pathogens and the creation of potentially carcinogenic DBPs (Hrudey 2009) while also keeping technological and economic constraints of water treatment plants in mind (Singer 1994, Li and Mitch 2018). Since the specific health risks associated with each species of DBP were relatively unknown, the regulation was based on the sum of THMs present in finished water (Singer 2006). However, the subsequent identification of several additional classes of DBPs in drinking water and a growing understanding of the potential toxicological and carcinogenic effects of individual species of DBPs lead to the creation of new MCL and maximum contaminant levels goals (MCLG) in the US (Li and Mitch 2018).

The current laws regulating drinking water disinfectant and disinfection by product regulation include the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules (DBPR; USEPA 1998, 2006). These regulations apply to community water systems and non-transient non-community systems that apply chemical disinfectants to drink water at any point during treatment (regardless of the number of customers served). The Stage 1 DBPR went into effect from 2002-2004 and expanded regulations to include HAA5, bromate, and chlorite. Under the Stage 1 DBPR the MCL for TTHM was lowered to 0.80 mg/L and MCLGs were created for individual DPB species within the regulated groups. The MCLG represents a non-enforceable public health objective that does not consider technological and economic limits of water treatment plants when defined, whereas the MCL is a legal threshold and enforceable regulation that does consider practical constraints on water treatment facilities (USEPA 1998). The Stage 1 DBPR also created maximum residual disinfectant levels (MRDL) for chlorine (4.0 mg/L), chloramines (4.0 mg/L), and chlorine dioxide (0.8 mg/L). Finally, the Stage 1 DBPR created a schedule and protocol for collecting DBP monitoring data at various stages of the treatment process.

The Stage 2 DBPR went into effect from 2012-2013 and supplemented the regulations established by the Stage 1 DBPR. Under the Stage 2 DBPR, water systems are required to identify areas of high DBP production within their treatment process for use as sampling sites. Each of these monitoring sites must have DBP levels in compliance with MCLs for TTHMs, HAA5, bromate, and chlorite, which is referred to as the locational running annual average (LRAA). The LRAA measure addresses a gap in Stage 1 DBPR compliance regulations, which allowed parts of a water distribution network to exceed DBP MCLs as long as the network as a whole averaged DBP levels below the MCLs (USEPA 2006).

Table 1. Maximum contaminant level (MCL) and maximum contaminant level goals (MCLG) for the 11 DBPs regulated by the US EPA’s Total Trihalomethane Rule (TTR 1979) and the Stage 1 (1998) and Stage 2 (2006) Disinfection Byproducts Rules (DBPR). Dashes indicate that no MCLG has been set for the DBP species. This table was modified from USEPA (2010).

DBP group	TTR 1979	Stage 1 Rule		Stage 2 Rule	
	MCL (mg/L)	MCL (mg/L)	MCLG (mg/L)	MCL (mg/L)	MCLG (mg/L)
Trihalomethanes (TTHM)	0.10	0.080		0.080	
Chloroform			-		0.07
Bromodichloromethane			Zero		Zero
Dibromochloromethane			0.06		0.06
Bromoform			Zero		Zero
Haloacetic acids (HAA5)	-	0.060		0.060	
Monochloroacetic acid			-		0.07
Dichloroacetic acid			Zero		Zero
Trichloroacetic acid			0.3		0.2
Bromoacetic acid			-		-
Dibromoacetic acids			-		-
Bromate	-	0.010	Zero	0.010	Zero
Chlorite	-	1.0	0.8	1.0	0.8

HOW DO THESE REGULATIONS COMPARE TO WHAT OTHER COUNTRIES ARE DOING (EUROPEAN UNION/AUSTRALIA, OTHERS)?

Overall, international regulations for DBPs are very similar to maximum contaminant levels (MCLs) under the Stage 1 and Stage 2 DBPR in the United States (summarized in Cortés and Marcos 2018). For example, in the US, the MCL for total THMs is 0.08 mg/L and guidelines for Europe, Canada, China, and Japan have been analogously set at 0.1 mg/L for total THMs. United States regulations for bromate (0.01 mg/L) and chlorite (1.0 mg/L) also compare with Canada and China, which set bromate and chlorite guidelines to 0.01 mg/L and from 0.7-1.0 mg/L, respectively. There is greater variation in the regulation of haloacetic acids, with only the US and Canada regulating the sum of five species, Japan and Australia regulating the individual concentrations three species, and China regulating the individual concentrations of two species. The guideline concentrations for the regulated haloacetic acids also vary widely, with HAA5 limits set at 60 mg/L (US) and 80 mg/L (Canada) and individual species limits from 0.02-2.0 mg/L for China, Japan, and Australia. Europe does not currently regulate any haloacetic acids, but there is a proposal for the revision of the EU Drinking Water Directive to include limits on HAA levels. Among the available data for global DBP regulations, Australia is an outlier in that its regulations allow much higher levels of trihalomethanes (0.25 mg/L), three haloacetic acid species (0.1-0.15 mg/L), bromate (0.02 mg/L), and chlorite (8.0 mg/L). Finally, the World Health Organization has set regulations on individual THMs (chloroform at 0.2 mg/L, bromoform at 0.1 mg/L, bromodichloromethane at 0.06 mg/L, and dibromochloromethane at 0.1 mg/L), HAAs (dichloroacetic acid at 0.05 mg/L and trichloroacetic acid at 0.02 mg/L), bromate (0.01 mg/L), and chlorite (0.7 mg/L).

WHAT ARE THE PRIMARY CONCERNS ASSOCIATED WITH THE CURRENT REGULATIONS?

Regulations concerning the maximum contaminant levels for DBPs and the protocol for monitoring the concentrations of these DBPs throughout the water treatment process have been established to limit the human health risks associated with using chemically-disinfected water for drinking, food preparation, and bathing (Singer 1994). The regulations attempt to strike a balance between disinfection of waterborne pathogens and minimization of DBP creation (Hrudey 2009) while keeping technological and economic constraints in mind (Singer 1994, Li and Mitch 2018). Thresholds for DBP levels in finished drinking water were chosen to reduce public health risks based on available toxicological and epidemiological data. The classes and individual species of DBPs were selected because trihalomethanes and haloacetic acids make up the majority of DBPs in finished drinking water following disinfection by chlorination (Krasner et al. 1989). Further, THMs and HAAs were thought to be surrogates for the hundreds of unregulated (and unmeasured) DBP species potentially present in the finished drinking water and indicators of the toxicity and human health risk associated with water use (Singer 2006).

Unfortunately, there is strong scientific evidence that the current Stage 1 and Stage 2 DBPRs fail to protect water consumers from exposure to potentially harmful species and concentrations of DBPs. US EPA regulations of DBPs have been updated several times since the first discovery of DBPs in finished drinking water in 1974 (Rook 1974). However, as argued by Singer (2006) these changes have consistently failed to consider the scientific evidence showing that the 11 regulated DBPs are inadequate surrogates for complex mixtures of potential hundreds of DBPs present in finished drinking water and therefore poor indicators of health risks associated with water use (Kolb et al. 2017).

First, only five of the nine bromine- and chlorine-containing haloacetic acids are regulated. The decision to regulate only five of these HAAs was made when analytical constraints limited the ability to quantify the four unregulated HAA species. By the mid-1990s the importance of the four unregulated species (account for 20-50% of HAA), especially for source water with elevated bromide levels, was recognized (Cowman and Singer 1996). Despite the commercial availability of the standards for the four unregulated HAAs before the finalization of Stage 1 DBPR, only five of the nine species were included for regulation (Singer 2006). The Stage 2 DBPR also failed to define MCL for the four unregulated HAA species, meaning that our current regulations do not accurately safeguard public exposure to haloacetic acids. The regulation of HAA5 instead of all nine species is particularly important when considering source waters with elevated bromide concentrations. When source waters containing high levels of bromide are disinfected with chlorine, DBP formation shifts to a greater proportion of brominated species, including the four unregulated brominated haloacetic acids (Cowman and Singer 1996). This means that the HAA5 measure underestimates HAA exposure, especially if the source water contains high levels of bromide.

Second, THM and HAA levels are regulated based on the sum of the species on a mg/L basis, meaning that the weights of individual species are added up to quantify TTHM and HAA5 levels. Since the molecular weights of DBPs increase with bromide incorporation, species containing only chloride have a higher weighting factor. This is a problem, because some of these chlorinated regulated species, such as chloroform, are considered less dangerous than brominated compounds like bromoform, which leads to the misrepresentation of public health risks (Singer 2006).

Third, regulating trihalomethanes and haloacetic acids as group sums (TTHM and HAA5) is not appropriate because the human health risks associated with DBP exposure vary between species (Singer 2006). This means that although two water samples may have the same TTHM or HAA5 values, the risk associated with consuming those water samples may be dramatically different depending on the proportions of individual DBP species that are contributing to those sums (Singer 2006). This is especially true for high bromide source waters, as there are greater health risks associated with brominated DBP species (Sawade et al. 2016, Kolb et al. 2017).

Finally, there is no evidence that the 11 regulated DBPs are surrogates for the unregulated DBPs or indicators of the health risks associated with water consumption (Krasner et al. 2006, Hrudey and Fawell 2015, Sawade et al. 2016). In fact, there is evidence that the unregulated and often unmeasured DBPs are drivers of toxicity (Richardson et al. 2007, Plewa et al. 2017). This is particularly concerning as water utilities switch to alternative disinfectants (chloramines, ozone, and chlorine dioxide) in attempts to comply with the Stage 1 and 2 DDBP rules. There is much less data on DBP formation and associated health risks of water consumption following treatment with alternative disinfectants. Recent work suggests that although alternative disinfectants may reduce the levels of regulated DBPs, these methods may promote the formation of unregulated DBPs that are potentially more genotoxic and cytotoxic (Richardson et al. 2007, Richardson and Kimura 2017, Samson et al. 2017). Increased formation of unregulated DBPs with alternative disinfectants is of particular concern if source waters contain elevated levels of bromide (Richardson et al. 1999).

CAN YOU FIND ANY PREDICTED CHANGES THAT MIGHT AFFECT REGULATION IN THE FUTURE?

Since there are no human or environmental health risks associated with bromide in itself, discharges of bromide to surface waters has never been regulated in the United States (WHO 2009, Good and Vanbriesen 2017). However, an accumulation scientific evidence over the past 40 years has identified bromide as an important precursor of disinfection by products (Cowman and Singer 1996, Singer and Reckhow 2011, States et al. 2013, Mctigue et al. 2014). Further, brominated DBPs are more genotoxic and cytotoxic than their chlorinated analogs, meaning there is potentially a greater human health risk associated with consuming water containing brominated DBPs (Richardson et al. 2007, Yang et al. 2014). Finally, greater source water bromide levels can lead to increased formation of unregulated DBP classes, including halonitromethanes, haloamides, haloacetronitriles (Krasner et al. 2006, Pressman et al. 2010), which may be more harmful than regulated DBPs (Richardson et al. 2007).

The US EPA has added bromide and total organic carbon (another important DBP precursor) to the Safe Drinking Water Act (SDWA) fourth Unregulated Contaminant Monitoring Rule (UCMR 4) as of December 2016 (USEPA 2016a). This means that the EPA has required drinking water utilities to monitor bromide and TOC to establish occurrence data that can be used to consider future regulation (Richardson and Ternes 2018). The US EPA has also included several haloacetic acid groups containing brominated species (HAA5; HAA6Br: bromochloroacetic acid, bromodichloroacetic acid, dibromoacetic acid, dibromochloroacetic acid, monobromoacetic acid, tribromoacetic acid; HAA9: bromochloroacetic acid, bromodichloroacetic acid, chlorodibromoacetic acid, dibromoacetic acid, dichloroacetic acid, monobromoacetic acid, monochloroacetic acid, tribromoacetic acid, trichloroacetic acid) in the UCMR 4. The most recent contaminant candidate list (CCL-4), which is a list of priority chemical and microbial contaminants selected by the US EPA for information collection and future regulation consideration, includes several nitrogen-containing DBPs and bromochloromethane (used as a fire-extinguishing fluid

and found as a brominated DBP in drinking water; (USEPA 2016b). Additionally, there is currently a plan to investigate the impacts of oil and gas industry wastewater discharges on drinking water quality in the US EPA's Final 2016 Effluent Guidelines Program Plan (USEPA 2018). The biennial "Water Analysis: Emerging Contaminants and Current Issues" review published in the journal *Analytical Chemistry* provides an excellent overview of updates on US EPA water contaminant monitoring and regulations, as well as a summary of the latest published research findings concerning emerging water contaminants and analytical methods (Richardson and Ternes 2018).

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ANTHROPOGENIC SOURCES OF BROMIDE

WHAT ACTIVITIES ARE LEADING TO INCREASES IN BROMIDE CONCENTRATIONS IN SOURCE WATER?

Starting in the 18th and 19th centuries, bromide was used at a small-scale for photograph development (silver bromide) and as a sedative in human medicine (potassium bromide; Soltermann et al. 2016). However, the first substantial anthropogenic release of bromide into the environment occurred during the proliferation of the global automobile industry from the 1920s to the 1990s (Thomas et al. 1997). During that period, brominated compounds were added to leaded gasoline to act as a scavenger and prevent lead deposition from damaging car engines. Engine combustion activities emitted these brominated compounds as methyl bromide (also called bromomethane; Thomas et al. 1997). Another historical anthropogenic source of bromide was the widespread agricultural use of methyl bromide as a fumigant and soil sterilizer from the 1960s to the 1980s (Winid 2015). When it was discovered that methyl bromide contributed to ozone layer depletion, its use was drastically reduced by the 2000s under the 1987 Montreal Protocol (Taylor 1994). Although most of the methyl bromide released into the environment volatilizes into the atmosphere, about 10-30% remains in the soil and is broken down into bromide (Wegman et al. 1981). Finally, bromide has been released as a waste product of potassium (potash) mining activities and found to elevate surface water bromide concentrations in several European countries, particularly the River Rhine (Flury and Papritz 1993) and the Llobregat River (Ventura and Rivera 1985). Salt mining still a major industry in various parts of the world and continues to create water quality issues when brines pollute source waters (Valero and Arbós 2010).

Current anthropogenic sources of bromide include energy extraction and utilization, coal-fired power plants, water treatment, flame retardants, pre-planting and post-harvest biocides, agricultural herbicides, municipal waste incinerators, landfill leachate, road deicers, and pharmaceuticals (Vainikka and Hupa 2012, Mctigue et al. 2014, VanBriesen 2014, Winid 2015).

Energy Extraction and Utilization Wastewater

Anthropogenic bromide contamination of surface waters from energy extraction and utilization activities in the US is well-documented (VanBriesen 2014). Wastewater from conventional oil and gas extraction (brine) is high in bromide and if it is not stored in an injection well, it is sent to a wastewater treatment plant (Weaver et al. 2015). Since wastewater treatment facilities are not required to meet discharge limits on dissolved solids, discharges from these facilities result in bromide loading in surface waters (Wilson and VanBriesen 2012). Hydraulic fracturing (“fracking”) is an unconventional gas extraction process in which shale rock is exploited via drilling and the high-pressure injection of water, sand, and other chemicals to release gas (Good and Vanbriesen 2017). Wastewater (flowback and produced water) from the fracking process is enriched by the minerals that compose shale, including bromide (Good and Vanbriesen 2017). The wastewater is subsequently discharged into surface waters, elevating the bromide concentration and potential for the creation of disinfection by-products (DBPs) following chemical disinfection (VanBriesen 2014).

Coal-fired Power Plants

Coal contains bromide at trace levels (usually >50 mg/L; Kolker et al. 2006), but these concentrations can vary depending on the source mine’s surrounding geology (Bragg et al. 1991). Coal combustion shifts bromide to bromine in flue gas (Klein et al. 1975). Bottom ash, fly ash, and gypsum do

not typically contain significant bromide levels following coal combustion. However, in plants that use a wet flue gas desulfurization (FGD) system, along with the intended conversion of gaseous sulfur dioxide to soluble sulfuric acid, gaseous chlorine and bromine are converted to soluble chloride and bromide in FGD wastewater (VanBriesen 2014). Power plant treatment systems do not remove halogens from FGD wastewater before releasing it to surface waters, so this is a significant source of anthropogenic bromide pollution in source waters (States et al. 2013). Further, since the US EPA's Air Toxics Standard was enacted, which requires mercury emissions to be reduced by 90% in 2017 (USEPA 2011), many coal-fired power plants have turned to bromine-addition technologies (calcium bromide) for enhanced mercury removal in FGD systems. As summarized by VanBriesen (2014), in FGD systems with added bromine for mercury control, bromine gas oxidizes elemental mercury gas to ionic mercury, which leads to the formation of mercury-halogen salts (HgBr_2). These salts are soluble and can be captured in FGD wastewater, which is then treated by a FGD wastewater plant to remove mercury prior to discharge. However, there is no treatment to remove the high levels of bromide in the FGD wastewater that result from bromine-addition. Thus, wastewater from wet FGD systems using bromine-addition for mercury control is an important anthropogenic source of bromide (Good and Vanbriesen 2017, Good and VanBriesen 2019).

Water Treatment (Bromine-chlorine Biocides)

Bromine-chlorine biocides are used as an anti-fouling agent in power plant cooling towers to prevent microbial growth (Winid 2015, WHO 2018). Wastewater produced by these cooling towers (blowdown) contains low bromide levels (1-3.5 mg/L) that may contribute to surface water bromide elevation (VanBriesen 2014). Paper and pulp mills also use bromide to prevent microbial contamination, with bromide levels of up to 100 mg/kg measured in wastewater sludge (Vainikka and Hupa 2012). Other applications of bromine-chlorine biocides include decontamination of water used for agriculture, chemical production, brewery pasteurization, and swimming pools (Vainikka and Hupa 2012). The widespread and regular use of bromine-chlorine biocides is of note because the final product yielded is typically bromide (Soltermann et al. 2016).

Flame Retardants

Brominated flame retardants are cheaper and more effective than those containing chlorine, so they are widely used throughout the world in electrical equipment, textiles, building and construction, and vehicles (Vainikka and Hupa 2012). Although BRFs can produce DBPs when exposed to an oxidizing agent (Pang et al. 2014), the primary concern associated with BRFs is the release of bromide-rich wastewater from production facilities (e.g. textile mills) into surface water (Mctigue et al. 2014).

Pre-planting and Post-harvest Biocides

Although the use of methyl bromide has drastically declined since it was discovered to deplete the ozone layer (Taylor 1994), small quantities are allowed for pre-planting soil fumigation and post-harvest quarantine of crops and logs (Johnson et al. 2012). As mentioned above, most of the methyl bromide volatilizes into the atmosphere, while about 10-30% remains in the soil and is broken down into bromide which can enter surface water (Wegman et al. 1981).

Agricultural Herbicides

Although the use of popular bromine-containing agricultural products (fumigants and pesticides) has been drastically reduced or eliminated due to environmental and health concerns, the use of bromacil as an herbicide continues today (Winid 2015). Bromacil is regularly applied to citrus and pineapple crop fields for weed control (Hu et al. 2019). Bromacil is both persistent and mobile in the environment, meaning that it can readily enter surface and groundwater surrounding agricultural areas (James and Lauren 1995). A recent study demonstrated that brominated DBPs were formed following chlorination of water containing bromacil (Hu et al. 2019).

Municipal Waste Incinerators

As described above, there are a variety of bromine-containing products (especially brominated flame retardants) that ultimately end up as solid fuel in municipal waste (Vainikka and Hupa 2012). Municipal waste incinerators have been shown to significantly contribute to elevated bromide in surface waters (Soltermann et al. 2016).

Landfill Leachate

Leachate from landfills (municipal solid waste storage sites), which can have high levels of bromide (Stuart et al. 2001), has been found to contaminate nearby surface and ground waters (Cozzarelli et al. 2011, Vodyanitskii 2016).

Road Deicers

Brine or road salt used as road deicers may represent nonpoint runoff bromide sources for surface waters in some regions (Kelly et al. 2010). However, recent work in North Carolina did not find that road deicers significantly contributed to surface water bromide levels (Greune 2014).

Pharmaceuticals

The number of pharmaceutical products that contain bromine is growing and includes natural products (bromotirosine) and synthetic anti-cholinergics (ipratropium bromide, oxitropium bromide and tiotropium bromide; Prakash et al. 2013). However, at the current scale of production and use for these compounds, it is unlikely that pharmaceuticals containing bromine are a significant driver of elevated bromide in surface waters (Focazio et al. 2008, Winid 2015).

WHAT ARE THE POTENTIAL INTERACTIONS BETWEEN ANTHROPOGENIC CLIMATE CHANGES AND INCREASING BROMIDE CONCENTRATIONS IN SURFACE WATER?

An increased frequency and severity of extreme weather events (droughts and flooding), increasing water temperatures, and sea level rise will be the major consequences of anthropogenic climate change on water resources (Delpla et al. 2009). In addition to water scarcity in times of extended drought, low surface water discharges will reduce the dilution capacity of source water (Yang et al. 2014). Diminished dilution capacity will lead to higher source water bromide levels and increased concentrations of brominated DBPs in finished drinking water (Cowman and Singer 1996). Alternatively, severe storms and flooding events can lead to increased contaminants in source water via surface run-off and the sediment re-suspension (Richardson and Kimura 2017). Increasing water temperature will increase the kinetics of reactions between DBP precursors and chemical disinfectants, leading to a greater concentration of

DBPs in finished drinking water (Delpla et al. 2009). Rising sea levels will lead to saltwater intrusion into coastal source waters. Saltwater intrusion will impair coastal aquifers and estuaries via increased water temperature and bromide content (Kolb et al. 2017). As discussed above, higher bromide levels in source water results in greater brominated DBPs in finished drinking water and thus greater potential risks of carcinogenicity and cytotoxicity for the consumer.

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DEALING WITH BROMIDE AND BROMINATED COMPOUNDS

HOW CAN BROMIDE BE REMOVED FROM SOURCE WATER?

Currently, there are no cost-effective and practical methods available to remove bromide from source water (Singer 1994). If anthropogenic bromide pollution of source water is stopped, bromide concentrations will be reduced via dilution and fewer brominated disinfection by-products (DBPs) will be present in finished drinking water over time (Good and Vanbriesen 2017). However, if bromide is continually added to source water, there are no cost-effective methods available at an industrial scale to reduce bromide concentrations prior to disinfection or remove brominated DBPs following disinfection. In addition to research and development of new preventative and control technologies, identifying anthropogenic bromide inputs to source water and preventing continued pollution is the best and only practical solution available right now to prevent elevated bromide in source water (Parker et al. 2014).

Despite a lack of practical bromide removal techniques, the impacts of anthropogenic bromide pollution of source water can be partially mitigated by:

- Limiting bromide-rich effluent to high-flow conditions when natural dilution is most effective (Weaver et al. 2016).
- Reducing the amount of bromide-rich discharge to surface water at one time by pulsing releases (Weaver et al. 2016).
- Implementing aquifer storage and recovery, which involves collecting raw source water when water quality is highest and bromide levels are minimal and storing it until needed (Singer 1994).

WHAT OPTIONS EXIST TO CHANGE THE DISINFECTION PROCESS TO PREVENT BROMINATED COMPOUNDS IN FINISHED DRINKING WATER?

Although there have been strides in optimizing water treatment processes and water distribution networks to reduce the formation of regulated DBPs, there are currently no cost-effective and practical methods to prevent brominated DBPs from forming in finished drinking water. However, as summarized in Rivera-Utrilla et al. (2019) there are several promising DBP precursor [halide and natural organic matter (NOM)] removal technologies in development that could eventually yield an efficient and economically viable option to reduce DBPs, including membrane, electrochemical, and adsorption methods.

- **Membrane bromide and NOM removal methods include reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED), and reverse electrodialysis (RED).**
 - RO involves the high-pressure movement of water through a semi-permeable membrane that rejects halides and other organic pollutants. Although RO is highly effective at removing bromide (99% bromide removed from seawater; Magara et al. 1996), there is a high cost associated with its implementation and maintenance that makes it an unpractical choice for public water utilities.
 - NF uses reverse osmosis and ultrafiltration to exclude halides and other nuisance compounds. NF is slightly less costly than RO and can remove halides almost as

- effectively as RO. However, the short operating lives of NF and RO membranes limit their practicality in public water utilities.
- In ED, ions are subjected to electrical currents between membranes with opposite charges, which remove them from the water. RED is similar, except that the membrane charges are periodically reversed. ED and RED methods are inexpensive compared to RO and NF, but have their membranes have short operating lives and are less efficient at halide removal.
 - **Electrochemical bromide removal methods include electrolysis and capacitive deionization (CDI).**
 - Electrolysis uses an electric current to oxidize bromide to hypobromite and hypobromous acid, which is then volatilized as bromine gas by carbon dioxide. This method has produced a 73% reduction in brominated trihalomethanes, but does not effectively remove NOM.
 - CDI involves a pair of porous electrodes that generate an electrical current and store halides within electrical layers. Membrane CDI improves halide removal by adding ion-exchange membranes. Although CDI is a promising option for halide removal, there is currently no technology designed for use at an industrial scale.
 - **Adsorption bromide and NOM removal methods include layered double hydroxides, double sol-gel, hydrated oxides, activated carbon-ag, silver-doped carbon aerogels, and magnetic ion-exchange resins.**
 - Adsorption methods are advantageous because they are easy to implement and cheap to maintain. Unfortunately, some of the materials are less selective for bromide, meaning that they do not remove the ion as effectively as the electrochemical and membrane methods. Depending on the compounds present in the source water, bromide might compete with organic material and other charged molecules for adsorption surface meaning that fewer bromide ions are successfully removed from the water.

CASE STUDIES

- **Desalination of the Llobregat River Water in Barcelona, Spain (Valero and Arbós 2010)**
 - The Llobregat and Ter rivers serve as source water for 4.5 million people in Barcelona, Spain. Potash mining near the Llobregat river since the 1920s has significantly elevated the river's salt content and discharges of urban and industrial sewage has increased the river's micropollutant and microbial levels. The elevated levels of bromide and NOM in the river led to high quantities of brominated disinfection byproducts in finished drinking water. Despite many updates to the Llobregat drinking water treatment plant (DWTP), including pre-oxidation with potassium permanganate, coagulation, flocculation, oxidation with chlorine dioxide, sand filtration, granular activated carbon (GAC) filtration, and final chlorination using chlorine gas, the elevated bromide levels and high water temperature of the Llobregat prevented water managers from achieving

acceptable disinfection byproduct levels according to European Union regulations. To reduce the levels of DBPs and achieve compliance with water quality regulations, the Llorbregat DWTP implemented an electro dialysis reversal (EDR) step following GAC filtration. Data collected over 28 months following EDR installation indicated >75% removal of bromide and comparable removal of other salts of concern while 90% water recovery was achieved (Valero and Arbós 2010, Valero et al. 2012).

- **California's Sacramento-San Joaquin Delta**

- The Sacramento-San Joaquin Delta provides source water for 23 million people living in California. The demand for water and water scarcity has surged over the past few decades, while the delta's water quality has steadily declined due to increased salinity and total organic carbon (TOC; Chow et al. 2007). The delta's bromide levels have increased due to saltwater intrusion, while TOC increase has been associated with agricultural runoff (Lund et al. 2015). California water utilities have addressed the declining water quality by implementing alternative disinfectants and by exploiting alternative water sources when the delta's water quality is too poor (bromide and TOC levels have seasonal shifts) for safe disinfection practices (CALFED 2005). Updating the water treatment plants and using alternative disinfectants has allowed California's water utilities to comply with DBP regulations. However, changes to the water treatment process are expensive and more updates will be necessary to cope with further declines in water quality. Rising sea levels and the failure of subsided western islands will present grand challenges for California's drinking water utilities in the near future (Chen et al. 2010).

- **Pennsylvania's Allegheny River Basin**

- Over 1.5 million people rely on the Pennsylvania's Allegheny River Basin as a drinking water source. Recently, dramatically elevated levels of bromide in the Allegheny River Basin's surface water has been attributed to wastewater from coal-fired power plants using bromine addition to control mercury emissions. Specifically, bromine is added to wet flue gas desulfurization (FGD) systems and high levels of bromide are present in wastewater. Although this wastewater is sent to wastewater treatment plants, the bromide is not removed and ends up in surface water. Researchers have documented bromide levels as high as 299 ug/L (States et al. 2013) and 599 ug/L (Wilson and VanBriesen 2012) in PA watersheds receiving coal-fired power plant wastewater discharges. Several papers from Carnegie Mellon University's Dr. Jeanne VanBriesen and colleagues have highlighted how bromine addition to wet FGD systems will elevate surface water bromide and subsequently increase brominated disinfection by-product formation in drinking water (VanBriesen 2013, 2014, Wang et al. 2016, Kolb et al. 2017). No practical solutions have been identified to remove bromide from source water (Good and VanBriesen 2019).

- **Coal Ash Basin Spills in North Carolina Rivers (Duke Energy Corporation 2015)**
 - In 2014, a coal ash basin at a facility owned by Duke Energy contaminated surface waters of the Dan River in Eden, North Carolina. Heavy metals and bromide present in the coal ash spread throughout NC and downriver to the North Carolina-Virginia border. A similar leak occurred at a Duke Energy steam electric plant that resulted in pollution of the Cape Fear River. Also, Duke Energy coal combustion facilities also knowingly discharged coal ash contents without permits into surface waters. Finally, although it was not a violation of US EPA regulations, Duke Energy's coal-fired power plants wet flue gas desulfurization systems used bromine-addition for mercury control, which further elevated surface water bromide levels throughout the state following wastewater discharge. The elevated bromide levels in various drinking water sources throughout North Carolina and Virginia lead to elevated disinfection by-product formation and an inability to meet US EPA regulations regarding trihalomethane and haloacetic acid levels (Greune 2014). Drinking water utilities upgraded their facilities to deal with the elevated bromide levels and purchased water from other facilities to meet customer needs in the meantime. Duke Energy plead guilty to nine violations of the Clean Water Act and has been working with a court-appointed monitor to achieve environmental compliance obligations (Duke Energy Corporation 2019).

- **Bromide and Iodide in Western Australia's Surface Waters**
 - Drinking water treatment in Western Australia is challenging because of high concentrations of DBP precursors: NOM (0.4-16 mg/L), bromide (400-8450 ug/L), and iodide (5-593 ug/L) in the source water (Gruchlik et al. 2015). It is especially concerning when source water contains high levels of bromide and iodide because brominated and iodinated DBPs are thought to be more cytotoxic and carcinogenic than their chlorinated analogs (Wagner and Plewa 2017). Saltwater intrusion and aridity contribute to elevated bromide and iodide levels in Western AU. Although there are several effective NOM removal methods, these methods do not remove halides and can lead to greater formation brominated DBPs when the source water bromide levels are elevated (Kristiana et al. 2011). Recent work has identified pre-ozonation followed by chloramination as a potential method to reduce iodinated DBPs because ozone oxidizes iodide to iodate. Unfortunately, practical bromide removal methods are still lacking (Gruchlik et al. 2015).

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