

**Drinking Water Quality and Risk Challenges from
Increasing Source Water Bromide:
Effects of Climate and Energy Changes**

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Dedication

To my parents. Even though they'll never read it, they're responsible for my endless curiosity.

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Abstract

Disinfection is a critical step in drinking water treatment, killing pathogenic organisms and ensuring the water is safe for consumption. However, disinfection byproducts (DBPs) form during treatment when disinfectants react with naturally occurring organic matter, bromide, iodide or other contaminants present in source waters. DBPs are of concern in drinking water because they are carcinogenic and teratogenic, and some DBPs are regulated. Source water bromide can shift DBP speciation toward higher risk brominated species and may shift some DBPs toward unregulated forms.

While naturally occurring bromide concentrations are typically quite low, elevated levels can be found in coastal groundwater and estuary sources and where surface waters are impacted by anthropogenic activities such as energy extraction and utilization activities. Elevated bromide concentrations in source waters may lead to higher risk to consumers, even while water continues to meet regulatory compliance requirements. TTHM does not adequately capture risk of the regulated species when source water bromide concentrations are elevated, and thus would also likely be an inadequate surrogate for many unregulated brominated species. Alternative surrogate measures, including THM₃ and the bromodichloromethane concentration, are more robust surrogates for species-specific THM risk at varying source water bromide concentrations.

Recently, climate change has been associated with increasing bromide concentrations in

coastal groundwater and estuaries sources resulting from saltwater intrusion and in inland surface water sources as a result of anthropogenic factors. This work evaluated elevated bromide concentrations resulting from saltwater intrusion in coastal groundwater systems and from anthropogenic discharges from coal fired power plants operating wet FGD units. Coastal utilities treating affected groundwater sources will likely meet regulatory levels for THMs, but even small changes in saltwater intrusion can have significant effects on finished water concentrations and may exceed desired health risk threshold levels due to the extent of bromination in the THM. As a result of climate change, drinking water utilities using coastal groundwater or estuaries should consider the implications of treating high bromide source waters.

In surface waters in the Monongahela River Basin, coal-fired power plants with wet FGD account for most of the total observed bromide concentrations at a drinking water intake downstream. For the modeled bromide load, coal power plant discharges contribute an additional 24 mg/L TTHM half of the time during the period evaluated, exceeding the 10^{-5} risk threshold. As source water bromide concentrations increase, TTHM may be inadequate as a surrogate measure for DBP risk. Alternative regulatory strategies may better protect human health.

Chapter 1

Introduction

Disinfection is an integral step in drinking water treatment, as it inactivates microbial contaminants present in source waters and ensures water is safe for consumers. During the drinking water treatment process, however, disinfectants added for pathogen control react with naturally occurring organic matter, bromide, iodide, or other common precursors present in source waters to form disinfection byproducts (DBPs). Variability of source water constituents can influence the efficacy of drinking water treatment, particularly with respect to the formation of toxic DBPs.

1.1 Disinfection byproducts and drinking water risk

First discovered in drinking water in the 1970s, researchers have identified DBPs as carcinogenic and teratogenic (NCI, 1976; Boorman et al., 1999; Bull et al., 2001; Cantor et al., 2010; Richardson et al., 1999; Villanueva et al., 2004; Richardson et al., 2007; Villanueva et al., 2015). Although more than 600 DBPs have been identified (Richardson et al., 2007), regulations to reduce their exposure are often based on measurements of only a few DBPs, including trihalomethanes (THMs) and haloacetic acids (HAAs) (Council of the EU, 1998; States, 2006; Becker et al., 2013; Regli et al., 2015), which serve as surrogates for DBP-associated risk.

When using chlorine-based disinfection, THMs are the most abundant class of DBPs formed. Disinfection byproduct regulation in the United States is based on an indicator or surrogate approach (Richardson et al. 2007; Bull 2012). The primary trihalomethanes include four regulated species: chloroform; bromodichloromethane, BDCM; dibromochloromethane, DBCM; and bromoform. The sum of the four regulated THM species is referred to as THM₄; within regulations, this sum is referred to as total trihalomethanes (TTHM), even though it does not contain iodinated THM. Three of the regulated species contain bromide, and the sum of these three species is referred to as THM₃. The maximum contaminant levels (MCLs) representing enforceable concentrations were set for the mass sum of four THMs (chloroform, BDCM, DBCM, bromoform) at 80 $\mu\text{g}/\text{L}$ (US EPA 1998; US EPA 2006).

In addition to the regulated DBPs, a number of other classes of disinfection byproducts are widely reported and studied in drinking water, including haloacetonitriles, halo ketones, halonitromethanes, haloaldehydes, halogenated furanones, haloamides, and nonhalogenated carbonyls (Weinberg et al. 2002; Krasner et al. 2006; Hebert et al. 2010; Chen et al. 2015). Some of these unregulated DBP species have been identified at concentrations similar to regulated species (Krasner et al. 2009), and unregulated DBPs may not be well represented by the class sum values used as surrogates in DBP regulations (Bull, 2012; Bull, Rice, Teuschler, and Feder, 2009; Bull, Rice, and Teuschler, 2009; Francis, VanBriesen, and Small, 2010; Hrudey et al., 2015; Krasner et al., 2006; Sawade, Fabris, Humpage, and Drikas, 2016; Weinberg, Krasner, Richardson, and Thruston, 2002).

Numerous epidemiological studies have established an association between the use of chlorinated drinking water and increased risk of bladder cancer (Richardson et al. (2007); Villanueva et al. (2015)). Hrudey et al. (2015) suggest that the strongest epidemiological data (e.g., (Villanueva et al. 2007; Salas et al. 2013, Cantor et al. 2010)) are associated with extensive bromine incorporation. Studies of negative reproductive outcomes have been mixed,

with associations seen only at the highest concentrations (Nieuwenhuijsen et al. 2009; Villanueva et al. 2015), and bromine incorporation is again implicated (Chisholm et al. 2008). Across multiple groups of DBPs, brominated forms are associated with negative outcomes at lower concentrations than their chlorinated analogs (Echigo et al. 2004; Plewa et al. 2004; Richardson et al. 2007). Initial concern related to THM in drinking water supplies focused on the bromohaloforms due to the elevated physiological effects compared to chloroform (Rook, 1974). Subsequent work confirmed bromine incorporation in DBPs is associated with higher risk (Motz et al., 2014; Chen et al., 2010; Wang and Huang, 2006; Nikolaou, 2004; Chang et al., 2001; Amy, 1994; Luong et al., 1980). Thus, the presence of bromide in source waters, which increases the formation of regulated and unregulated brominated DBPs, increases the risk associated with use of chlorinated drinking water (Hong et al. 2007; Yang et al. 2014; Regli et al. 2015).

1.2 Bromide as a DBP precursor

Early studies identified bromide as a precursor to DBP formation (Luong et al., 1980; Lange and Kawczynski, 1978; Rook, 1974), and later work highlighted source water bromide as a potential concern for drinking water utilities (Amy et al., 1993; Obolensky and Singer, 2005; Hua et al., 2006; Obolensky et al., 2007). Bromide present in source water can increase the formation of DBPs and shift speciation to more brominated forms. As bromide reacts with chlorine or chloramine used for disinfection, it is oxidized to hypobromous acid. Hypobromous acid reacts more quickly than hypochlorous acid, resulting in increased bromide incorporation into DBPs and higher concentrations of DBPs.

The relationship between bromide concentrations in source water and DBP concentrations in disinfected water has been studied for many decades (Luong et al. 1982; Hellergrossman et al. 1993; Pourmoghaddas et al. 1993; Symons et al. 1996; Ates et al. 2007; Tian et al. 2013).

Laboratory studies indicate that, in general, increasing bromide concentrations increase the total DBPs formed (on a molar and mass basis) (Hua et al. 2006; Bond et al. 2014) as well as increasing the bromine incorporation into the formed DBPs (Symons et al. 1993; Krasner et al. 1996; Diehl et al. 2000; Ates et al. 2007). Bromide can also alter the speciation of unregulated DBPs formed in drinking water (Richardson et al. 1999; Richardson et al. 2003; LeRoux et al. 2012; Pan and Zhang 2013; Zhai et al. 2014). Site-specific studies at drinking water utilities confirm bromide is an important predictor of brominated DBPs (Duong et al. 2003; Ye et al. 2009; Chang et al. 2010; Charisiadis et al. 2015). Elevated bromide in source water was associated with elevated DBPs and bromine incorporation in surveys of U.S. drinking water utilities (Amy et al. 1993; McGuire et al. 2002; Weinberg et al. 2002), and bromide was a significant predictor for all DBP species (Obolensky and Singer 2005). Amy et al. (1994) noted that virtually any level of bromide present in a water source can potentially form brominated chlorination byproducts, such as THMs (Amy et al. 1994). Thus, due to the higher total concentrations and more brominated DBPs formed, elevated source water bromide concentrations may lead to elevated risk to consumers, even when TTHM and HAA levels meet regulatory requirements.

1.3 Bromide in drinking water sources

Bromide is naturally occurring in the environment, generally at low concentrations. Elevated bromide concentrations have been identified in sources associated with fossil fuels. Davis et al. (Davis, Fabryka-Martin et al. 2004) surveyed groundwaters in the U.S. and report concentrations in potable groundwater vary from 0.0032 to 0.058 mg/L (median value 0.016 mg/L). Bromide is rarely observed at significant concentrations in fresh surface water systems (e.g., inland rivers and lakes in the U.S.), with typical levels between 0.014-0.2 mg/L (Bowen 1966; Bowen 1979). Concentrations in rain are typically below 0.01 mg/L as bromide ion (Flury and Papritz 1993), with slightly higher values in coastal areas due to seaborne aerosols. U.S.

drinking water sources were characterized during the ICR (USEPA 1996), and source water bromide values were reported to range from below detection ($< 20 \mu\text{g/L}$) to 2.23 mg/L ($2230 \mu\text{g/L}$) with a mean of $69 \mu\text{g/L}$ (0.069 mg/L) and a median of $36 \mu\text{g/L}$ (0.036 mg/L) (McGuire et al. 2002). McGuire and Hotaling (2002) summarize the ICR data and classify bromide values above $100 \mu\text{g/L}$ (0.1 mg/L) as “high” and values above $500 \mu\text{g/L}$ (0.5 mg/L) as “very high” (McGuire and Hotaling 2002). Approximately 20% of the samples reported bromide source water concentrations above $100 \mu\text{g/L}$, while 30% of reported samples were below the method detection limit for the study ($20 \mu\text{g/L}$) (McLain et al. 2002). The American Water Works Association (AWWA) Research Foundation sponsored a nation-wide survey of 100 utilities specifically focused on source water bromide and its role in DBP formation (Amy et al. 1994). For a random selection of large plants (serving $> 50,000$ people), source water bromide concentrations ranged from $2\text{-}426 \mu\text{g/L}$, with a mean of $61 \mu\text{g/L}$ and a median of $42 \mu\text{g/L}$. The 90th percentile value for bromide in this data set was $102 \mu\text{g/L}$ (Amy et al. 1993).

Figure 1.1 is a box-plot of the observed bromide concentrations from the ICR for each region (by Hydrologic Unit Code 2 (HUC2) watershed), separated by geographic regions (western, mid-west, and eastern). The red horizontal dashed line represents the detection limit for the data set; values reported as below detection were imputed using Regression on Order Statistics (ROS) (Helsel 1990). Each regional box plot includes a solid line for its median and an open circle for its mean. The box extending to the 25th and 75th percentile concentrations, and the whiskers extending to the minimum (usually imputed) and maximum concentrations. Regional trends are clear, with the Eastern region showing low bromide concentrations in HUC regions 01, 02, 03, 04 (median values in $\mu\text{g/L}$ of 10, 31, 29, and 29, respectively), and the mid-west showing higher levels, with the median always above detection (median values for HUC regions 05-11 in $\mu\text{g/L}$ are 35, 34, 44, 36, 57, and 36, respectively). The western region shows more variability, with significantly elevated bromide in HUC regions 12, 13, and 15, which are Texas and the southwest, with much lower levels in the north west

(HUC regions 16 and 17 with medians below detection). Figure 1.2 and Figure 1.3 presents these data at the HUC4 level on a map of the United States; dividing them between surface water (Figure 1.2) and groundwater (Figure 1.3). The coloration of these figures is based on the quartiles, which are significantly different between surface waters (median of 30 $\mu\text{g}/\text{L}$, interquartile range 13 to 65 $\mu\text{g}/\text{L}$) and groundwater (median of 66 $\mu\text{g}/\text{L}$, interquartile range of 32-166 $\mu\text{g}/\text{L}$). Elevated values in coastal groundwater systems can be seen in California, Texas, and Florida. White indicates regions where no data were available, primarily in inland regions, the Pacific Northwest, and along the eastern seaboard.

As shown in Figures 1.1 through 1.3, naturally occurring bromide concentrations in source waters are typically quite low (ICR reported surface water median 30 $\mu\text{g}/\text{L}$; groundwater median 66 $\mu\text{g}/\text{L}$). However, elevated levels can be found in coastal groundwater and estuary sources (Ged and Boyer 2015; CALFED 2007; Chen et al. 2010; Amy et al. 1994) and where surface waters are affected by anthropogenic activities such as road salt application (Dailey et al. 2014) and energy extraction and utilization activities (Landis et al. 2016; Wilson et al. 2014; Cravotta and Brady 2015; Cravotta 2008; McAuley and Kozar 2006; Ruhl et al. 2012).

Historically, elevated bromide concentrations were of primary concern to drinking water utilities using coastal sources (McGuire et al., 2002). To address issues of elevated bromide in estuary-influenced sources, the CALFED Drinking Water Quality Program in California has set a source water bromide concentration target of 50 $\mu\text{g}/\text{L}$ (0.05 mg/L) to protect the public from the health effects associated with brominated disinfection byproducts (Holm et al., 2007). To assess the feasibility of meeting the bromide target, CALFED funded 70 pilot projects (at a cost of \$83.1 million) to test alternative strategies for bromide control (Holm et al., 2007). Due to technological feasibility, most of the projects focused on reducing agricultural runoff affecting source waters, but relocating intakes or implementing advanced treatment technologies (e.g., granular activated carbon) were estimated to have the greatest

effect on reducing DBP precursors in source waters (Holm et al., 2007).

Recently, climate change has been associated with increasing bromide concentrations in coastal groundwater and estuary sources resulting from saltwater intrusion (Ged and Boyer 2015; Cromwell et al. 2007; Kolb et al. 2017). Seawater contains significantly higher concentrations of bromide than freshwater (WHO, 1996). As sea levels rise, saltwater intrusion in coastal aquifers and estuary systems will increase and could affect drinking water supplies (Sawyer et al, 2016; Yuan et al., 2015; Loaiciga et al., 2012; Webb and Howard, 2011; Yechieli et al., 2010; Werner and Simmons, 2009; Heberger et al., 2009; USEPA, 2008; Masterson and Garabedian, 2007). Several areas in the United States have already experienced increased saltwater intrusion resulting from sea level rise (Barlow and Reichard, 2009; Chen et al., 2010; CISA/NOAA, 2012; DRBC, 2008; Motz et al., 2014; Oude Essink et al., 2010). Warmer water temperatures may also influence the formation of DBPs during drinking water treatment.

In recent years, elevated bromide concentrations have been observed in inland surface waters as a result of anthropogenic factors (Landis et al., 2016; Wang et al., 2016; Wilson et al., 2014). Increasing development of shale gas resources and surface discharge of partially treated produced water has been implicated in increased bromide discharges to surface waters in Pennsylvania (States et al., 2013a; Wilson and VanBriesen, 2013). In 2011, the PA Department of Environmental Protection (PADEP) requested natural gas operators to cease utilizing wastewater facilities discharging to surface water supplies (PADEP 2011). Coal-fired power plants are also known to discharge bromide when wet flue-gas desulfurization is deployed to prevent acid rain (Good and VanBriesen, 2016, 2017; Soltermann et al., 2016; Winid, 2015). The Mercury and Air Toxics Standards (MATS) requires significant mercury reductions (USEPA, 2012), which could result in increased use of bromide at power plants, and bromide is not regulated in power plant discharges (USEPA, 2015). Thus, inland surface water systems may see increased source water bromide from a variety of sources, and

changing bromide concentrations may lead to changing risk from drinking water.

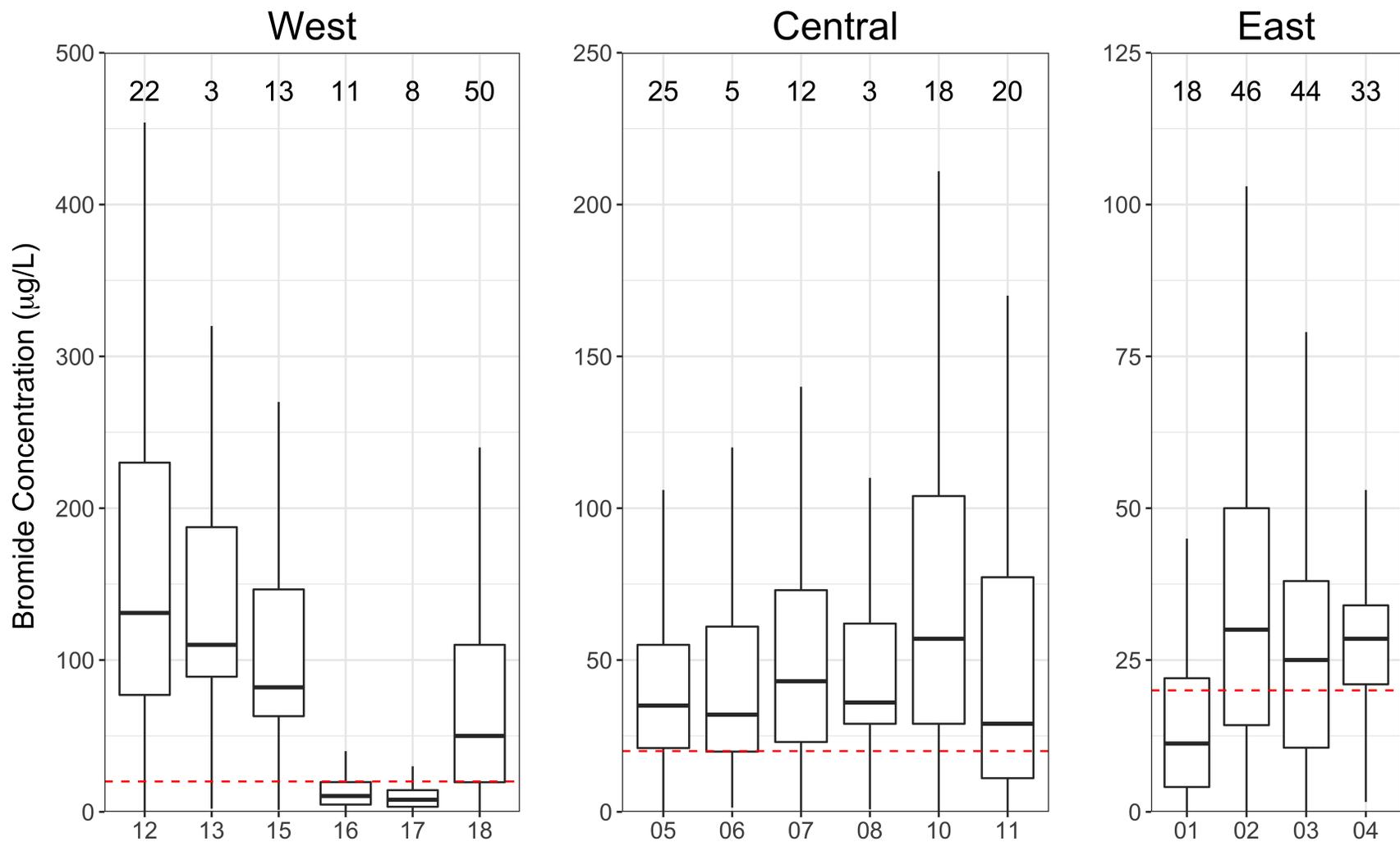


Figure 1.1: Influent bromide concentration measured at drinking water utilities during the ICR by HUC2 (all water sources) for watersheds in the Western (left panel), central (middle panel), and Eastern (right panel) states.

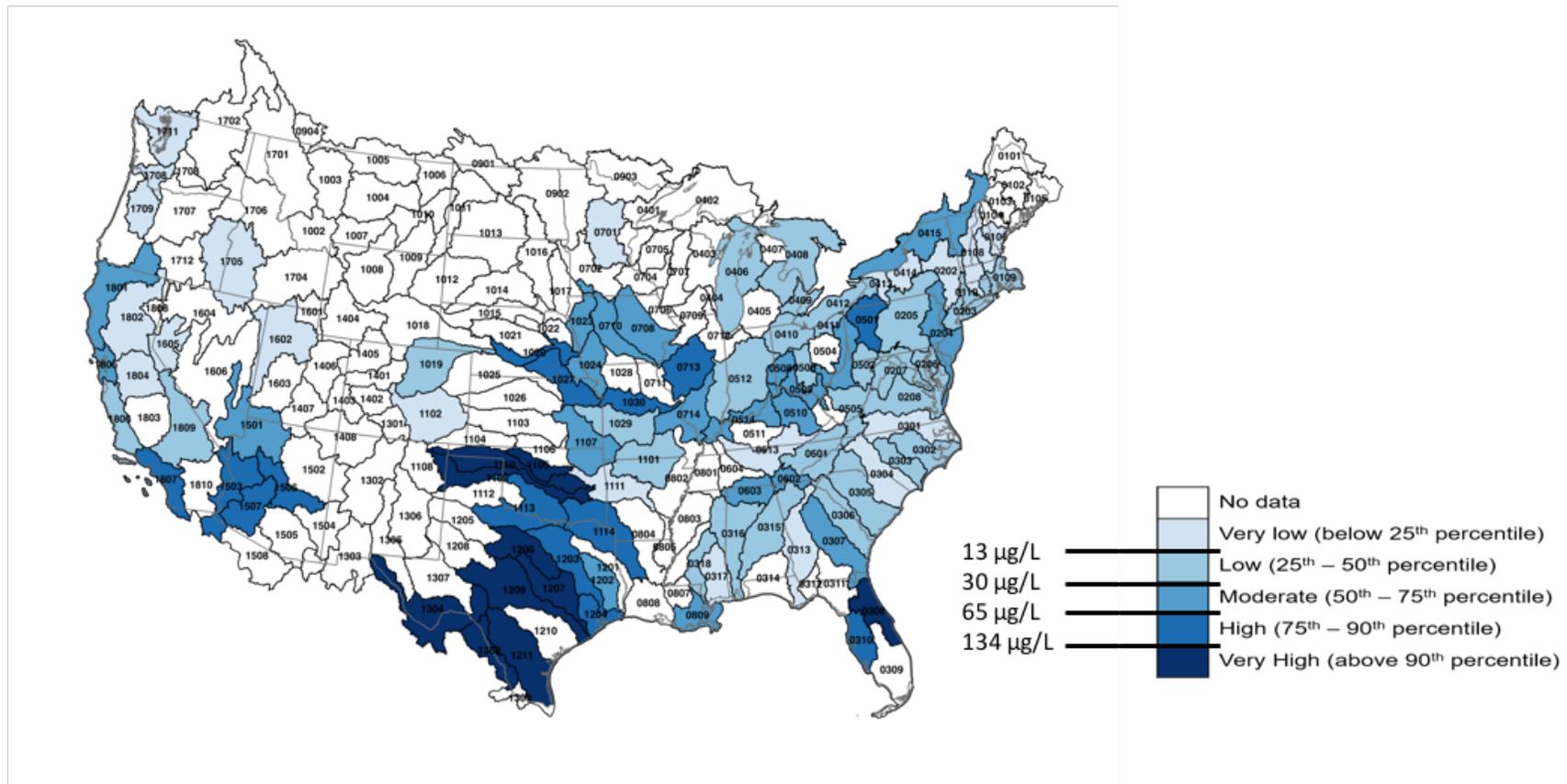


Figure 1.2: ICR reported bromide concentrations by HUC4 for surface water.

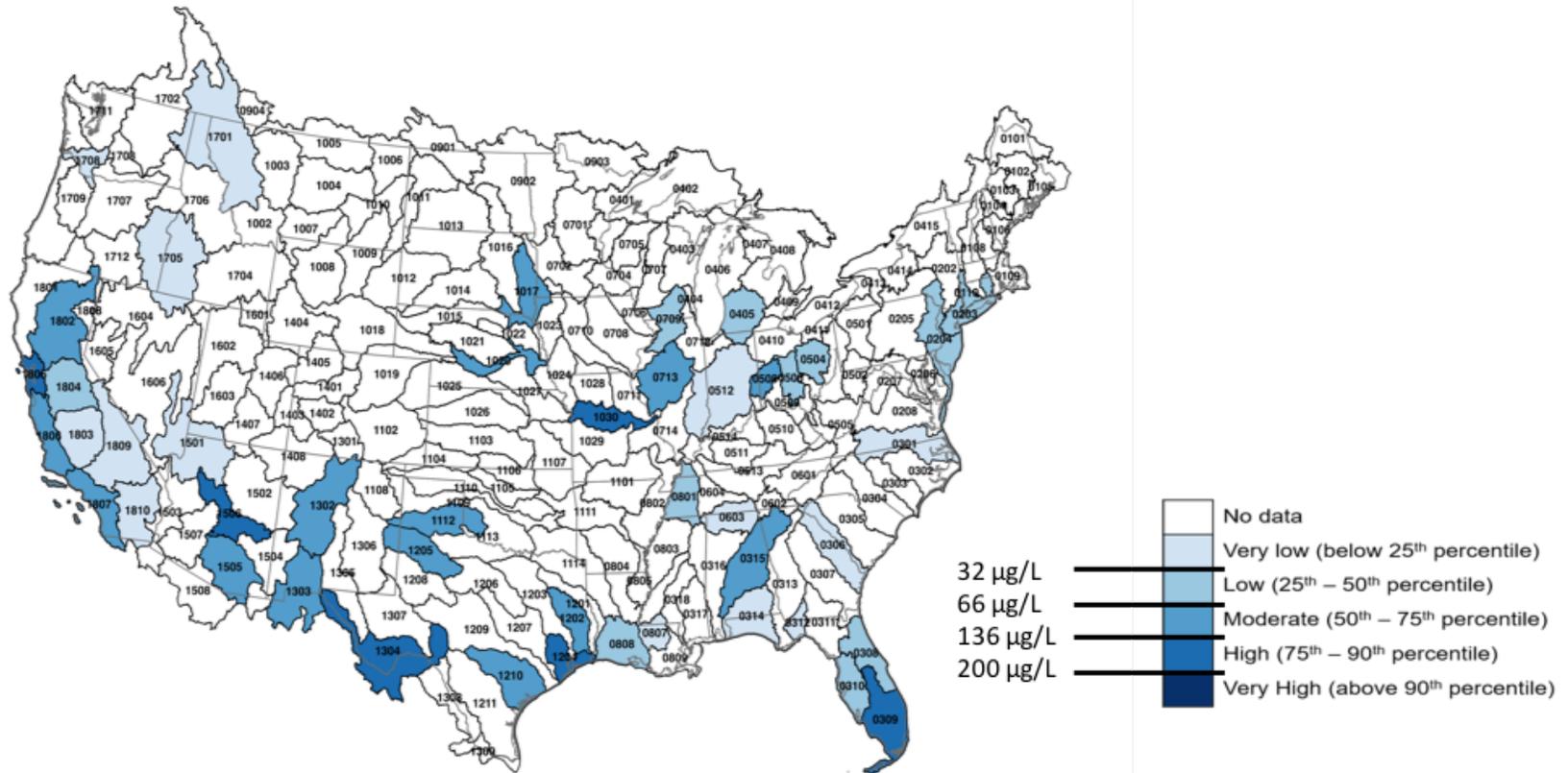


Figure 1.3: ICR reported bromide concentrations by HUC4 for groundwater.

1.4 Research questions and objectives

With changing bromide concentrations in source waters, it is unclear if current regulatory compliance goals will be protective of human health. Thus, the present work aims to improve understanding of the potential effects of changing source water bromide concentrations (resulting from seawater intrusion in coastal aquifers and anthropogenic discharges to inland surface waters), on DBP formation, bromine incorporation, and human health risk. Additionally, this work examines the suitability of total trihalomethane (TTHM, measured as THM₄) as a surrogate measure to adequately represent risk for source waters with variable bromide concentrations. Furthermore, alternative risk surrogates that may be more suitable for waters with variable bromide concentrations (e.g., individual THM species concentrations) are evaluated. Three research objectives address this research question:

1. Evaluate the suitability of THM₄ as a surrogate measure for risk at elevated source water bromide concentrations;
2. Evaluate the effect of climate-induced increased bromide due to saltwater intrusion in groundwater on THM₄ formation, speciation and risk; and
3. Evaluate the effect of anthropogenic bromide discharges from coal fired power plants operating wet flue gas desulfurization units on surface water used as a drinking water source, and evaluate the impact of these discharges on finished water quality and risk.

This dissertation is comprised of 5 chapters to address these research objectives. Chapter 1 is this introductory chapter. Chapter 2 reviews the regulatory history of DBPs in the United States and assesses the use of TTHM as a surrogate measure for DBP risk when source water bromide concentrations are elevated. Alternative metrics are also evaluated to assess how compliance thresholds correspond to risk as source water bromide concentrations increase. Chapters 3 and 4 consider two causes of increasing source water bromide: saltwater intrusion and coal power plant discharges. Chapter 3 focuses on the effects of elevated bromide for

coastal groundwater systems impacted by sea level rise in New Jersey. Chapter 3 assesses the effect of coal power plant discharges to surface water supplies in Pennsylvania. These chapters demonstrate the effects of elevated source water bromide from varying sources, with a focus on THM formation and risk. Finally, Chapter 5 summarizes the conclusions and implications of this research and highlights additional research to further this work.

Chapter 2

Disinfection byproduct regulatory compliance surrogates and bromide-associated risk¹

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Abstract

Natural and anthropogenic factors can alter bromide concentrations in drinking water sources. Increasing source water bromide concentrations increases the formation and alters the speciation of disinfection byproducts (DBPs) formed during drinking water treatment. Brominated DBPs are more toxic than their chlorinated analogs, and thus have a greater impact on human health. However, DBPs are regulated based on the mass sum of DBPs within a given class (e.g., trihalomethanes and haloacetic acids), not based on species-specific risk or extent of bromine incorporation. The regulated surrogate measures are intended to protect against not only the species they directly represent, but also against unregulated DBPs that are not routinely measured. Surrogates that do not incorporate effects of increasing bromide may not adequately capture human health risk associated with drinking water when source water bromide is elevated. The present study analyzes trihalomethanes (THMs), measured as TTHM, with varying source water bromide concentrations, and assesses its correlation with brominated THM, TTHM risk and species-specific THM concentrations and associated risk. Alternative potential surrogates are evaluated to assess their ability to capture THM risk under different source water bromide concentration conditions. The results of the present study indicate that TTHM does not adequately capture risk of the regulated species when source water bromide concentrations are elevated, and thus would also likely be an inadequate surrogate for many unregulated brominated species. Alternative surrogate measures, including THM₃ and the bromodichloromethane concentration, are more robust surrogates for species-specific THM risk at varying source water bromide concentrations.

2.1 Introduction

Disinfection is a critical step in drinking water treatment, which kills pathogenic organisms and ensures water is safe for use. However, disinfection byproducts (DBPs) form during treatment when chemical disinfectants react with natural organic matter, bromide, iodide, and other chemicals present in source waters. Since their initial discovery in the early 1970s, more than 600 DBPs have been identified in chlorinated water (Richardson et al, 2007). DBPs are of concern in drinking water because they are reported to be associated with cancer in epidemiological and animal studies (Villanueva et al, 2004, Villanueva et al., 2015, Cantor et al., 2010, Richardson et al., 1999, Richardson et al, 2007, Bull et al., 2001). Different DBP species have different effects, with brominated DBPs associated with negative health outcomes at lower concentrations than their chlorinated analogs (Hrudey et al., 2015, Yang et al., 2014, Chisholm et al., 2008, Richardson et al., 2007, Echigo et al., 2004).

In response to the risk associated with use of water containing DBPs, regulations have been developed in the U.S. and other countries to limit human exposure (Australian Government, 2011, Health Canada, 2006, USEPA, 2006b, The Council of the European Union, 1998). In the U.S., DBP regulations address the occurrence of two individual byproducts (bromate and chlorite) and two common classes of DBPs (trihalomethanes (THMs) and haloacetic acids (HAAs)). DBP regulatory limits that are set based on class-sum values do not distinguish among different species within each class (which may have different risks). Although these class-sum values are considered surrogates for unregulated as well as regulated DBPs present in the water, studies have shown that they may not be adequate (Hrudey et al., 2015, Sawade et al., 2016, Bull, 2012, Weinberg et al., 2002) nor provide information about differential risk across classes (Bull et al., 2009a, Bull et al., 2009b). Increasing source water bromide can shift DBP speciation toward higher risk brominated species (Sohn et al., 2006) and alter class-sum value representativeness (Francis et al., 2009). Thus, changing bromide concentrations in source waters may lead to higher risk to consumers even while water continues to meet

regulatory compliance requirements (Sawade et al., 2016). With more than 260 million people exposed to DBPs in drinking water (USEPA, 2005), even small changes in risk can be significant (Regli et al., 2015).

2.1.1 THMs and drinking water regulations

THMs, the most abundant class of DBPs formed during chlorine-based disinfection, were first reported in drinking water in 1974 (Bellar et al., 1974, Rook, 1974), and concern focused initially on the bromohaloforms as they were expected to have physiological effects greater than CHCl_3 (Rook, 1974). Subsequently, in 1975, the U.S. Environmental Protection Agency (EPA) conducted the National Organics Reconnaissance Survey (NORS) for Halogenated Organics in Drinking Water to measure four THM species (chloroform (CHCl_3), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (CHBr_3)) as well as 1,2-dichloroethane and carbon tetrachloride in the treated water of 80 public drinking water utilities across the US (Symons et al., 1975). Concentrations varied widely: CHCl_3 (less than 0.1-311 $\mu\text{g/L}$; median = 21 $\mu\text{g/L}$); BDCM (0-116 $\mu\text{g/L}$; median = 6 $\mu\text{g/L}$); DBCM (0-100 $\mu\text{g/L}$; median = 1.2 $\mu\text{g/L}$); and CHBr_3 (0-92 $\mu\text{g/L}$; median = below detection).

Soon after, the National Cancer Institute published a report on the carcinogenicity of THMs (NCI, 1976), establishing precedence for the regulation of DBPs in drinking water. As a result, EPA established an interim standard, setting the allowable maximum contaminant level (MCL) at 100 $\mu\text{g/L}$ for total trihalomethanes (TTHM) (USEPA, 1979). TTHM was defined as the sum of the mass-based concentrations (typically reported in $\mu\text{g/L}$) of four species: CHCl_3 , BDCM, DBCM and CHBr_3 .

The Stage I Disinfectants and Disinfection byproducts (D/DBP) Rule, promulgated in 1998, lowered the MCL for TTHM from 100 to 80 $\mu\text{g/L}$ and established non-enforceable maximum contaminant level goals (MCLGs) for the four THM species ($\text{CHCl}_3 = 0 \mu\text{g/L}$; BDCM = 0

$\mu\text{g/L}$; DBCM = $60 \mu\text{g/L}$; $\text{CHBr}_3 = 0 \mu\text{g/L}$) (USEPA, 1998). The MCLGs were set to zero for the three species that were initially identified as probable human carcinogens in 1998, while DBCM was set higher at that time as data on its carcinogenicity was incomplete (USEPA, 1990). The updated MCL for TTHM was developed as a surrogate measure for excess cancer risk as a result of exposure to mixtures of DBPs through drinking water (USEPA, 2006b), with bladder cancer as the relevant outcome for the cost-benefit analysis in the regulation (Regli et al., 2015, USEPA, 2005). Additionally, Stage I included removal requirements for total organic carbon (TOC) in source water. Requiring reductions in this DBP precursor was intended to reduce DBP formation across all classes (not just THMs), thus, lowering the risk associated with use of the treated water. Advanced treatment technologies used for TOC removal, such as enhanced coagulation and granular activated carbon, do not remove bromide (Krasner et al., 2016, Summers et al., 1993). The use of these advanced treatment technologies to meet TOC regulations alters the interaction of bromide and TOC in the formation of DBPs, resulting in differential formation of brominated DBPs.

To better inform the Stage II D/DBP rule and also the Long-Term 2 Enhanced Surface Water Treatment Rule (USEPA, 2006a, USEPA, 2006b), EPA issued an Information Collection Rule (ICR) to collect nation-wide data (USEPA, 1996). The ICR data collection effort included the monitoring and reporting of various water quality parameters, and a variety of different DBPs, including THMs, from source water, treated water, and water in the distribution system over an 18-month period (Wysock et al., 2002). The results of this national survey (McGuire et al., 2002) confirmed prior work that had identified THMs and HAAs as the dominant forms of DBPs in chlorinated drinking water (e.g., Symons et al., 1975, Krasner et al., 1989, Amy et al., 1994). However, the ICR data suggested that other DBP classes (e.g., haloacetonitriles, halonitromethanes) were formed in appreciable quantities. Although these non-regulated DBP classes were also correlated with THM and HAA, as observed in prior work (e.g., Oliver, 1983, Krasner et al., 1989), the ICR survey led to a more in-depth

study by EPA of additional non-regulated DBPs of potential concern in the 2002 U.S. Nationwide DBP Occurrence Study (Krasner et al., 2006, Weinberg et al., 2002). The two dominant classes are considered surrogates for other DBPs (Regli et al., 2015). While the use of these surrogates enabled routine monitoring and compliance evaluation (Bull, 2012, Richardson et al., 2007), some analyses question the use of TTHM as a surrogate for risk as unregulated DBPs may not be well represented by measurements of the four THMs (Hrudey et al., 2015, Sawade et al., 2016, Bull, 2012, Bull et al., 2009a, Bull et al., 2009b, Krasner et al., 2006, Weinberg et al., 2002), particularly when bromide is elevated (Francis et al., 2010).

In 2006, following the ICR survey and in response to the expanded epidemiological data showing human health risk from disinfected water, the Stage II D/DBP Rule updated the MCLG for CHCl_3 to $70 \mu\text{g/L}$, reflecting new information that suggests that CHCl_3 is not a human carcinogen (Hrudey and Fawell, 2015, USEPA, 2001). The Stage II D/DBP Rule also modified compliance requirements for TTHM and HAA5 from a running annual average (RAA) across sampling locations within the distribution system to a location-specific running annual average (LRAA) with a focus on selection of locations that had previously reported elevated DBPs (USEPA, 2006b). This change was made to reduce high rates of exposure at specific locations within the distribution system. This change resulted in new sampling locations for some utilities and in new challenges meeting the MCL even for utilities previously in compliance (Roberson, 2008).

2.1.2 Health effects of DBPs

Despite the extensive use of TTHM as an exposure metric for DBP epidemiological work (Simmons et al., 2004, Teuschler and Simmons, 2003), recently, Hrudey et al. (2015) suggested that the strongest epidemiological data (e.g., Salas et al., 2013, Cantor et al., 2010, Villanueva et al., 2007) are associated with extensive bromine incorporation into THM that

is associated with elevated source water bromide. Villanueva et al. (2007) found that exposure to TTHM through ingestion, dermal absorption and inhalation was associated with an increase in bladder cancer risk; those exposed to 50 $\mu\text{g}/\text{L}$ or higher TTHM had twice as much risk as those exposed to 8 $\mu\text{g}/\text{L}$ or less. The region Villanueva et al. (2007) studied had elevated source water bromide (Hrudey et al., 2015), and thus, the reported TTHM was likely more brominated than would be observed in regions with lower bromide concentrations. Similarly, Cantor et al. (2010) considered the association between THM species and bladder cancer; they found that polymorphisms in glutathione S-transferase and cytochrome P450 genes that code for enzymes in the biotransformation of brominated THM and α -haloacids were associated with cases, suggesting a possible mechanism for the effect of brominated THMs on bladder cancer risk. Salas et al. (2013) used several statistical models to evaluate bladder cancer risk associated with exposure to TTHM in the Villanueva et al. (2007) study and found that TTHM exposure produced a strong dose-response relationship with bladder cancer risk. Additionally, Salas et al. (2013) identified a monotonically increasing association of risk with concentration for brominated THMs and a flat association for the CHCl_3 concentration using Principal Component Analysis, indicating that brominated THMs were more strongly associated with bladder cancer risk than was CHCl_3 .

In addition to epidemiological work, laboratory-based carcinogenicity studies have been performed for most regulated DBPs, which were all found to be carcinogenic in rodents (Richardson et al., 2007, USEPA, 1987, USEPA, 1990, USEPA, 1993). Some studies have shown that brominated THMs are also genotoxic (IARC, 1999a, IARC, 1999b), indicating mutagenicity (damage to DNA, or deoxyribonucleic acid). As a result of this evidence, in 2006 EPA classified BDCM and CHBr_3 as probable human carcinogens and DBCM as a possible human carcinogen (USEPA, 2006b).

Further, the observed toxicity in laboratory studies suggests potential for teratogenicity

(Plewa et al., 2002). Epidemiological studies of negative reproductive outcomes have reported mixed results, with associations seen only at high concentrations (Hoffman et al., 2008, Levallois et al., 2012) or when infants have certain genetic polymorphisms (Infante-Rivard, 2004), or for particular DBP species (Villanueva et al., 2015, Nieuwenhuijsen et al., 2009). Interpretation of species-specific analyses have been equivocal. For example, Savitz et al. (2006) reported no association between TTHM concentration in drinking water and pregnancy loss; however, they reported a weak association between BDCM and pregnancy loss when comparing the highest quartile and the highest water consumption with lower exposures. Chisholm et al. (2008) studied the role of brominated DBPs on negative reproductive outcomes in Australia using a mass-based bromination fraction for an exposure metric, and reported that women exposed to high levels of highly brominated THMs (92% brominated by mass, on average) experienced a statistically significant increase in the risk of birth defects, particularly birth defects associated with the cardiovascular system (Chisholm et al., 2008).

2.1.3 Source water bromide and brominated DBP risk

Bromide was identified early as a precursor for DBP formation (Luong et al., 1980, Lange and Kawczynski, 1978, Rook, 1974). Subsequent work confirmed bromide is a primary precursor and a potential challenge for drinking water utilities in reducing the risk associated with brominated DBPs (Obolensky et al., 2007, Hua et al., 2006, Obolensky and Singer, 2005, Amy et al., 1993, Amy et al., 1994). When bromide is present in source water treated with disinfectants, it is oxidized to form bromine. Bromine then reacts with organic chemicals present in source water to form brominated DBPs. The presence of bromide increases the rate of formation of DBPs and shifts the speciation of DBPs to more brominated forms (Motz et al., 2014, Chen et al., 2010, Wang and Huang, 2006, Nikolaou, 2004, Chang et al., 2001, Amy et al., 1994, Luong et al., 1980). For THMs specifically, increasing bromide increases the molar concentration of THM (Hua et al., 2006), and the formation of brominated DBPs

(Ates et al., 2007a, Diehl et al., 2000, Krasner et al., 1996, Symons et al., 1993). Luong et al. (1982) report 15%-30% of source water bromide is converted to brominated THMs, while Amy et al. (1991) report as much as 50% of bromide is incorporated into brominated THMs, with incorporation observed even at very low bromide concentrations ($<10 \mu\text{g/L}$) (Amy et al., 1993, Amy et al., 1994). Bromide also alters the speciation of DBPs formed in drinking water (Pan et al., 2014, Zhai et al., 2014, Krasner et al., 2008, Richardson, 2003, Richardson et al., 1999). While the relationship between bromide concentration and formation of uncharacterized DBPs is complex (Ates et al., 2007b, Hua et al., 2006, Zhai et al., 2014), bromination of unregulated DBPs increases when bromine incorporation into THM increases (Francis et al., 2009).

As noted above, brominated DBPs are of particular concern because they are toxic at lower concentrations than their chlorinated analogs (Cantor et al., 2010, Plewa et al., 2004). Increasing bromide in source water is associated with increasing genotoxicity and cytotoxicity in water disinfected with chlorine or chloramine (Sawade et al., 2016, Yang et al., 2014). Also as noted, epidemiological studies identify brominated DBPs as more of a concern (Cantor et al., 2010). Thus, the presence of bromide in source waters, which increases the formation of brominated DBPs, increases the risk associated with use of chlorinated water (Regli et al., 2015, Yang et al., 2014, Hong et al., 2007). To assess relative risk, EPA assigns cancer slope factors (CSFs) to DBPs with potential cancer risks. CSFs are reported in the Integrated Risk Information System (IRIS) from EPA (USEPA, 2016). The oral CSFs for the THM species are 6.2×10^{-2} per mg/kg-day for BDCM (USEPA, 1987), 8.4×10^{-2} per mg/kg-day for DBCM (USEPA, 1990), and 7.9×10^{-3} per mg/kg-day for CHBr_3 (USEPA, 1993). IRIS does not report a CSF for CHCl_3 , and recent work has called into question the carcinogenicity of CHCl_3 (Hrudey and Fawell, 2015, USEPA, 2001).

2.1.4 Current and future challenges in source water bromide

Historically, elevated bromide concentrations were of primary concern for coastal groundwater and estuary sources (Krasner et al., 1994, McGuire et al., 2002). Several studies have identified elevated bromide in coastal sources as an important precursor for DBP formation (Holm et al., 2007, Krasner et al., 1994, Krasner et al., 1996), and more recent work has considered the effect of increased bromination due to saltwater intrusion (Kolb et al., 2017, Ged and Boyer, 2014). In recent years, elevated bromide concentrations have been observed in inland surface waters as a result of anthropogenic factors (Landis et al., 2016, Wang et al., 2017, Greune, 2014, McTigue et al., 2014, Wilson et al., 2014). Increasing development of shale gas resources and surface discharge of partially treated oil and gas wastewater have been implicated in increased bromide discharges to surface waters in Pennsylvania (Vengosh et al., 2017, States et al., 2013a, States et al., 2013b, Wilson and VanBriesen, 2013). The effects of bromide discharges from oil and gas wastewater on drinking water intakes in Pennsylvania have also been evaluated (Landis et al., 2016, Weaver et al., 2016). While recent changes have reduced the volume of unconventional produced water being discharged partially treated, conventional oil and gas wastewaters remain a problem in the region (Vidic et al., 2013), and contamination associated with injection facilities has recently been reported (Akob et al., 2016), increasing potential pathways of concern for this wastewater reaching drinking water sources.

Similarly, coal-fired power plants are known to discharge bromide when wet flue gas desulfurization is deployed to prevent acid rain (Soltermann et al., 2016, Winid, 2015). The Mercury and Air Toxics Standards (MATS) requires significant mercury reductions (USEPA, 2012b), which could result in increased use and discharge of bromide at power plants (USEPA, 2015, McTigue et al., 2014). Good and VanBriesen (2016) recently assessed the role of power plant bromide discharges on downstream drinking water plants in the Allegheny River, demonstrating significant contributions to source water concentrations and the potential for much

higher levels associated with mercury control technologies. Thus, inland surface water systems may see increased bromide concentrations from a variety of sources, and this may lead to changing risk from drinking water DBPs.

In addition to anthropogenic bromide sources, natural changes in bromide are anticipated in many locations. Krasner et al. (1994) assessed the effects of degraded water quality on the Sacramento-San Joaquin River Delta and concluded that watershed management would be important to control DBP formation in coastal river delta systems. The CALFED Bay-Delta Water Quality Program (Holm et al., 2007) identified sources of elevated bromide in California and estimated costs associated with managing anticipated changes. Climate change poses additional risks for drinking water sources that could affect source water bromide concentrations. Surface water bodies are at risk of increasing TOC concentrations due to increased and more extreme precipitation patterns (Ritson et al., 2014, Skjelkvale et al., 2005, Delpla et al., 2015, Sawade et al., 2016, Li et al., 2014), while changing patterns of rainfall and drought can change bromide concentrations (Roberson, 2002). Further, ground-water and estuary sources in coastal regions are at risk of increased source water bromide concentrations as a result of sea level rise and saltwater intrusion into fresh water supplies (Holm et al., 2007, DVRPC, 2004, Navoy, 1991), which could affect DBP formation and speciation (Kolb et al., 2017).

Under these changing bromide conditions, it is unclear if meeting current regulatory compliance levels will be protective of human health. Previously, Regli et al. (2015) evaluated this question by estimating risk increases associated with source water bromide concentration increases. Regli et al. (2015) used U.S. EPA risk calculations for bladder cancer to determine that a 50 $\mu\text{g}/\text{L}$ increase in source water bromide would be expected to cause a 10^{-3} to 10^{-4} increase in lifetime bladder cancer risk for consumers of treated water from that source. For some plants in their study, a smaller increase (10 $\mu\text{g}/\text{L}$) in source water

bromide was predicted to cause an increase in risk as well (Regli et al., 2015). This work highlighted the critical role of bromide in altering DBP risk, assessed based on TTHM; however, it did not consider the differences in risk associated with different species of THM. The present work considered species-specific risk changes associated with changing bromide concentrations. Further, it evaluates the suitability of current regulatory class-sum values as well as several other potential DBP surrogates to adequately represent THM-derived water risk when source waters have elevated bromide concentrations.

2.2 Methods

2.2.1 Data source

Source water and THM data were obtained from the ICR database (USEPA, 2000). The ICR was a data collection effort through EPA requiring large water utilities (those serving greater than 10,000 people) to collect samples for various chemical and biological constituents at the plant intake, throughout the treatment process, and in the distribution system (Wysock et al., 2002). Samples were collected and analyzed using standard protocols and methods monthly between July 1997 and December 1998 (Roberson, 2002). The ICR database has been widely studied (Regli et al., 2015, Li et al., 2014, Francis et al., 2010, Obolensky et al., 2007). It remains the most comprehensive data collection initiative for drinking water plants in the U.S., despite some concerns with its representativeness due to regional variations in unusually warm and wet climactic conditions during 1998 (Roberson, 2002). The ICR database includes records from 296 drinking water utilities, representing 500 treatment plants (McGuire et al., 2002). Data used in the present analysis are a subset of the ICR and include source water bromide and THM species data (1199 total observations, including missing and censored data) for surface water utilities in the U.S. using chlorine as a disinfectant at the time of the study.

2.2.2 Data preparation and censored data handling

The THM species data were reported quarterly, whereas bromide data were reported monthly. Source water bromide observations were paired with their associated THM species concentrations based on the sampling period for each utility, resulting in 1199 bromide-THM observations including missing and censored data. The resulting subset of bromide data was not statistically different from the complete set of observed values ($p > 0.05$). Six bromide values were adjusted due to data entry error prior to performing statistical analyses using these data (following McGuire and Hotaling, 2002). The data were transformed to an approximately normal distribution using a Box-Cox distribution (Box and Cox, 1964):

$$y(x|\lambda) = \begin{cases} x^\lambda & \text{for } \lambda > 0 \\ \log(x) & \text{for } \lambda = 0 \end{cases} \quad (2.1)$$

where x represents the data and y the transformation. The ICR THM data were previously characterized using a log-normal distribution (i.e., $\lambda = 0$) (Obolensky, 2007, Travis and Land, 1990). Francis et al. (2009), however, found that the THM data deviated from the log-normal distribution and identified the data as Box-Cox normal under the power transformation ($\lambda = 0.5$). Analysis of the bromide-THM paired data confirmed that the data are Box-Cox normal under the power transformation.

2.2.3 Data augmentation and sampling

Many bromide and THM species data were reported below the detection limit. Additionally, a large number of bromide observations were omitted from the analysis due to the bromide-THM data pairing. Due to the reduced data, and the much smaller sample size for THM data associated with elevated source water bromide concentrations, Markov Chain Monte Carlo (MCMC) simulations were performed. The simulation of these data avoided potential downward bias in the assessment of differences in high bromide versus low bromide concentration source waters with respect to THM concentration and speciation that might have resulted

from the different sample sizes. Using simulated data based on the observed concentrations of THMs enables a more robust analysis of uncertainty among groups where observed data are lacking (USEPA, 1997). MC simulations have been used previously to study DBPs in order to reduce the effect of below detection limit data on statistical inferences (Francis et al., 2010, Regli et al., 1992) or to compensate for insufficient data in a region of interest (Kolb et al., 2017).

To account for the missing and censored data, a data augmentation step using Multivariate Imputation by Chained Equations (MICE) was executed to estimate the parameters of the multivariate Box-Cox distribution using the R computing language (R Core Team, 2015, van Buuren and Groothuis-Oudshoorn, 2011). MICE incorporates multiple imputation using a MCMC Gibbs' sampling algorithm and has been used in numerous studies analyzing data with missing observations (Azur et al., 2011, van Buuren and Groothuis-Oudshoorn, 2011, White et al., 2011, van Buuren and Oudshoorn, 1999). The MICE-derived parameters for the Box-Cox normal transformed data are shown in Table 2.1. Using these estimated parameters, sample data was generated ($n = 10,000$) for a correlated multivariate Box-Cox normal distribution using the `mvtnorm` package in R (Genz and Bretz, 2009, Genz et al., 2017). The sample data was then transformed back to the respective concentration using the inverse of the power transformation.

The simulated bromide-THM paired data were binned according to the bromide concentration. Data where the bromide concentration was at or below the 10th percentile ($7.2 \mu\text{g/L}$) were identified as "very low"; data above the 10th percentile but below the 25th percentile ($7.2\text{-}19.2 \mu\text{g/L}$) were identified as "low"; data above the 25th percentile but below the 75th percentile ($19.2\text{-}65.1 \mu\text{g/L}$) were identified as "moderate"; data above the 75th percentile but below the 90th percentile ($65.1\text{-}92.2 \mu\text{g/L}$) were identified as "high"; and data above the 90th percentile ($92.2 \mu\text{g/L}$) were identified as "very high." The bromide bins for the

Table 2.1: Summary of missing and below detection data for source water quality and operational parameters

	Bromide	CHCl ₃	BDCM	DBCM	CHBr ₃
Mean	-1.61	6.32	3.12	1.15	-0.31
Bromide	1.00	–	–	–	–
CHCl ₃	-0.17	1.00	–	–	–
BDCM	0.38	0.42	1.00	–	–
DBCM	0.69	-0.23	0.69	1.00	–
CHBr ₃	0.69	-0.34	0.20	0.69	1.00

MCMC: Markov Chain Monte Carlo; BDCM: bromodichloromethane; DBCM: dibromochloromethane.

simulated data are consistent with observed values. Summary statistics for the THM species in each bromide bin are provided in Table 2.2.

Figure 2.1 shows the cumulative distribution function (CDF) for the source water bromide concentration (top). The dashed red vertical lines demarcate the percentiles used to classify the bromide concentration. Solid lines show the 50th percentile, median value (38.1 $\mu\text{g/L}$) and the mean concentration (45.9 $\mu\text{g/L}$). All values are identified on the x-axis marking. The bottom five panels show the bromide distributions within the very low, low, moderate, high and very high bromide bins (note the different y axis values for each panel). The boxplot boxes represent the median, 25th and 75th percentiles, the diamond shows the mean and the hinges extend to 1.5 times the interquartile range.

2.2.4 Assessing bromine incorporation into DBPs

Due to the association of bromination with increased risk, the relative contribution of brominated THMs in TTHM has been used to characterize finished water in previous studies. The Bromine Incorporation Factor (BIF) was originally developed by Gould et al. (1983) to assess

Table 2.2: Distribution of simulated THM species data by source water bromide bin. The mean is shown in regular font, the median in bold, and the standard deviation in italic. Data in $\mu\text{g/L}$.

	CHCl_3	BDCM	DBCM	CHBr_3	TTHM
Very high	15.7	11.8	10.2	3.8	41.4
>90th percentile (92.2)	12.4	11.2	9.5	3.5	39.4
	<i>13.1</i>	<i>6.0</i>	<i>5.2</i>	<i>2.1</i>	<i>18.0</i>
High	17.3	9.5	6.3	2.2	35.3
\leq 90th percentile (92.2)	14.6	8.6	5.7	1.8	32.7
>75th percentile (65.1)	<i>13.6</i>	<i>5.4</i>	<i>3.9</i>	<i>1.6</i>	<i>17.6</i>
Moderate	20.1	7.3	3.1	1.0	31.6
\leq 90th percentile (65.1)	17.1	6.5	2.4	0.7	28.6
>75th percentile (19.2)	<i>14.7</i>	<i>4.7</i>	<i>2.7</i>	<i>1.0</i>	<i>17.8</i>
Low	22.2	5.5	1.3	0.4	29.4
\leq 90th percentile (19.2)	19.4	4.8	0.8	0.2	26.2
>75th percentile (7.2)	<i>15.4</i>	<i>4.0</i>	<i>1.5</i>	<i>0.6</i>	<i>17.8</i>
Very low	24.7	4.6	0.8	0.3	30.4
\leq 90th percentile (7.2)	22.5	3.9	0.4	0.1	28.3
	<i>16.1</i>	<i>3.7</i>	<i>1.0</i>	<i>0.5</i>	<i>18.3</i>

MCMC: Markov Chain Monte Carlo; BDCM: bromodichloromethane; DBCM: dibromochloromethane.

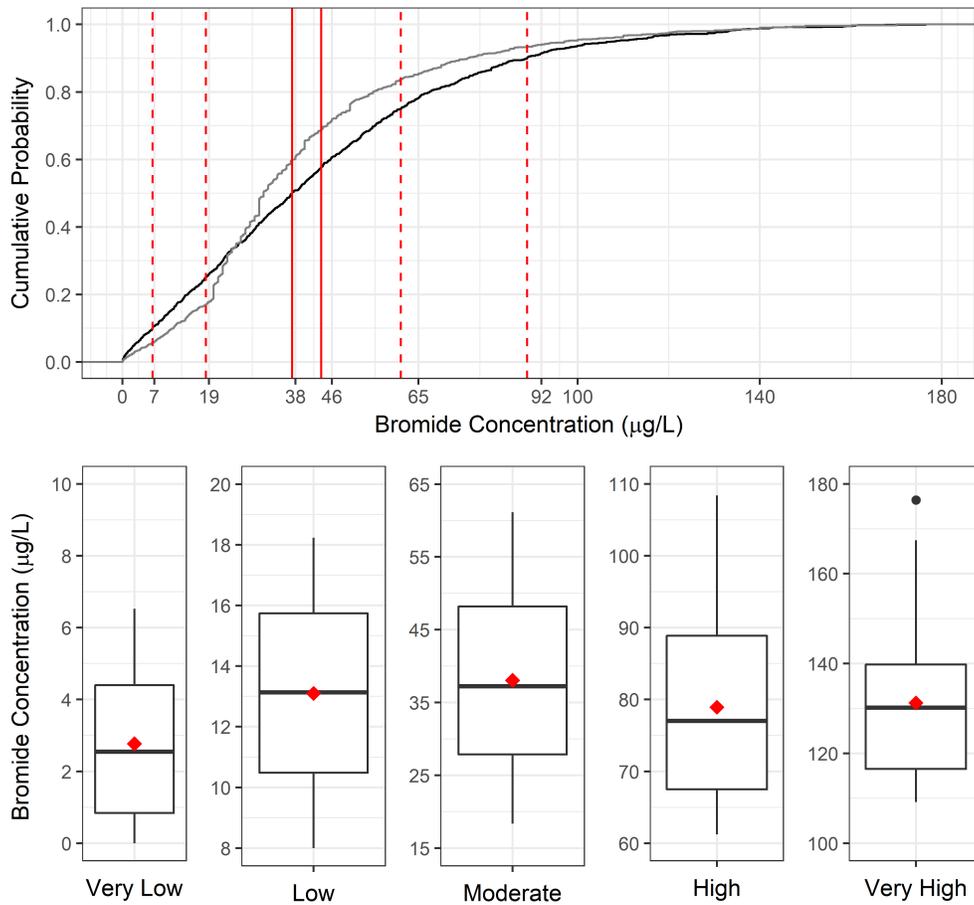


Figure 2.1: Estimated cumulative distribution function for the source water bromide concentration (top) and the distribution of bromide within bromide bins (bottom, with different axes).

the extent of bromine incorporation in TTHM (Equation 2.2), and BIF has been used in numerous studies (Tian et al., 2013, Francis et al., 2010, Rathbun, 1996, Symons et al., 1993). The value can be normalized to represent the fraction of total molar bromine in a DBP class (following Obolensky and Singer (2005)), and the normalized BIF is also called the Bromine Substitution Factor (BSF) (Equation 2.3). In this form, it allows comparison across groups of DBPs (e.g., THMs, HAAs) and facilitates interpretation as a percent incorporation (Hua and Reckhow, 2012, Hua et al., 2006). BSF has been used in recent work to characterize bromide incorporation in THMs (Wang et al., 2017, Hua et al., 2006).

$$BIF = \frac{\sum_{n=1}^3 n[CHCl_{3-n}Br_n]}{\sum_{n=0}^3 n[CHCl_{3-n}Br_n]} \quad (2.2)$$

where concentrations are in molar units (mol/L), and n represents the number of bromine atoms in the individual THM species.

$$BSF = \frac{\sum_{n=1}^3 n[CHCl_{3-n}Br_n]}{3 \times \sum_{n=0}^3 n[CHCl_{3-n}Br_n]} \quad (2.3)$$

where concentrations are in molar units (mol/L), and n represents the number of bromine atoms in the individual THM species.

Because the regulatory threshold for TTHM is a mass-based standard, an alternative to BIF and BSF (molar-based values) is to assess bromine incorporation on a mass basis (Mao et al., 2014, Zhang et al., 2011, Sohn et al., 2006). Similar to BIF and BSF, percent bromination indicates the portion of brominated THM species compared to the total TTHM concentration (Equation 2.4) with mass concentrations rather than molar. Brominated THMs have higher mass than chlorinated analogs, and thus have a greater effect on TTHM when a mass-based calculation is used. Handke (2009) suggested that this mass-based analysis was appropriate to determine source water bromide concentrations of concern for drinking water utilities in

Pennsylvania.

$$\% \text{Brominated by mass} = \frac{\sum_{n=1}^3 n[\text{CHCl}_{3-n}\text{Br}_n]}{\sum_{n=0}^3 n[\text{CHCl}_{3-n}\text{Br}_n]} \quad (2.4)$$

where concentrations are in mass units ($\mu\text{g/L}$), and n represents the number of bromine atoms in the individual THM species.

BIF, BSF and percent bromination have all been used to assess changes in DBPs observed at plants where source water bromide has changed. Wang et al. (2017) report that BSF and percent by mass for TTHM were correlated with source water bromide concentrations for six drinking water plants in southwestern Pennsylvania analyzed during a three year field study. Greune (2014) reports increasing BIF in TTHM with increasing bromide concentration for 78 water treatment facilities in North Carolina assessed over a year. States et al. (2013a, 2013b) report bromide concentrations less than $50 \mu\text{g/L}$ led to 40%-60% bromination by mass in TTHM in finished water at the Pittsburgh water utility during a period of changing source water bromide concentrations (2010-2011). Handke (2009) reports similar results for drinking water plants in Pennsylvania in regions experiencing changing bromide levels during 2008.

2.2.5 Risk characterization

The World Health Organization (WHO) recommends a 10^{-5} risk target for DBPs, representing 1 additional cancer case for every 100,000 people exposed (WHO, 2011). During the DBP rulemaking process, the EPA aimed to meet between 10^{-4} and 10^{-6} risk targets to balance consumer risk and the economic cost of meeting target thresholds (USEPA, 1998). Despite this target risk threshold, most of the THM data reported in the ICR fall between 10^{-4} and 10^{-5} risk, based on the analysis described in the D/DBP rule-making documentation (USEPA, 2005). Further, EPA describes risk values for all four THM species calculated using the CSFs described previously, and Region 8 EPA reports target concentrations for

Table 2.3: THM species concentrations associated with different risk thresholds.

	Cancer slope factor (CSF) (per mg/kg-day)	Concentration at associated risk level ($\mu\text{g/L}$)			Reference
		10^{-4} risk	10^{-5} risk	10^{-6} risk	
		BDCM	6×10^{-2}	60	
DBCM	8.4×10^{-2}	40	4	0.4	USEPA (1990)
CHBr ₃	7.9×10^{-3}	400	40	4	USEPA (1993)
TTHM	–	500	50	5	–

10^{-6} risk levels using the reference dose used to compute the MCLGs for CHCl_3 and DBCM. A summary of the reported risk data and species concentrations evaluated for different risk values calculated using CSFs are shown in Table 2.3. The present analysis assesses TTHM risk at these threshold values calculated using two different approaches.

Regli et al. (2015) estimated bladder cancer risk associated with increased source water bromide concentrations using odds ratios (ORs), consistent with the approach used in the Stage II Economic Analysis (USEPA, 2005). In epidemiological studies, ORs compare the odds of disease status in a population with elevated exposure to the constituent of interest, to the odds of disease status in a population with low or no exposure to the constituent of interest. With respect to bladder cancer risk, ORs compare the odds of developing bladder cancer for a population exposed to some level of TTHM compared to the odds of developing bladder cancer in a population with low or no TTHM exposure. Regli et al. (2015) report the results of a pooled analysis of six case-control studies indicating that the OR of bladder cancer risk is continuously increasing with increase in TTHM concentration and duration of exposure. Regli et al. (2015) use a simplified linear dose-response relationship developed for the Stage II Economic Analysis in which the OR of developing bladder cancer given no

exposure to TTHM is 1.00 and increases with all non-zero exposures as shown in Equation 2.5 (USEPA, 2005). Regli et al. (2015) modified EPA approach using a weighted slope, shown in Equation 2.6. Using this approach, Regli et al. (2015) estimated baseline odds to be 0.02090, or approximately 2 bladder cancer cases per 100 unexposed individuals. Thus, the risk associated with TTHM concentrations greater than zero can be calculated as shown in Equation 2.7, where r is the risk associated with the TTHM concentration of concern. Utilizing this approach considers the mass sum (TTHM) to estimate risk and cannot be used to estimate how THM speciation alters risk.

$$OR = 1 + 0.00581 \times \text{Average Lifetime THM}_4 \text{ Concentration} \quad (2.5)$$

$$OR = e^{\text{THM}_4 \text{ Concentration} \times 0.00427} \quad (2.6)$$

$$OR = \frac{r}{1 - r} = 0.02090 \times e^{\text{THM}_4 \text{ Concentration} \times 0.00427} \quad (2.7)$$

As an alternative to the TTHM-based risk assessment described in the D/DBP rule and used in Regli et al. (2015), we also consider assessment the risk-based on the individual THM species. To assess risk associated with mixtures of different chemical species in water, EPA advises the use of an additive response method using CSFs (Choudhury et al., 2000). CSFs represent the upper-bound estimate of lifetime human cancer risk and indicate the probability that, as the result of exposure to an environmental constituent, an individual will develop cancer (Choudhury et al., 2000, Hrudey and Charrois, 2012). IRIS does not report an oral CSF for CHCl_3 , and thus it is not included in the species-specific analysis here (USEPA, 2001). The carcinogenicity of chloroform with respect to drinking water exposure pathways remains unclear (Richardson et al., 2007, USEPA, 2001) and thus, this species-specific analysis may underestimate this risk.

For the additive analysis, drinking water consumption risk is estimated by multiplying the CSF and the lifetime average daily dose (LADD, in mg/kg-day, see Equation 2.8) (Theodore and Dupont, 2012). LADD is calculated by multiplying the individual species concentration (C), intake rate (IR), and exposure duration (ED) and dividing by body weight (BW) and lifetime (LT) (see Equation 2.9) for each THM species. EPA estimates the adult intake rate to be 2 L of water per day, the average body weight of an adult to be 70 kg, and the average lifetime to be 70 years (USEPA, 2012a, Asante-Duah, 2002). Finally, the exposure duration is taken to be 70 years when estimating lifetime exposure.

$$\textit{Drinking water cancer risk} = LADD \times CSF_{oral} \quad (2.8)$$

$$LADD = \frac{C \times IR \times ED}{BW \times LT} \quad (2.9)$$

Then, TTHM additive risk is calculated by summing the individual CSF-derived THM species risks that were computed following Equation 2.8 incorporating their individual concentrations through Equation 2.9. This approach also allows for the derivation of target concentrations given a specific risk threshold, which was done to include CSF-derived values in Table 2.3. The CSF-based approach for DBP risk analysis has been previously used by Wang et al. (2017) and Bergman et al. (2016).

Given that the MCLG for DBCM is 60 $\mu\text{g/L}$ and EPA has designated it as a possible (not probable) human carcinogen (USEPA, 1990), it is surprising that the CSF for DBCM is higher than other brominated THMs. Since the CSF and MCLG are contradictory, in the present work, risk-based analysis for DBCM is likely to identify significant risk associated with concentrations well below the MCLG, which may be surprising to those familiar with the MCLG and the objective of setting the MCLG to be protective of human health. These values, based on the latest information on carcinogenicity, suggest that a DBCM concentra-

tion below the MCLG may still be of significant concern. Further, it is important to include DBCM-associated risk calculations as the role of brominated THM as a surrogate for risk associated with unregulated DBPs may be significant, given recent research that suggests brominated DBPs are more toxic than chlorinated DBPs (Yang et al., 2014).

2.3 Results and discussion

2.3.1 MCMC simulation

Figure 2.2 shows the THM species concentrations (each vertical band of five stacked plots, with CHCl_3 to the left and CHBr_3 to the right) compared to the TTHM concentration (left vertical axis, repeating) for the observed (shown in black) and simulated data (shown in color) by bromide bin (identified on the right vertical axis, with low bromide at the bottom and very high bromide at the top). Figure 2.2 indicates that the simulated data adequately represent the observed values and augment the sparse data in the high and very high bromide bins as was the intention.

2.3.2 THM species risk analysis

Risk calculated using the OR method (following Equation 2.7 and Regli et al. (2015)) is strongly correlated with CHCl_3 ($\rho = 0.98, 0.95, 0.91$ for very low, low, and moderate bromide concentrations, respectively; data not shown). When source water bromide is elevated, speciation shifts from CHCl_3 to more brominated forms (top middle panels in Figure 2.1), which is expected to increase risk. However, since the TTHM concentration does not change proportionally to the changing risk associated with the brominated THM species, the OR, based on TTHM, could indicate a lower risk than anticipated based on species-specific risk values that change with concentration of the brominated species. As noted in the methods, species-specific risk calculated using CSFs is expected to capture the effect of changing

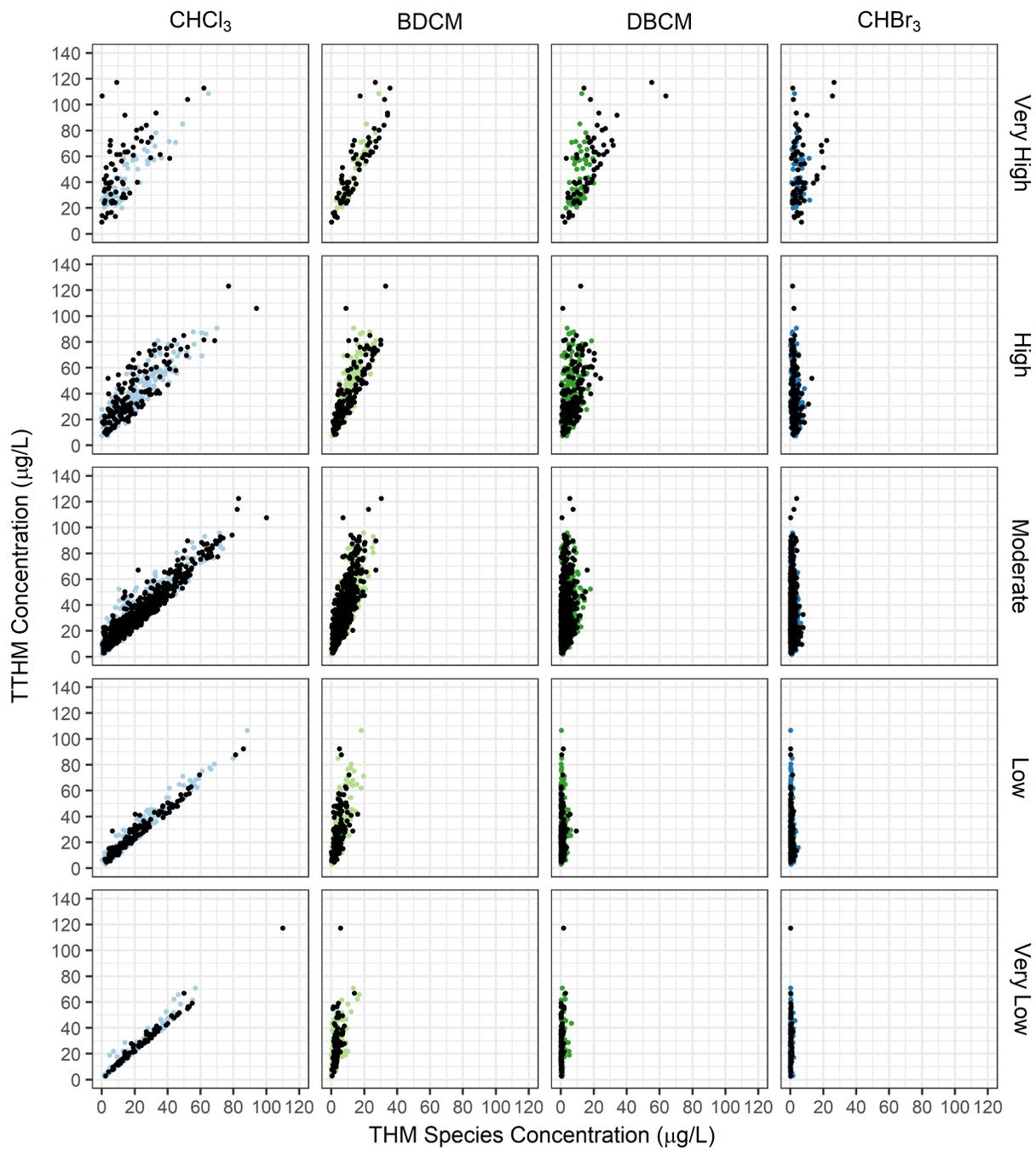


Figure 2.2: THM species concentrations versus TTHM concentration for each source water bromide bin.

bromination and thus are used here.

Figure 2.3 shows the cumulative probability distribution functions for the three brominated THM species risk and for TTHM additive risk by bromide bin for the simulated data. The bromide bins are indicated on the right-hand side of each subfigure. The colored lines show the brominated THM species (colored) and TTHM (in black). The red dashed vertical lines indicate the 10^{-4} , 10^{-5} , and 10^{-6} risk thresholds.

The likelihood of exceeding the risk threshold increases as source water bromide increases, as expected. CHBr_3 does not play a major role in exceeding the risk threshold, due to low concentrations of CHBr_3 observed, while BDCM and DBCM both contribute significantly to the computed risk. When source water bromide is classified as high or very high, the probability of meeting the 10^{-5} risk threshold is 5.8% and 1.8%, respectively. Only in the very low bromide bin is the likelihood of meeting the 10^{-5} risk threshold greater than 50% for TTHM additive risk. In the high and very high bromide bins, BDCM and DBCM have similar risk distributions. Individually, the BDCM has a 26% and 14% probability, and the DBCM has a 34% and 11% probability of meeting the 10^{-5} risk threshold, in the high and very high bromide bins, respectively.

2.3.3 TTHM and alternative risk surrogates

Figure 2.4 shows the CDFs for the simulated TTHM concentrations for low, moderate, high and very high source water bromide bins that meet the 10^{-5} risk threshold (represented as dashed lines) and that exceed the 10^{-5} risk threshold (represented as solid lines). The vertical red dashed line indicates the MCL for TTHM. Figure 2.4 shows that almost all values that meet the risk threshold (of 10^{-5}) also meet the MCL and nearly all of the values that exceed the risk threshold also meet the MCL. An ideal metric would show that the values that exceed the target concentration threshold also exceed the risk threshold and those that meet

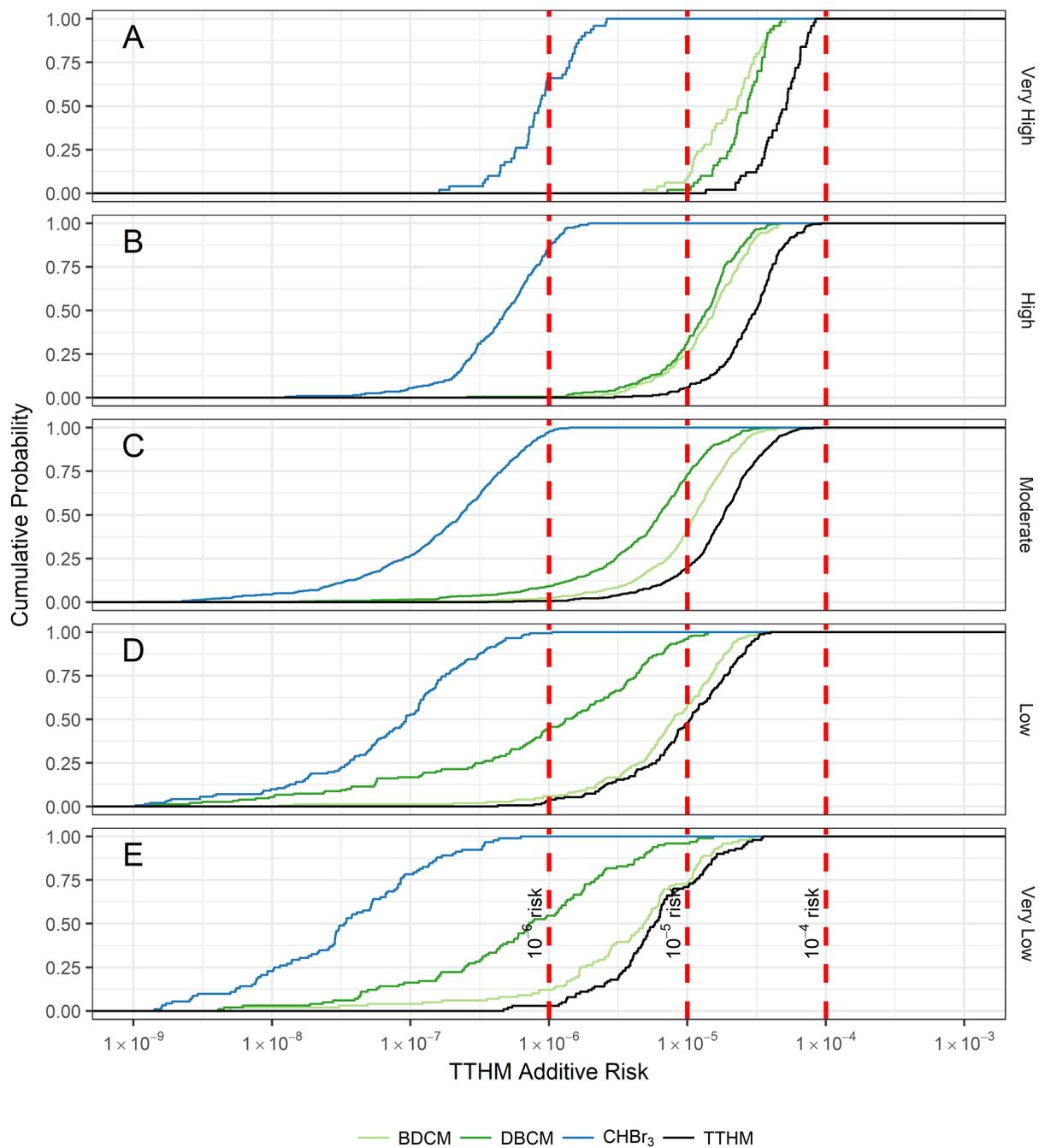


Figure 2.3: Cumulative probability distributions for simulated brominated THM species risk and TTHM additive risk (plotted on a log scale) for very low, low, moderate, high and very high source water bromide bins.

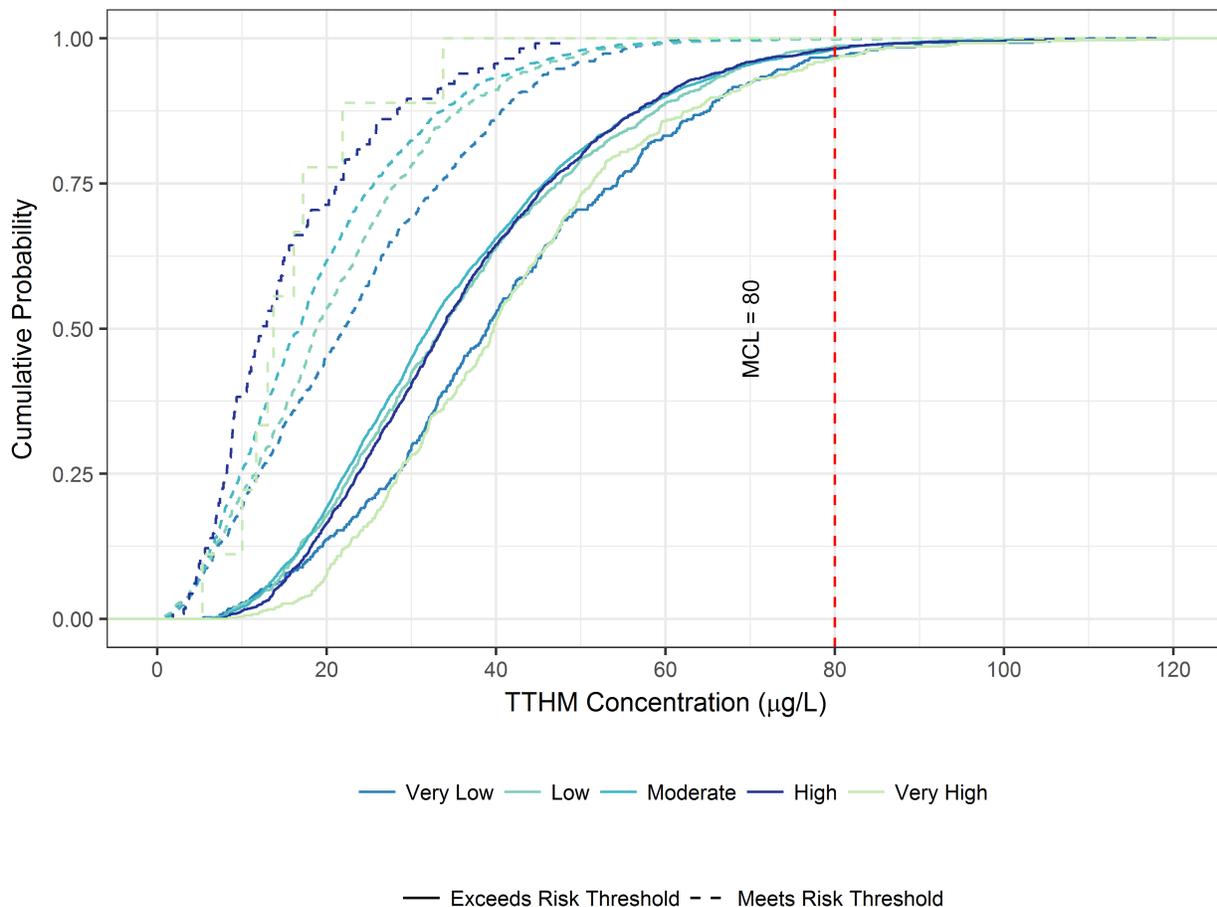


Figure 2.4: Cumulative probability distributions for simulated TTHM for very low, low, moderate, high and very high source water bromide bins for data that meet the 10^{-5} risk threshold (dashed lines) and that exceed the 10^{-5} risk threshold (solid lines).

the target concentration are below the risk threshold. Considering the MCL for TTHM, this would mean that all observations that exceed the risk threshold also exceed the MCL, and observations that meet the risk threshold also meet the MCL, with no overlap in their representative distribution functions. Thus, as demonstrated in Figure 2.4, using TTHM as the sole surrogate for drinking water would fail to adequately identify conditions that produce water with elevated risk from the brominated THM species. The suitability for TTHM to act as a surrogate for other unregulated brominated compounds would also be questionable since bromination of unregulated DBPs appears to mirror THM bromination (Francis et al., 2009).

Table 2.4: Spearman correlation coefficients for TTHM additive risk (calculated using CSFs) versus the potential surrogate measures for DBP risk. The darker shade indicates strong correlation and the lighter shade indicates weak correlation.

	THM ₃	TTHM	BSF	% Bromination	BDCM	DBCM
Total	0.99	0.59	0.55	0.59	0.92	0.90
Very high	0.99	0.70	0.24	0.33	0.89	0.93
High	0.99	0.65	0.25	0.33	0.90	0.91
Moderate	0.99	0.60	0.41	0.47	0.92	0.87
Low	0.99	0.56	0.50	0.56	0.95	0.76
Very low	0.99	0.63	0.44	0.52	0.94	0.51

TTHM: total trihalomethane; CSFs: cancer slope factors; DBP: disinfection byproduct; THM: trihalomethane; BSF: Bromine Substitution Factor; BDCM: bromodichloromethane; DBCM: dibromochloromethane.

Table 2.4 shows the Spearman rank correlation coefficients for the TTHM additive risk and a set of potential surrogates: TTHM, THM₃ (the mass sum of the brominated species), BSF, percent bromination by mass, and individual species concentrations for BDCM and DBCM. TTHM is moderately correlated with TTHM additive risk at all bromide concentrations, with highest correlation for very high bromide ($\rho = 0.70$). THM₃ is strongly correlated with TTHM additive risk at all source water bromide levels. BSF and percent bromination by mass are not well correlated with TTHM additive risk at any source water bromide concentration ($\rho \leq 0.50$ and $\rho \leq 0.56$, respectively). BDCM is well correlated with TTHM additive risk for all source water bromide concentrations and DBCM is well correlated when source water bromide is in the moderate or higher bins. This finding suggests that BDCM and DBCM concentrations and THM₃ may be useful surrogates to protect against THM species-derived risk when source water bromide is elevated.

Figure 2.5 and Figure 2.6 show potential surrogates for THM risk (each vertical band) plot-

ted against the computed TTHM risk (left axis, repeating) by bromide bin (indicated on right axis). Figure 2.5 includes THM₃ and TTHM mass-sum concentrations. Figure 2.6 shows alternative surrogates for comparison: BSF, percent bromination by mass, and the individual species concentrations for BDCM and DBCM. The dashed black horizontal lines show the 10^{-4} and 10^{-5} risk thresholds and the dashed black vertical lines show specific values for each potential surrogate for comparison. For THM₃, 50 or 10 $\mu\text{g}/\text{L}$ concentrations are shown for comparison (corresponding to the sum of the 10^{-5} species-specific risk levels for the three brominated species and the difference between the MCL and the MCLG for CHCl_3 , respectively). For TTHM, we show 80 $\mu\text{g}/\text{L}$ (the current MCL) as the sole vertical line. For BSF, we selected 0.5 BSF or 50% bromination on a molar basis, and for percent bromination by mass, we show 33% and 80% (following Handke, 2009). For BDCM and DBCM, we plot the 10^{-5} risk levels, corresponding to 6 and 4 $\mu\text{g}/\text{L}$, respectively. These plotted values are not intended as proposed regulatory values, but rather are used to highlight the differences in how the current regulatory approach compares with other potential surrogate values under changing source water conditions. The quadrants represented by these lines then indicate: meeting the risk threshold and the surrogate comparison value (lower left); meeting the surrogate comparison value but not meeting the risk threshold (upper left); not meeting the surrogate comparison value or the risk threshold (upper right); and not meeting the surrogate comparison value but meeting the target risk (lower right).

A good surrogate would show an exceedance when the risk threshold is exceeded and not show an exceedance when the risk threshold is not exceeded. Thus, all values would fall in the upper right quadrant or lower left quadrant, when comparing the plotted values and the current regulatory threshold. Values in the lower right represent false positives (surrogate comparison value exceeded but risk below threshold), and values in the upper left represent false negatives (surrogate comparison value not exceeded but risk above threshold). For protection of human health, the goal would be to choose a surrogate (and an associated value

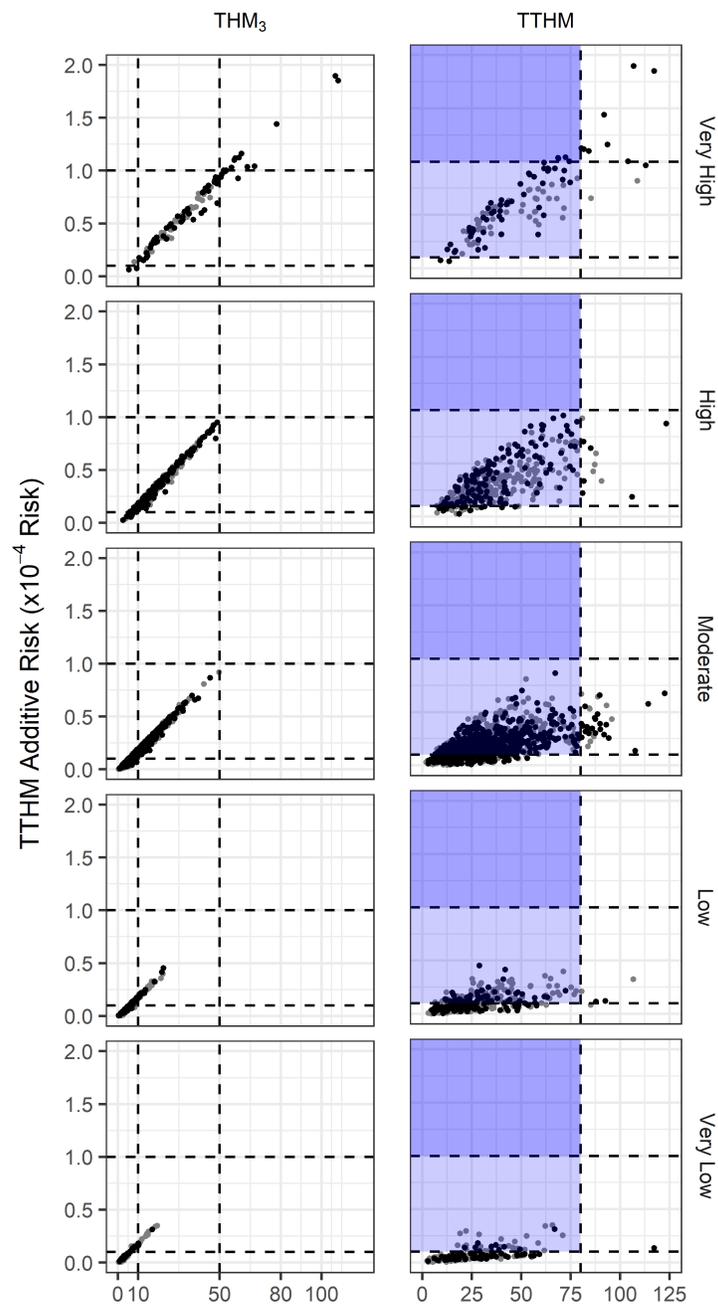


Figure 2.5: THM₃ and TTHM concentration ($\mu\text{g}/\text{L}$) versus TTHM additive risk (plotted as $\times 10^{-4}$ risk) by source water bromide bin.

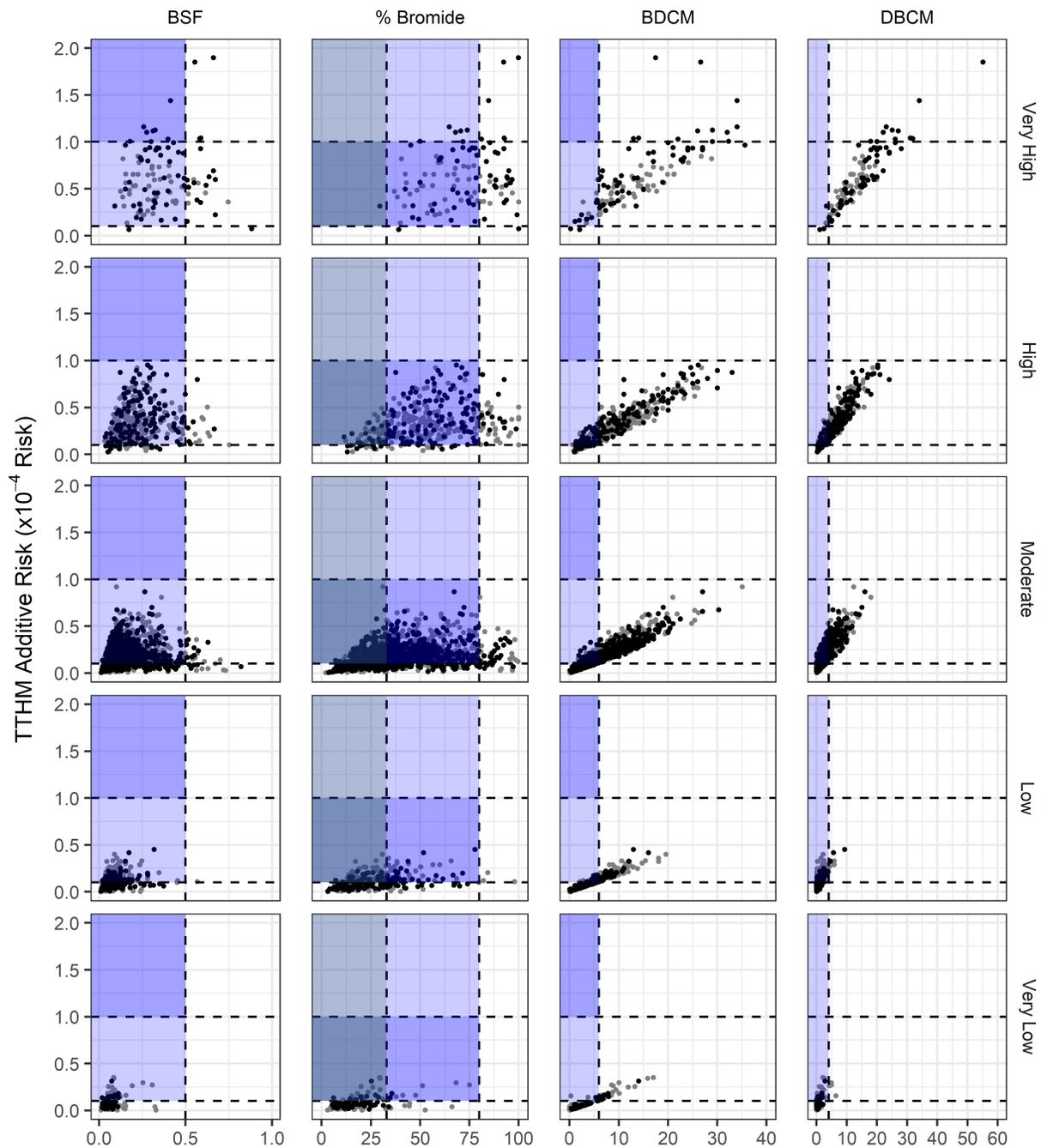


Figure 2.6: BSF, percent bromination by mass, BDCM concentration ($\mu\text{g/L}$) and DBCM concentration ($\mu\text{g/L}$) versus TTHM additive risk (plotted as $\times 10^{-4}$ risk) by source water bromide bin.

for that surrogate) with a low false negative value, or few values in the upper left quadrant. Although false positives (lower right) do not increase human health risk since they trigger action when the risk threshold was not exceeded, they could lead to unnecessary additional treatment costs and unnecessary public notification of exceedance. The target region then is shown in blue highlighting in Figure 2.5, Figure 2.6, with darker blue indicating the upper left quadrant for a 10^{-4} risk threshold and lighter blue indicating the upper left quadrant for a 10^{-5} risk threshold.

In Figure 2.5, THM₃ and TTHM show similar trends, although THM₃ has less variability at low source water bromide concentrations, due to the dominance of CHCl₃ in TTHM at low bromide concentrations. The relationship between TTHM additive risk and TTHM is linear at very high source water bromide but less so at lower bromide concentrations. In the moderate, high and very high bromide bins, some values fall into the upper left quadrant, exceeding the 10^{-4} risk threshold, suggesting that TTHM may be inadequate to protect consumers of drinking water even when bromide in source water is quite low (the moderate bin in this analysis had a lower bound of 19.1 $\mu\text{g/L}$). THM₃ shows an improved linear correlation for all source water bromide bins. Fewer false negatives would be reported for high and very high bromide source waters if the comparison value was 50 $\mu\text{g/L}$. The 10 $\mu\text{g/L}$ threshold would report no false negatives for all source water bromide bins and under most circumstances provide protection at the 10^{-5} risk threshold, suggesting that a THM₃ MCL would be more protective than the TTHM MCL when bromide exceeds moderate ranges (> 65 $\mu\text{g/L}$ in this analysis).

In Figure 2.6, BSF and percent bromination by mass do not demonstrate a linear relationship with TTHM additive risk in any bromide bin. Risk appears to be highest for low to moderate BSF (0.3 to 0.5), with very low and high or very high values showing lower risk. This is likely due to the higher risk values associated with the mono-brominated form (BDCM) compared

with the di- and tri-brominated forms (DBCM and CHBr_3). Risk appears to increase with increasing bromination by mass, although the relationship is not linear. For the high and very high source water bromide categories, the 33% comparison value would be protective at a 10^{-4} risk threshold (gray-blue upper left quadrant in column 2 of Figure 2.6, while the 80% bromination would be protective at low and moderate bromide concentrations. An intermittent value of 50% brominated (not delineated in the figure) would be nearly as protective as the 33% value.

The relationship between BDCM and TTHM additive risk is approximately linear across all source water bromide bins ($r^2 > 0.80$). Similarly, the relationship between DBCM and TTHM additive risk is approximately linear across all bromide bins, but the relationship is particularly strong at high and very high bromide ($r^2 > 0.84$). For BDCM and DBCM, targets of 6 and 4 $\mu\text{g}/\text{L}$, respectively, would capture all of the samples that exceed the 10^{-4} risk threshold. Detecting concentrations below these levels suggest that water would have low THM species-specific risk, even when source water bromide concentrations are elevated or changing. However, the DBCM MCLG has been set at 60 $\mu\text{g}/\text{L}$, a value rarely exceeded in the data set. Thus, in order for DBCM to be useful as a risk metric, its target threshold would need to be set below its MCLG or its MCLG would have to be revised in response to the data used to select its CSF.

Based on the results in Figure 2.5 and Figure 2.6, the potential metrics to consider further are THM_3 and the BDCM concentration. Figure 2.7 shows the CDFs for these surrogates by source water bromide bin for data that meet the 10^{-5} risk threshold (dashed lines) and exceed the 10^{-5} risk threshold (solid lines). The black vertical dashed lines show the comparison values for each surrogate. By assessing the data that exceed the risk threshold, we can determine which measure would best protect against this risk. The best surrogate would trigger non-compliance when the risk threshold is exceeded (denoted by the solid lines) and

have a low probability of triggering non-compliance when the risk threshold is not exceeded (denoted by the dashed lines). If the proposed surrogate meets both of these conditions, there would be a low false positive and a low false negative rate. Although a false positive would not be of concern for public health, it could increase treatment costs for the utility.

For the THM₃ concentration, a 50 $\mu\text{g}/\text{L}$ comparison value would lead to few false positives (meeting the risk threshold but exceeding the proposed target) in all bromide bins because the cumulative probability is above 90% for all of the dashed lines. However, the likelihood of exceeding the risk threshold and meeting the comparison value (false negative) would occur for nearly all observations for a comparison value of 50 $\mu\text{g}/\text{L}$. The false negative rate for a comparison value of 10 $\mu\text{g}/\text{L}$ is 3% when source water bromide is very high, 16% when it is high, 49% when it is moderate, 78% when it is low and 91% when it is very low. Thus, as source water bromide increases, the rate of false negatives decreases. For low bromide waters, setting a THM₃ threshold of 10 $\mu\text{g}/\text{L}$ provides little differentiation between waters that meet or exceed the risk threshold because almost all THM₃ values are below 10 $\mu\text{g}/\text{L}$. At the lower comparison values, there is a tradeoff between an increase in false positives and a decrease in false negatives.

For the BDCM concentration target of 6 $\mu\text{g}/\text{L}$, there would be no false positives reported (instances that meet the risk threshold but exceed the standard) since all cases of meeting the standard have BDCM concentrations below 6 $\mu\text{g}/\text{L}$. The false negative rate would not exceed 30% across all of the bromide bins since none of the cases of exceeding the risk threshold (shown as solid lines) exceed 30% at a concentration of 6 $\mu\text{g}/\text{L}$. As the source water bromide concentration increases, the false negative rate would decrease.

Figure 2.7 shows the tradeoff between false positives (triggering non-compliance despite meeting the desired risk threshold) and false negatives (not triggering non-compliance de-

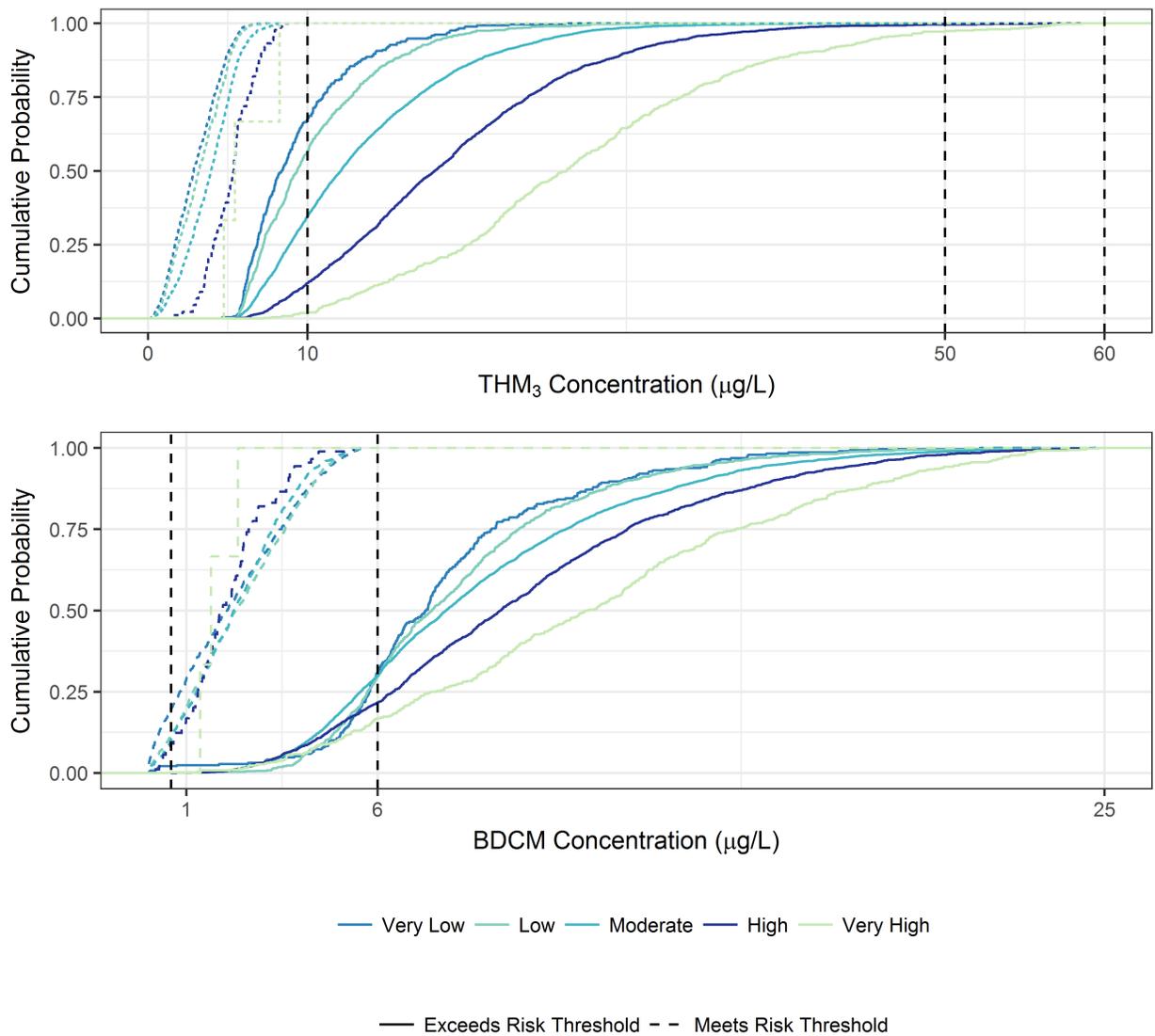


Figure 2.7: Cumulative probability distributions for simulated THM₃, and BDCM concentration ($\mu\text{g/L}$) for very low, low, moderate, high and very high source water bromide bins for data that meet the 10^{-5} risk threshold (dashed lines) and data that exceed the 10^{-5} risk threshold (solid lines).

Table 2.5: False negative rates for THM risk surrogate measures by bromide bin. The target threshold is 80 $\mu\text{g}/\text{L}$ for TTHM, 50 $\mu\text{g}/\text{L}$ for THM₃, 6 $\mu\text{g}/\text{L}$ for BDCM, and 4 $\mu\text{g}/\text{L}$ for DBCM.

	TTHM	THM ₃	BDCM	DBCM
Very high	95.4	96.0	17.4	6.40
High	93.6	95.2	23.6	29.5
Moderate	76.3	77.7	27.3	53.5
Low	49.1	50.3	18.7	46.6
Very low	27.4	29.0	11.1	27.8
Total	71.8	73.1	23.2	42.7

spite exceeding risk thresholds). Both surrogate measures have a low false positive rate for all bromide bins, but higher false negative rates. BDCM shows less variability in the false negative rate across bromide bins, but THM₃ has a lower false negative rate at high and very high source water bromide for the comparison values shown in Figure 2.7.

Table 2.5 shows the false negative rates, measured as a percentage, for TTHM, THM₃, BDCM and DBCM with target thresholds of 80, 50, 6 and 4 $\mu\text{g}/\text{L}$, respectively. The false positive rates are not shown because they are close to zero across all bromide bins for every surrogate measure. These surrogate measures showed positive correlation with TTHM risk, as shown in Table 2.4. The comparison values for TTHM and THM₃ have high false negative rates, particularly as source water bromide increases. The BDCM and DBCM comparison values have much lower false negative rates, while maintaining low false positive rates. Overall, BDCM has a low false positive and false negative rate at a comparison value of 6 $\mu\text{g}/\text{L}$, suggesting that this parameter might be a useful surrogate for THM species-specific risk.

2.4 Conclusion

As source water bromide concentrations increase as a result of anthropogenic discharges or climate change, TTHM may be inadequate as a surrogate measure for risk associated with increasingly brominated DBPs. Alternative regulatory strategies should consider the projected increases in source water bromide concentrations, as well as the feasibility of implementing alternative metrics for finished water risk. The present study identified value in considering brominated THM (THM₃) or the individual species BDCM as surrogates for protection of human health when source water bromide concentrations are changing.

Acknowledgments

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Chapter 3

Climate change impacts on bromide, trihalomethane formation, and health risks at coastal groundwater utilities¹

¹Kolb, C., Pozzi, M., Samaras, C., and VanBriesen, J. M. (2017). "Climate Change Impacts on Bromide, Trihalomethane Formation, and Health Risks at Coastal Groundwater Utilities." *ASCE-ASME J. Risk Uncertainty Eng. Syst., Part A: Civ. Eng.*, 3(3): 04017006. doi: 10.1061/AJRUA6.0000904.

Abstract

In some regions, sea level rise due to climate change is expected to increase saltwater intrusion in coastal aquifers, leading to increased salt levels in drinking water wells relying on these supplies. Seawater contains elevated concentrations of bromide, which has been shown to increase the formation and alter the speciation of disinfection byproducts (DBPs) during the treatment process. DBPs have been associated with increased risk of cancer and negative reproductive outcomes, and they are regulated under drinking water standards to protect human health. This paper incorporates statistical simulation of changes in source water bromide concentrations as a result of potential increased saltwater intrusion to assess the associated impact on trihalomethane (THM) formation and speciation. Additionally, the health risk associated with these changes is determined using cancer slope factors and odds ratios. The analysis indicates that coastal utilities treating affected groundwater sources will likely meet regulatory levels for THMs, but even small changes in saltwater intrusion can have significant effects on finished water concentrations and may exceed desired health risk threshold levels due to the extent of bromination in the THM. As a result of climate change, drinking water utilities using coastal groundwater or estuaries should consider the implications of treating high bromide source waters. Additionally, extra consideration should be taken for surface water utilities considering mixing with groundwater sources, as elevated source water bromide could pose additional challenges for health risk, despite meeting regulatory requirements for THM.

3.1 Introduction

Climate change poses several risks to freshwater supplies, which could affect the availability and sustainability of coastal freshwater aquifers (USGCRP 2014; IPCC 2013). Increasing global average mean temperature is expected to cause thermal expansion in the oceans and melting of glaciers, leading to rising sea levels (USGCRP, 2014; IPCC, 2013). As a result, coastal aquifers are expected to be subject to increased saltwater intrusion (Sawyer et al., 2016; Yuan et al., 2015; Loaiciga et al., 2012; Webb and Howard, 2011; Yechieli et al., 2010; Werner and Simmons, 2009; Heberger et al., 2009; USEPA 2008; Masterson and Garabedian, 2007). The expected increase in saltwater intrusion into coastal aquifers and estuaries may impair drinking water resources through warming groundwater and increasing salt content.

Climate-induced sea level rise is expected to alter natural groundwater flow patterns, causing an inland migration of the saltwater-freshwater interface (Badaruddin et al., 2015; Carretero et al., 2013; Giambastiani et al., 2007; Barlow, 2003). Although dependent on aquifer characteristics and regional hydrology, many regions of the United States have already experienced increased saltwater intrusion as a result of climate change and anthropogenic factors (Motz et al., 2014; CISA and USC, 2012; Chen et al., 2010; Oude Essink et al., 2010; Barlow and Reichard, 2010; DRBC 2008). With future sea level rise, intrusion in these regions may be exacerbated.

Saltwater intrusion causes drinking water wells near the coast to contain higher concentrations of salts, measured as total dissolved solids (TDS). TDS and several specific constituents (chloride and sulfate) are regulated under the U.S. Environmental Protection Agency (EPA) drinking water regulations (USEPA, 1991). TDS, chloride, and sulfate are regulated with secondary standards, meaning that they are of concern due to aesthetic effects rather than due to human health impacts. In general, water containing high concentrations of salt is objectionable to consumers at much lower concentrations than would cause any health concern

(WHO, 1996). An increase in seawater content of just 2% can lead to waters too saline for drinking water consumption, based on the secondary standards of 500 mg/L TDS and 250 mg/L chloride (Ged and Boyer, 2014).

In addition to these aesthetic concerns, seawater contains significantly higher concentrations of bromide than freshwater, resulting in increased bromide concentrations in source water affected by saltwater intrusion (WHO, 2010). Elevated bromide concentrations in source water increase the formation and alter the speciation of disinfection byproducts (DBPs) during drinking water treatment (Motz et al., 2014; Chen et al., 2010; Wang and Huang, 2006; Nikolaou 2004; Chang et al., 2001; Amy, 1994; Luong et al., 1980).

Disinfection byproducts are formed when organic carbon reacts with disinfectants added to drinking water for pathogen control. DBPs have been associated with cancer and negative reproductive outcomes in various epidemiological studies (Villanueva et al., 2015, 2004; Cantor et al., 2010; Richardson et al., 2007), and thus they are regulated to protect human health (Becker et al., 2013; Regli et al., 2015; USEPA, 2006a). When source water containing bromide is disinfected, the bromide is oxidized to form bromine, which then reacts with organic matter present in source water to form brominated and mixed bromo-chloro DBPs. Bromide in source waters increases the rate and extent of DBP formation, generally because the rate of bromination of organic matter is higher than the rate of chlorination (Heeb et al., 2014; Westerhoff et al., 2004). Brominated DBPs are associated with negative outcomes at lower concentrations than their chlorinated analogs (Cantor et al., 2010; Richardson et al., 2007), and thus, the presence of bromide in source waters increases the risk associated with the use of chlorinated drinking water (Regli et al., 2015; Yang et al., 2014; Hong et al., 2007). DBPs are regulated through two class sums that act as surrogates for risk. The mass sum of four trihalomethanes is called total trihalomethanes (TTHM) and includes chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and

bromoform (CHBr_3). Additional trihalomethanes can form with iodide; however, these are not regulated. For clarity, in this work, TTHM will refer to the regulatory compliance term, and THM_4 will refer to the sum of the concentrations of the four regulated THMs. The current regulatory limit, the maximum contaminant level (MCL), for TTHM in drinking water is $80 \mu\text{g/L}$ (USEPA 2006a).

Previous work has demonstrated saltwater intrusion in estuaries increases DBP production in finished drinking water (Krasner et al., 1996, 1994). The impact of saltwater intrusion in coastal aquifers on DBP formation was explored by Ged and Boyer (2014), who simulated saltwater intrusion scenarios for a coastal aquifer in Florida. An increase in the source water bromide concentration of $936 \mu\text{g/L}$ (associated with intrusion of 2% seawater) led to an increase in finished water total trihalomethane concentration (THM_4) of $163 \mu\text{g/L}$ (Ged and Boyer 2014), well above the MCL. Thus, the finished water THM_4 concentration found by Ged and Boyer (2014) would be of significant concern, requiring use of an alternative source or additional treatment to remove DBPs prior to distribution to consumers.

Previous work has also considered the effect of climate change on source water changes that affect treatability of surface waters. Several recent studies have assessed the changes in organic carbon concentrations, a known DBP precursor, as a result of changes in precipitation and temperature (Delpla et al., 2015; Sawade et al., 2016; Li et al., 2014; Ritson et al., 2014). Li et al. (2014), for example, conducted an analysis on the impacts of climate change for a surface water utility drawing from the Ohio River. The study used Monte Carlo analysis to assess baseline and expected future source water quality conditions for surface waters under climate change and predicted finished water DBP concentrations using an empirical drinking water model developed by the EPA (USEPA, 2001b). Results from the analysis indicate that climate-induced changes in source water could result in potential violations of regulatory limits for DBPs in the finished water, necessitating treatment modifications at

the plant (Li et al., 2014).

The present work considers the impact of saltwater intrusion for coastal groundwater utilities located in New Jersey. Several utilities located in the state utilize estuary-impacted groundwater from the Delaware River, which has been shown to be susceptible to saltwater intrusion events (Navoy et al., 2004; Ervin et al., 1994; Hull and Titus, 1986). Scenarios with different levels of saltwater intrusion are assessed for their effect on bromide concentration and trihalomethane formation and speciation. Additionally, an increase in source water temperature is evaluated to capture the potential influence of warming water temperatures on DBP formation. Furthermore, the risk associated with increased THM formation and changing speciation is examined using species-specific and THM₄ risk parameters.

3.2 Methods

3.2.1 Site description

Five water utilities utilizing coastal groundwater supplies in New Jersey as their source of supply were selected as a regional case study. These utilities were selected because previous studies have shown the Potomac-Raritan-Magothy (PRM) aquifer system to be at risk of increased salinity as a result of sea level rise (Navoy et al., 2004; Ervin et al., 1994; Hull and Titus, 1986). The aquifer is influenced by the Delaware River estuary system where sea level rise is expected to shift the freshwater-saltwater interface further upstream. A drought in the 1960s caused elevated chloride concentrations to move as high as intakes in Philadelphia, PA, (at river mile 100 from the mouth), demonstrating the extent of intrusion that could occur under sea level rise as a result of climate change (Hull and Titus, 1986). During this same drought, chloride concentrations increased from 20 to 80 mg/L in some production wells in the PRM aquifer (Hull and Titus, 1986). Hull and Titus (1986) assessed

the potential effects of sea level rise on the Delaware River estuary system and predicted that chloride concentrations above 250 mg/L might be detected in some groundwater sources as a result of a 250 cm increase in sea level.

3.2.2 Data collection

Data were obtained through the information collection rule (ICR) database (USEPA, 2000a). The EPA established the ICR in 1996 and required water utilities serving populations greater than 100,000 people to collect data monthly from July 1997 to December 1998 in response to the National Primary Drinking Water Regulations (USEPA, 1996). The ICR data collection program included plant design and operation parameters, as well as water quality sampling data throughout the treatment processes and in the distribution system. Data from the ICR has been used in numerous studies to assess the impact of source water quality on DBP formation (Regli et al., 2015; Li et al., 2014; Francis et al., 2010; Obolensky et al., 2007). In this paper, ICR data were used for identifying the baseline conditions, as they are the most comprehensive publicly available data.

Data from five groundwater plants in New Jersey were used for the source water characterization and subsequent analysis. Although not all of these drinking water treatment plants draw on the PRM, groundwater characteristics in the region are similar.

3.2.3 Data processing

Several source water quality parameters influence the formation and speciation of DBPs, including pH, temperature, total organic carbon (TOC) concentration, ultraviolet absorbance at 254 nm (UV_{254}), bromide concentration (Br^-), chlorine dose (Cl_2), and chlorine contact time. Of these parameters, sea level rise as a result of climate change is expected to influence source water bromide concentrations and temperature for groundwater sources through aquifer recharge. Data for these parameters were extracted from the ICR database by sam-

pling period (monthly samples between July 1997 and December 1998); a total of 84 samples were used in the analysis.

The data extracted from the ICR database included below detection and missing values. To ensure an adequate sample size for model validation and to accurately characterize the source water quality data, a lognormal distribution was fit to the observed data (Obolensky 2007; Travis and Land, 1990) and used to impute the missing values. The robust semiparametric regression on order statistics (ROS) method for multiple imputation (Helsel 2005; Helsel and Cohn, 1988) was used to determine summary statistics for the source water quality parameters. Using the NADA package in the R computing language (Lee 2015), missing data were imputed from a truncated lognormal distribution based on the ROS-derived estimates of the means and standard deviations. For data missing at random, samples were generated for each missing value from the entire distribution. Table 3.1 shows a summary of below detection and missing observations of source water quality parameters for the five drinking water utilities used in the analysis. Table 3.2 shows a summary of the estimated mean and standard deviation of source water quality parameters for the five drinking water utilities. The plants selected for the current analysis had below-average TOC and bromide concentrations (TOC = 0.48 mg/L and bromide = 0.050 mg/L) compared to the mean concentrations for all groundwater plants included in the ICR database (TOC = 1.83 mg/L and bromide = 0.103 mg/L) (USEPA, 2000a).

3.2.4 Baseline scenario analysis

A baseline scenario was developed using the source water quality data extracted from the ICR database and was used to facilitate comparison with simulated future saltwater intrusion scenarios. Monte Carlo (MC) simulations, with 10,000 independent runs, were carried out from a correlated multivariate lognormal distribution of source water quality following the approach of Li et al. (2014). The means, standard deviations, and correlation among

Table 3.1: Summary of missing and below detection data for source water quality and operational parameters.

Parameter	Number (%) of observations below detection	Number (%) of missing observations	Detection limit
pH	0 (0%)	1 (1%)	–
Temp (°C)	0 (0%)	1 (1%)	–
TOC (mg/L)	59 (70%)	6 (7%)	0.5
UV ₂₅₄ (nm/cm)	20 (24%)	3 (4%)	0.009
Br ⁻ (mg/L)	24 (29%)	9 (11%)	0.02
Cl ₂ (mg/L)	0 (0%)	18 (21%)	–
Time (h)	0 (0%)	32 (38%)	–

Note: Br⁻ = bromide concentration; Cl₂ = chlorine dose; Temp = source water temperature; Time = chlorine contact time; TOC = total organic carbon concentration; UV₂₅₄ = ultraviolet absorbance at 254 nm.

Table 3.2: Observed source water quality and operational parameters.

Parameter	Mean	Standard Deviation
pH	7.56	0.302
Temp (°C)	14.6	2.09
TOC (mg/L)	0.561	0.310
Br ⁻ (mg/L)	0.0521	0.0665
UV ₂₅₄ (nm/cm)	0.0121	0.00479
Cl ₂ (mg/L)	1.56	0.592
Time (h)	3.25	1.72

Note: Br⁻ = bromide concentration; Cl₂ = chlorine dose; Temp = source water temperature; Time = chlorine contact time; TOC = total organic carbon concentration; UV₂₅₄ = ultraviolet absorbance at 254 nm.

Table 3.3: Correlation matrix for water quality parameters.

Parameter	pH	Temp	TOC	Br ⁻	UV ₂₅₄	Cl ₂	Time
pH	1.00	-0.0484	-0.521	0.128	0.222	-0.00446	-0.129
Temp	-	1.00	0.342	0.357	0.260	-0.429	-0.409
TOC	-	-	1.00	0.0222	0.129	-0.286	-0.240
Br ⁻	-	-	-	1.00	0.215	-0.129	-0.0584
UV ₂₅₄	-	-	-	-	1.00	-0.285	-0.357
Cl ₂	-	-	-	-	-	1.00	0.749
Time	-	-	-	-	-	-	1.00

Note: Br⁻ = bromide concentration; Cl₂ = chlorine dose; Temp = source water temperature; Time = chlorine contact time; TOC = total organic carbon concentration; UV₂₅₄ = ultraviolet absorbance at 254 nm.

parameters estimated using ROS techniques were used to simulate the baseline source water quality scenario. The correlation matrix, calculated using the observed and imputed data, is shown in Table 3.3.

3.2.5 Climate change analysis

Scenarios were developed for expected changes in groundwater bromide concentrations and temperature increases as a result of saltwater intrusion. As described previously, sea level rise increases the risk of saltwater intrusion in coastal aquifers, with the potential to contaminate coastal groundwater supplies. All other source water parameters were assumed to remain at baseline levels. Although evidence suggests changes in TOC concentrations are possible as a result of climate change, these effects are expected to be predominately in surface waters as a result of changes to precipitation patterns (Ritson et al., 2014; Tang 2013; Skjelkvale et al., 2005). Operational parameters were assumed to remain constant from the baseline scenario to assess how the utility would perform using existing infrastructure. Additional MC simulations, again with 10,000 independent runs, were carried out for each future scenario.

Based on the analysis of Ged and Boyer (2014), five bromide scenarios were assessed to capture the range of possible bromide concentrations as a result of saltwater intrusion. Ged and Boyer (2014) conducted laboratory mixing experiments using groundwater and seawater samples to assess the impacts of saltwater intrusion on source water quality for a drinking water utility utilizing coastal groundwater in southern Florida. They concluded that with just 2% seawater mixing, the resultant source water would reach the regulatory limit for TDS and chloride under the secondary drinking water standard. As a result, they performed five experiments with 0.1, 0.2, 0.4, 1.0, and 2.0% seawater mixing. The seawater mixing experiments resulted in bromide concentration increases of 21, 68, 159, 465 and 936 $\mu\text{g/L}$, respectively. In the present study, these values were added to the mean baseline bromide concentration to create five saltwater intrusion scenarios.

Previous work suggests that groundwater temperatures are expected to increase as a result of increasing global average temperatures (Kurylyk et al., 2014; Gunawardhana and Kazama, 2011; Cromwell et al., 2007). As ocean water temperatures increase, saltwater intrusion could increase coastal groundwater temperatures due to increased mixing. Additionally, interactions with warmer surface waters have the potential to influence groundwater temperatures. Gunawardhana and Kazama (2011) predict an increase in groundwater temperatures between 1.2 and 3.3°C by 2080. For this analysis, a 2°C increase in water temperatures was explored to investigate potential impacts of warming on DBP formation.

3.2.6 Trihalomethane model selection and validation

In the present work, 12 models for total trihalomethane (THM_4) from the literature, identified by Ged et al., (2015), were tested against observed finished water quality data for the five groundwater utilities in New Jersey (Chen and Westerhoff, 2010; Hong et al., 2007; Al-Omari et al., 2005; Sohn et al., 2004; Serodes et al., 2003; Rodriguez et al., 2000; Amy et

al., 1998; Chang et al., 1996; Rathbun, 1996; Malcolm Pirnie, 1993; Montgomery-Watson, 1993; Urano et al., 1983). Additionally, three species-specific model ensembles, comprising the four regulated species – chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and bromoform (CHBr_3) – were tested against the observed data (Amy et al., 1998; Malcolm Pirnie 1993; Montgomery-Watson 1993).

The Malcolm Pirnie model ensemble was selected for the present work due to its predictive capabilities when validated against occurrence data in several studies (Boyer 2015; Ged et al., 2015; Malcolm Pirnie, 1993) and because it provided the best prediction for the data at the particular plants in the present study. The model required the ammonia concentration, which was unavailable in the baseline dataset; however, a sensitivity analysis showed the predicted THM_4 concentration was not sensitive to an assumption of no ammonia in this source water.

3.2.7 THM species concentration

Using the statistical models from Malcolm Pirnie (1993), the THM_4 and THM species concentrations were simulated from the baseline and future scenario source water distributions. The predicted DBP concentrations represent finished water quality prior to entering the drinking water distribution system. These models do not predict THM concentrations after distribution and, thus, cannot be compared directly to regulatory compliance goals, which are for water quality at the point of consumption. However, utilities often have a target of 80% of the MCL for water leaving the treatment works (Becker et al., 2013; Roberson et al., 1995); thus, finished water THM_4 above $64 \mu\text{g/L}$ might be of concern to the utility. Further, individual THM species exhibit different toxicity (Regli et al., 2015; Yang et al., 2014; Hong et al., 2007), and the EPA has established maximum contaminant level goals (MCLGs) for individual species concentrations (CHCl_3 , 0.07 mg/L; CHCl_2Br , 0 mg/L; CHClBr_2 , 0.06 mg/L; and CHBr_3 , 0 mg/L) to reflect their relative risk (USEPA, 2006a). As such, individual

species concentrations, especially CHCl_2Br and CHBr_3 , are important considerations for the protection of public health.

3.2.8 Bromide incorporation in THM_4

In addition to DBP concentrations, the relative contribution of brominated THMs to the THM_4 concentration may be important to characterize finished water quality risk (Hrudey et al., 2015; Regli et al., 2015; Francis 2011; Chisholm et al., 2008). Francis (2011) suggests that the bromine incorporation might provide a useful means by which to measure the relative risk of THM_4 , and bromine incorporation is used to assess levels of concern for source waters in Pennsylvania (Handke 2009).

The bromine incorporation factor (BIF) is a unitless measure developed by Gould et al. (1983), and it has been used in various studies to assess the degree and the rate of formation of bromide incorporation into THM_4 (Tian et al., 2013; Francis et al., 2010; Rathbun, 1996; Symons et al., 1993). BIF is measured as the molar ratio of brominated THM to THM_4 , and it ranges from 0 to 3, depending on the degree of bromine incorporation (Gould et al., 1983). As an alternative to BIF, Hua et al. (2006) developed the bromine substitution factor (BSF), which normalizes the BIF to values between 0 and 1. This measure, in contrast to BIF, allows for comparison across DBP classes and facilitates interpretation as a measurement of the percent of bromide incorporation on a molar basis (Hua and Reckhow, 2012; Hua et al., 2006). The BSF is calculated as shown in Equation 3.1, where each bracketed value is the molar concentration of the chemical constituent

$$BSF = \frac{1 \times [\text{CHCl}_2\text{Br}] + 2 \times [\text{CHClBr}_2] + 3 \times [\text{CHBr}_3]}{3 \times ([\text{CHCl}_3] + [\text{CHCl}_2\text{Br}] + [\text{CHClBr}_2] + [\text{CHBr}_3])} \quad (3.1)$$

In addition to these molar criteria, an alternative mass-based measure of bromine incorporation in finished water DBPs has also been used to assess the relative contribution of brominated DBPs to the regulatory threshold for THM_4 (Mao et al., 2014; Zhang et al.,

2011; Sohn et al., 2006). Since brominated forms of THMs are heavier than chloroform, they have a disproportionate effect on THM₄ computed on a mass basis. Thus, increasing bromination increases the likelihood that THM₄ will exceed the mass-based THM₄ standard of 80 $\mu\text{g}/\text{L}$. The percent bromination indicates the portion of brominated species to the total THM concentration on a mass basis and is calculated as shown in Equation 3.2, where each bracketed value is a mass concentration of the chemical constituent

$$\% \text{Brominated by mass} = \frac{[\text{CHCl}_2\text{Br}] + [\text{CHClBr}_2] + [\text{CHBr}_3]}{[\text{CHCl}_3] + [\text{CHCl}_2\text{Br}] + [\text{CHClBr}_2] + [\text{CHBr}_3]} \times 100 \quad (3.2)$$

3.2.9 Risk analysis

The EPA recommends the use of cancer slope factors (CSFs), available from the Integrated Risk Information System (IRIS; USEPA, 2016), defined as the upper bound estimate of lifetime human cancer risk, in assessing the probability that an individual develops cancer as the result of exposure to a given chemical present in the environment (Hrudey and Charrois 2012; USEPA, 2000b). Although various approaches for estimating risk are often used, the EPA recommends an additive response method to calculate the risk for DBP mixtures wherein the risk of individual DBP species concentrations are calculated and then summed to estimate the total exposure risk for a given class of DBPs (USEPA, 2000b). For the THM class, the species oral CSFs are 6.2×10^{-2} per mg/kg-day for bromodichloromethane (USEPA 1987a), 8.4×10^{-2} per mg/kg-day for dibromochloromethane (USEPA, 1987b), and 7.9×10^{-3} per mg/kg-day for bromoform (USEPA 1993). No CSF is given in IRIS for chloroform; however, previous work reported a CSF of 6.1×10^{-3} per mg/kg-day (Faust 1992). Inclusion of this CSF does not significantly change the results (not shown). Since recent work calls into question the carcinogenicity of chloroform (Hrudey et al., 2015; USEPA, 2001a), and IRIS does not list a CSF, chloroform risk was not included in the present analysis. Thus, the present study estimates the individual brominated THM species risk associated with

increases in source water bromide as a result of sea level rise.

The EPA has estimated the carcinogenic risk of DBPs in drinking water through chronic oral exposure studies (USEPA, 2005a) and suggests conducting drinking water risk estimation by multiplying the oral CSF and lifetime average daily dose (LADD, in mg/kg-day), as shown in Equation 3.3 (Theodore and Dupont, 2012). LADD is calculated as concentration (C) times intake rate (IR) times exposure duration (ED), divided by body weight (BW) and lifetime (LT), as shown in Equation 3.4 (Asante-Duah, 2002). According to the 2012 EPA Drinking Water Standards and Health Advisories document, the ingestion rate for a 70-kg adult is estimated to be 2 L of water per day for an exposure duration of one day (USEPA 2012), measured over a lifetime of 70 years (Asante-Duah, 2002).

$$\textit{Drinking water cancer risk} = LADD \times CSF_{oral} \quad (3.3)$$

$$LADD = \frac{C \times IR \times ED}{BW \times LT} \quad (3.4)$$

Additionally, a separate risk analysis was conducted using the odds ratio method following the Economic Analysis of the Stage 2 D/DBP Rule (USEPA, 2005b). Following Regli et al., (2015), the baseline odds of developing bladder cancer without DBP exposure (0.0290), the average lifetime risk of developing bladder cancer (2.4%), and a weighted slope (0.00427) were used to calculate the increased risk associated with a higher THM₄ concentration in the finished water, as shown in Equation 3.5 (adapted from Regli et al., 2015).

$$\textit{Increased risk} = \frac{0.0209 \times e^{[THM_4] \times 0.00427}}{1 + 0.0209 \times e^{[THM_4] \times 0.00427}} - \textit{baseline risk} \quad (3.5)$$

3.2.10 Mixing analysis

One common adaptation strategy to reduce the impact of diminished source water quality is to mix current supplies with alternative sources (Breach 2011; Peet et al., 2001; Lovins et al., 2005; Owen, 2003). As has been demonstrated in the literature (Delpla et al., 2015; Sawade et al., 2016; Li et al., 2014; Ritson et al., 2014), surface waters are at risk of encountering elevated TOC concentrations in their source water due to climate change impacts. As a result, traditional practices of mixing ground and surface waters may not be a viable option in the future if surface water plants struggling to meet water quality criteria incorporate groundwater with elevated bromide concentrations. This dual impact of increased bromide and TOC concentrations could exacerbate DBP formation and increase risk for drinking water consumers.

In order to evaluate the potential impacts surface water?groundwater mixing could have on DBP formation, data for surface water plants in the New Jersey was extracted from the ICR database to assess: (1) the potential impact of expected changes in source water TOC; and (2) the impact of mixing ground and surface waters under the projected future conditions. Skjelkvale (2005) studied the regional trends in surface water chemistry for various regions across North America and Europe from 1990 to 2001. According to their study, the Atlantic region has experienced an increase in dissolved organic carbon (DOC) concentrations of 0.06 mg/L per year, which could be linked to changing climate conditions (Skjelkvale et al., 2005). DOC is typically the primary component of TOC; thus, the trends are assumed to be equivalent. The present study examines potential increases in the mean TOC concentration of 0.60, 1.2, 1.8, 2.4, and 3.0 mg/L for surface water plants in New Jersey.

The mixing of ground and surface waters is then simulated to assess the potential impact of mixing as an adaptation strategy to meet regulatory criteria for source waters. Because surface waters typically require higher levels of treatment than groundwater, the operating

parameters (chlorine dose and contact time) for the surface water utilities are used for the mixing scenarios.

3.3 Results and discussion

3.3.1 THM species concentration

Figure 3.1 shows the mean THM species concentrations for the baseline and saltwater intrusion scenarios with no change in temperature (top panel) and a 2°C increase in temperature (bottom panel). The 0.1, 0.2, and 0.4% saltwater intrusion scenarios for both temperature scenarios show minimal changes in the THM species concentrations. For the 1 and 2% saltwater intrusion scenarios, corresponding to an increase in the mean source water bromide concentration of 465 and 936 $\mu\text{g/L}$, respectively, notable increases in the mean finished water THM₄ concentration are predicted as expected. The 2% saltwater intrusion scenario would be of particular concern for drinking water utilities as the mean THM₄ concentration leaving the plant exceeds 80% of the MCL, a common threshold set by many utilities for water at the end of treatment (Becker et al., 2013; Roberson et al., 1995). Drinking water utilities treating affected groundwater sources, of particular concern for utilities already facing saltwater intrusion (Barlow and Reichard, 2010), will likely face increased challenges with respect to THM formation as sea levels rise.

Based on these results, the projected increase in groundwater temperature affects finished water THM₄ for the 2% saltwater intrusion scenario but has little effect at lower saltwater intrusion scenarios. Thus, the dominant change of concern at lower intrusion levels is the increase in bromide. This is confirmed by consideration of other salts that are present in seawater. At intrusion levels below 1%, TDS, chloride, and sulfate are all below their secondary drinking water standards (results not shown), confirming the results of Ged and Boyer (2014).

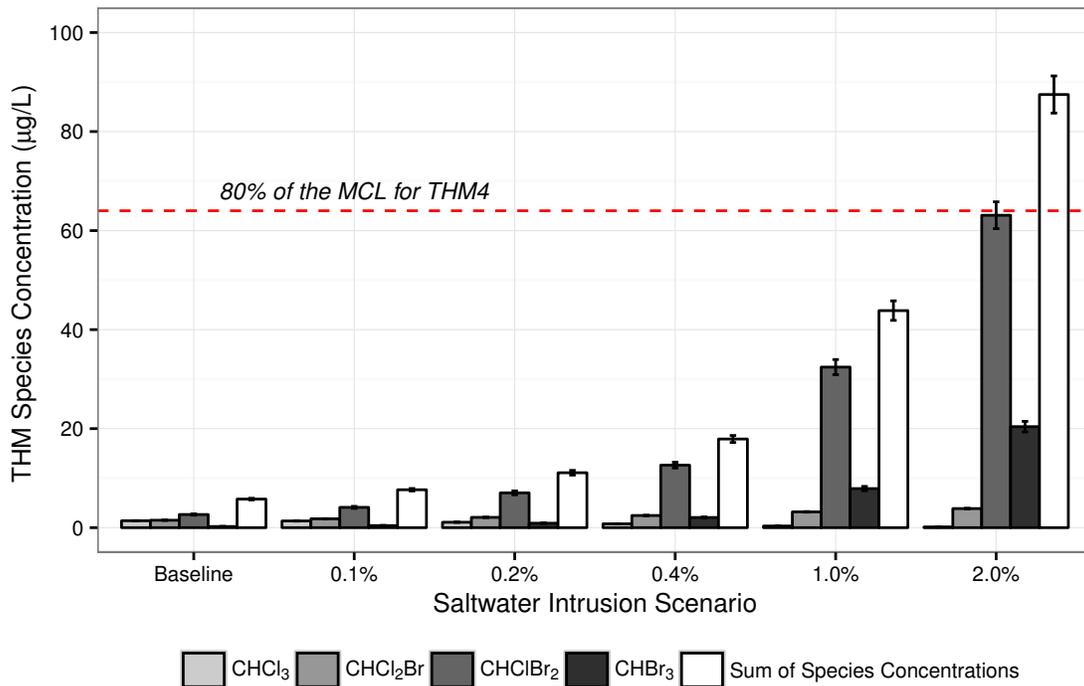
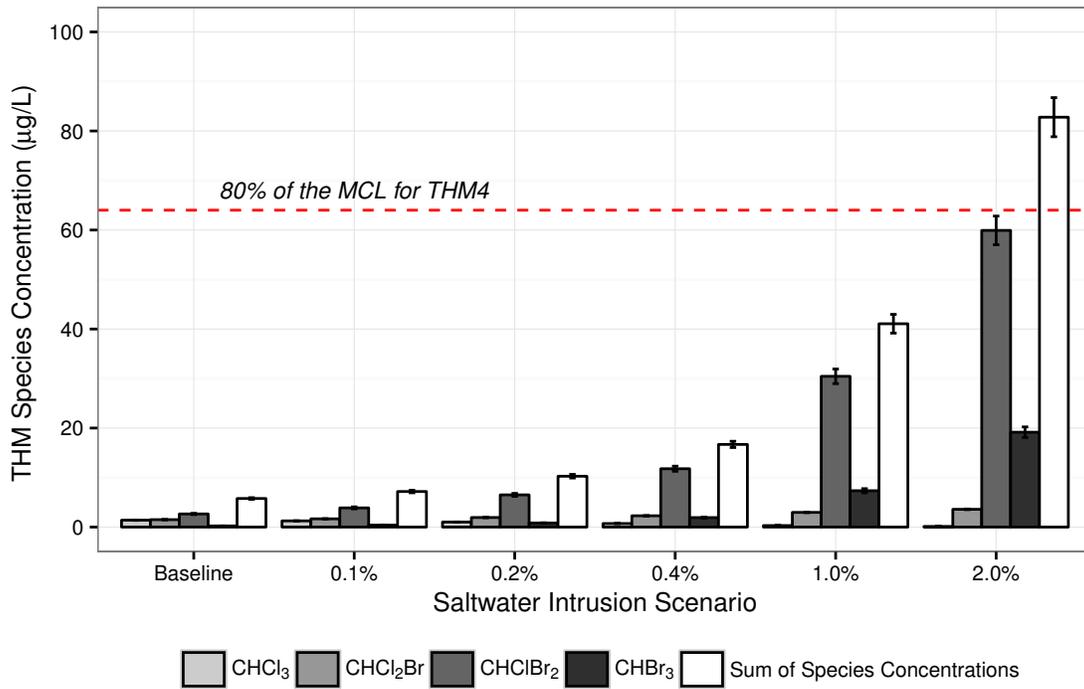


Figure 3.1: Mean THM species concentrations for the baseline and climate scenarios with (a) no change in temperature; (b) a 2°C change in temperature; dashed line shows 80% of the maximum contaminant level (MCL) for THM₄.

3.3.2 Bromide incorporation into THM₄

The BSF indicates the relative incorporation of brominated species relative to the THM₄ concentration. As brominated THMs have been associated with more significant health impacts than their chlorinated analogs (Regli et al., 2015; Yang et al., 2014; Hong et al., 2007), the BSF may provide additional insight into utility concern regarding THM changes in finished water. Figure 3.2 shows the BSF computed from the simulated THM speciation concentrations for the baseline and saltwater intrusion scenarios with no temperature change. The results for a 2°C temperature change were similar and, thus, are not shown. The mean simulated BSF of the baseline scenario, where mean source water bromide was 52.1 µg/L is 0.35, with 25th and 75th percentiles of 0.29 and 0.4, respectively. Generally, the BSF increases as source water bromide concentrations increase as expected. Zhang et al. (2011) identified source water bromide concentrations of 100 µg/L as leading to BSF values of concern for drinking water utilities. A source water bromide concentration of 100 µg/L corresponds approximately to the 0.2% saltwater intrusion scenario in this analysis, where the mean BSF is about 0.4. The mean BSFs for the 0.4, 1, and 2% saltwater intrusion scenarios all exceed 0.5 (0.56, 0.66, and 0.7, respectively).

The percent bromination by mass has been used to evaluate the impact of increasing source water bromide concentrations on bromide incorporation in finished water THM₄ (States et al., 2013; Handke, 2009). Figure 3.3 shows the percent bromination by mass computed from the simulated THM speciation concentrations for the baseline scenario and increased bromide scenarios with no temperature change. The results for a 2°C temperature change were similar and, thus, are not shown. The mean simulated percent bromination by mass of the baseline scenario where mean source water bromide was 52.1 µg/L is 75%, with 25th and 75th percentiles of 68% and 80%, respectively. Generally, the percent bromination by mass increases as source water bromide concentrations increase as expected. All the saltwater intrusion scenarios result in greater than 80% bromination of THM, and the highest values

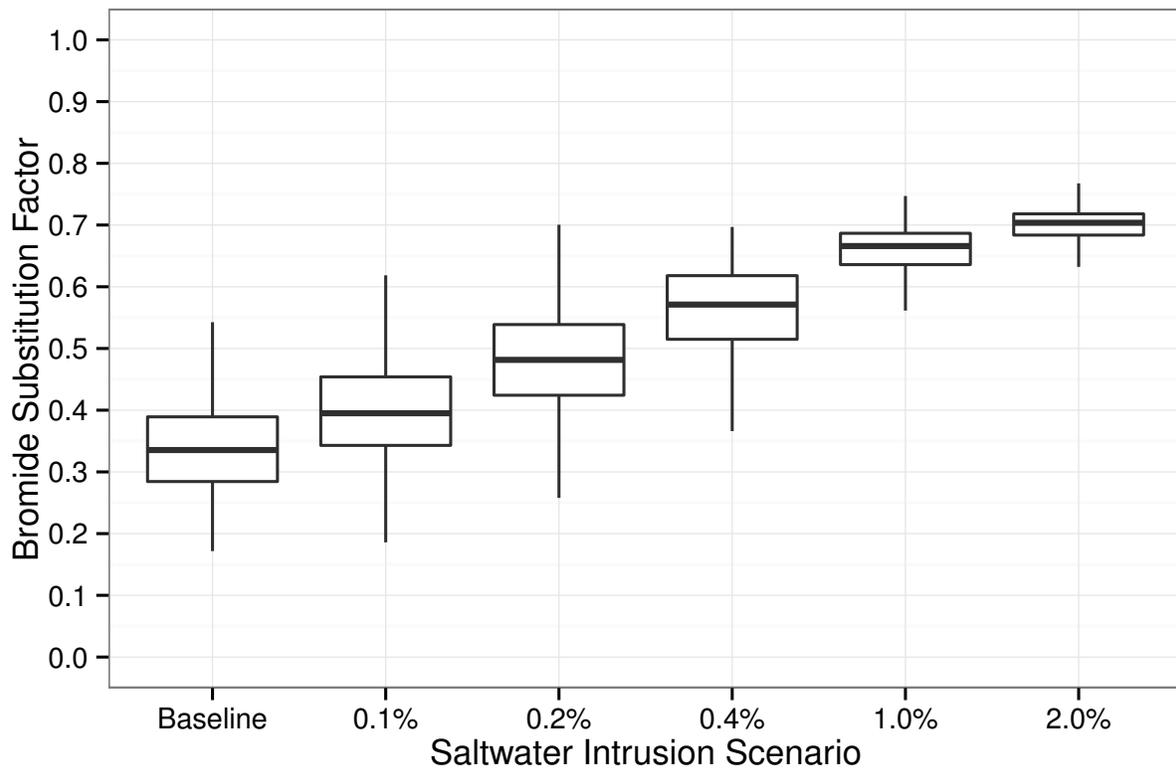


Figure 3.2: Boxplot of the simulated BSF for the baseline scenario and climate change scenarios with no change in temperature; box shows the median with bold black centerline and the 25th and 75th percentiles; bars show the 5th and 95th percentiles.

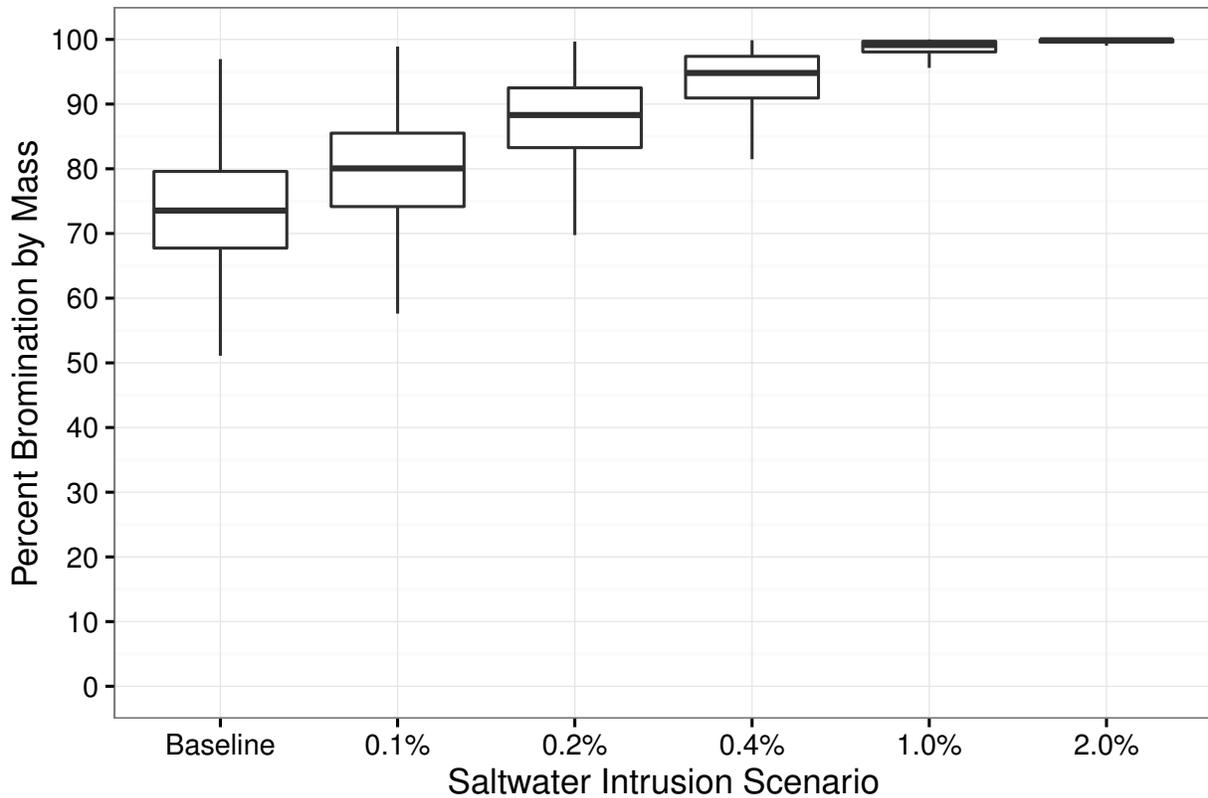


Figure 3.3: Boxplot of the simulated percent bromination by mass for the baseline scenario and climate change scenarios with no change in temperature; box shows the median with bold black centerline and the 25th and 75th percentiles; bars show the 5th and 95th percentiles.

(1 and 2%) result in more than 90% bromination in the finished water THM. These results are consistent with Handke (2009), who found that a source water bromide concentration of $170 \mu\text{g/L}$ from a sample in the Monongahela River led to between 85 and 95% bromination of THM. Similarly, States et al., (2013) found that source water bromide concentrations of 50 and $150 \mu\text{g/L}$ resulted in 62 and 83% bromination, respectively. As BSF and the percent bromination of THMs increases as a result of increased source water bromide, drinking water utilities utilizing affected groundwater sources will need to consider alternative treatment technologies to reduce the risk to consumers.

3.3.3 THM₄ and species risk

Figure 3.4 shows the THM species risk computed from the simulated THM speciation concentrations for the baseline and for each increased bromide scenario with no change in temperature using cancer slope factors. The results for a 2°C temperature change were similar and, thus, are not shown. The cumulative risk is shown on the far right bar in each scenario. The mean simulated risk of the baseline scenario (where mean source water bromide was 52.1 µg/L) is 9.3×10^{-6} , or approximately nine cancer cases per 1 million people exposed. The remaining seawater-mixing scenarios contain simulated samples that exceed one cancer case per 100,000 people exposed. The primary component of risk quickly shifts to dibromochloromethane due to the dominance of the dibromochloromethane concentration in the THM as source water bromide increases, indicating that meeting the regulatory limit for THM₄ may not sufficiently reduce consumer risk. The regulatory framework is built around THM₄ as a surrogate measure for DBP risk, but at high source water bromide concentrations, this surrogate measure may no longer accurately characterize the risk of brominated THMs in the finished water. Thus, these results suggest that utilities will need to consider methods to control bromination rather than just control THM₄, and regulators will need to consider whether THM₄-focused regulations are sufficient to protect drinking water consumers.

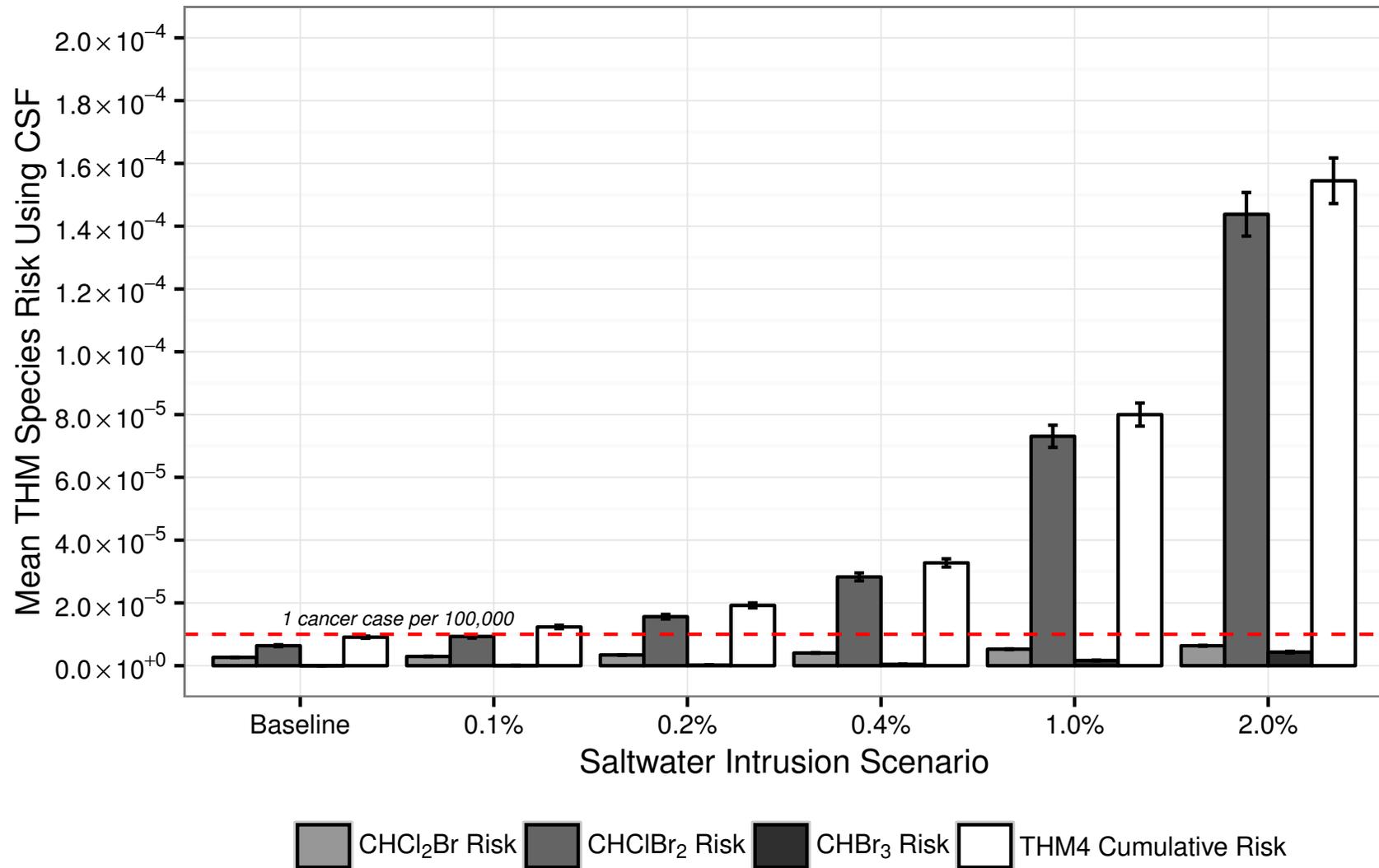


Figure 3.4: Simulated brominated THM species risk for the baseline scenario and climate change scenarios with no change in temperature using the cancer slope factors for the brominated THM species; dashed line shows the threshold of one additional cancer case per 100,000 people exposed.

Figure 3.5 shows the change in THM₄ risk from the baseline scenario computed using odds ratios (Regli et al., 2015). All scenarios are expected to lead to increased THM₄ risk from the baseline scenario of 10⁻⁴ added lifetime risk of bladder cancer. The 95th percentile for the 2% mixing scenario exceeds an added lifetime risk of bladder cancer of 10⁻². Although the increase in THM₄ explored in this analysis exceed those explored by Regli et al., (2015), these results are consistent with their findings. For example, Regli et al., (2015), the results are consistent. For example, Regli et al., (2015) found that a 1 μg/L increase in the THM₄ concentration resulted in an estimated 10⁻⁴ increase in total risk. The present analysis suggests that seawater intrusion of 0.2% leading to source water bromide increase of 21 μg/L would result in an increased bladder cancer risk of between 10⁻⁴ and 10⁻³.

3.3.4 Mixing scenario results

Surface water utilities needing to adapt to changing source water conditions may decide to incorporate groundwater sources. If potential groundwater sources become contaminated due to saltwater intrusion in coastal regions, the potential for increased THM formation and increasing bromination of THMs may continue to pose a risk for surface water utilities trying to meet regulatory levels. This analysis assesses the potential impacts for a typical surface water utility in New Jersey utilizing New Jersey groundwater sources.

Figure 3.6 shows the simulated THM species concentrations for surface water utilities in New Jersey for a baseline case, as well as five scenarios with elevated TOC concentrations. The figure shows that all scenarios result in THM₄ concentrations above 80% of the MCL, but speciation is dominated by chloroform, which is typical for low-bromide surface waters. As TOC concentrations increase, the bromination of the THM₄ does not change, but the chloroform concentration continues to increase.

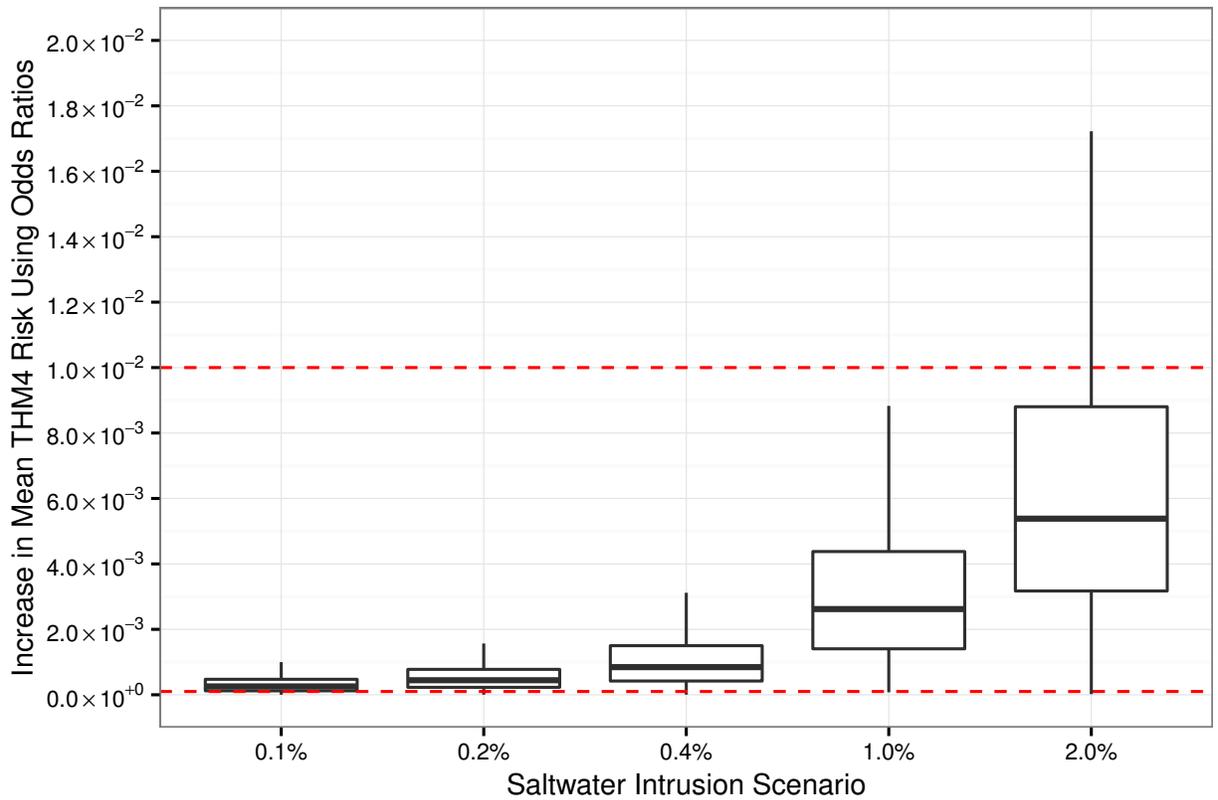


Figure 3.5: Simulated increase in risk of bladder cancer from the baseline scenario THM₄ risk for each saltwater intrusion scenario with no change in temperature using the odds ratio method; dashed lines show the thresholds of 10^{-4} additional lifetime cancer risk and 10^{-2} additional lifetime cancer risk.

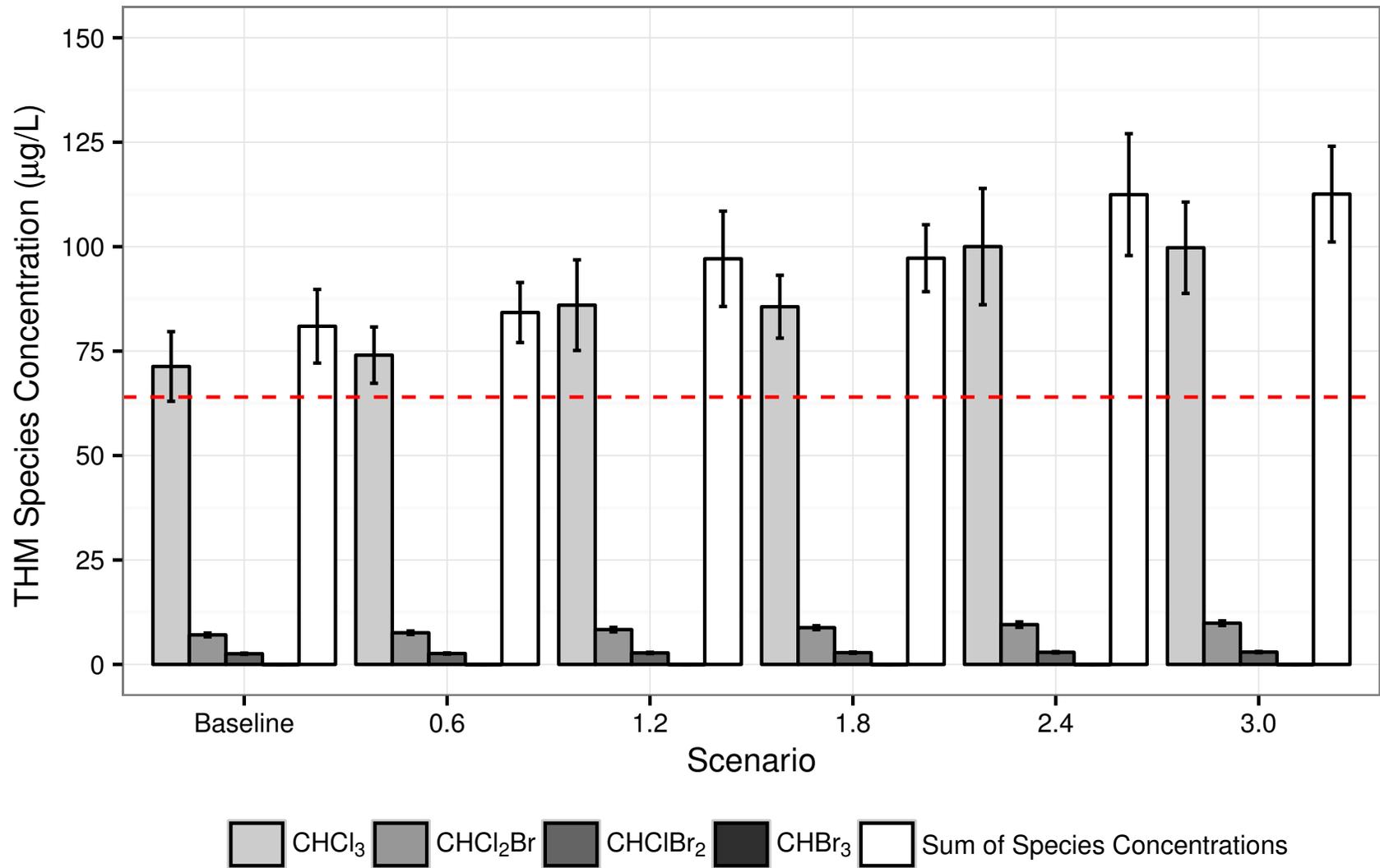


Figure 3.6: Mean THM species concentrations for the baseline surface water and TOC scenarios with no change in temperature; dashed line shows 80% of the maximum contaminant level (MCL) for THM₄.

If the typical surface water utility incorporated groundwater into the treatment process as a means to reduce THM formation, mixing with New Jersey groundwater sources could shift the THM speciation to more brominated forms. Figures 3.7 and 3.8 show the effect on THM formation and speciation for two mixing scenarios. Figure 3.7 shows how the typical surface water would respond to mixing with a high-bromide groundwater, and Figure 3.8 shows how surface water with high TOC would respond to mixing with a high-bromide groundwater. Both figures indicate that mixing source waters could reduce THM₄ formation below the regulatory level, but THM₄ speciation would shift to more brominated forms.

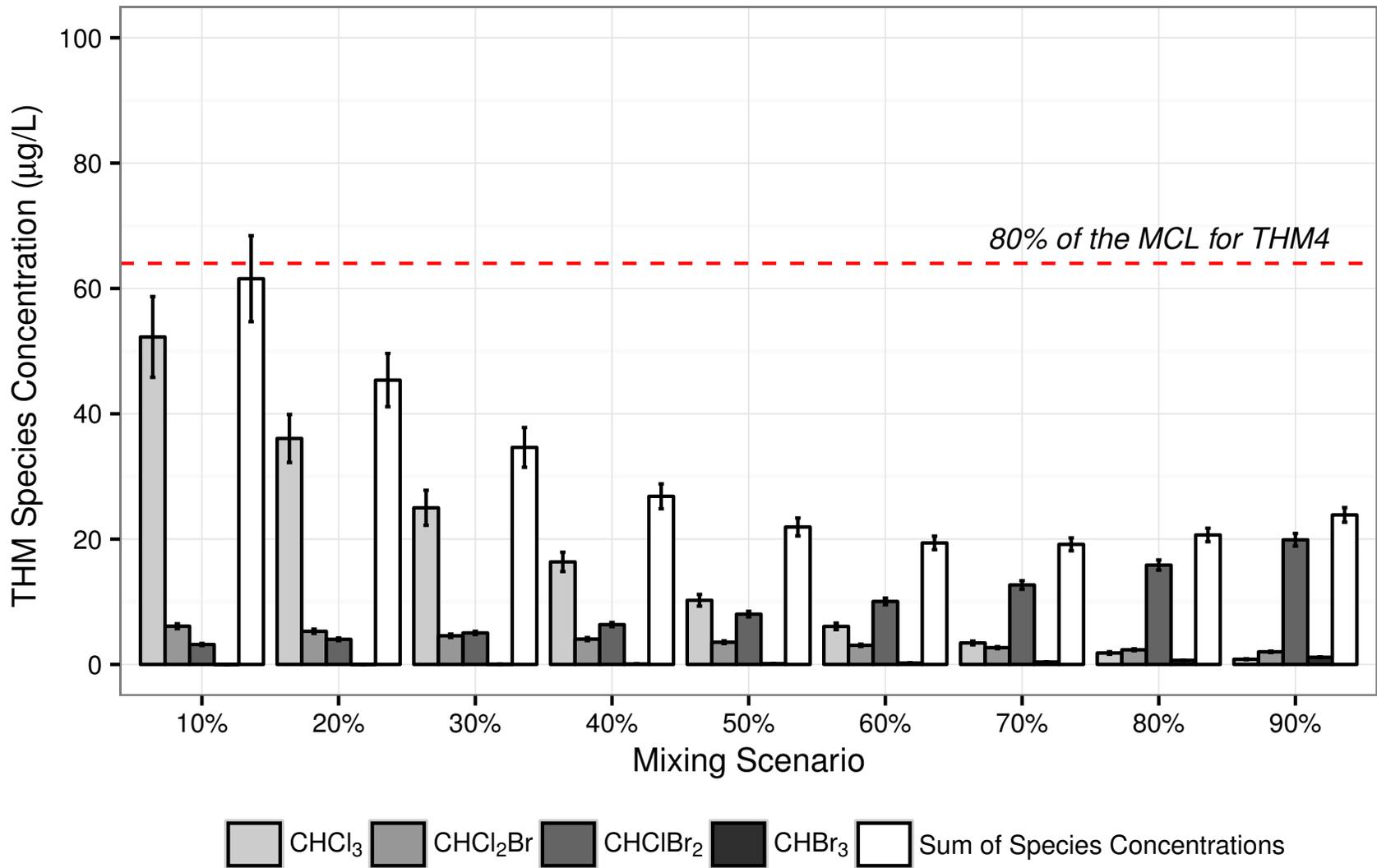


Figure 3.7: Simulated THM species concentrations for the groundwater/surface water mixing scenarios with the baseline surface water and 2% seawater mixing scenario; the mixing scenario describes the fraction of groundwater mixed with the surface water source; dashed line shows 80% of the maximum contaminant level (MCL) for THM₄.

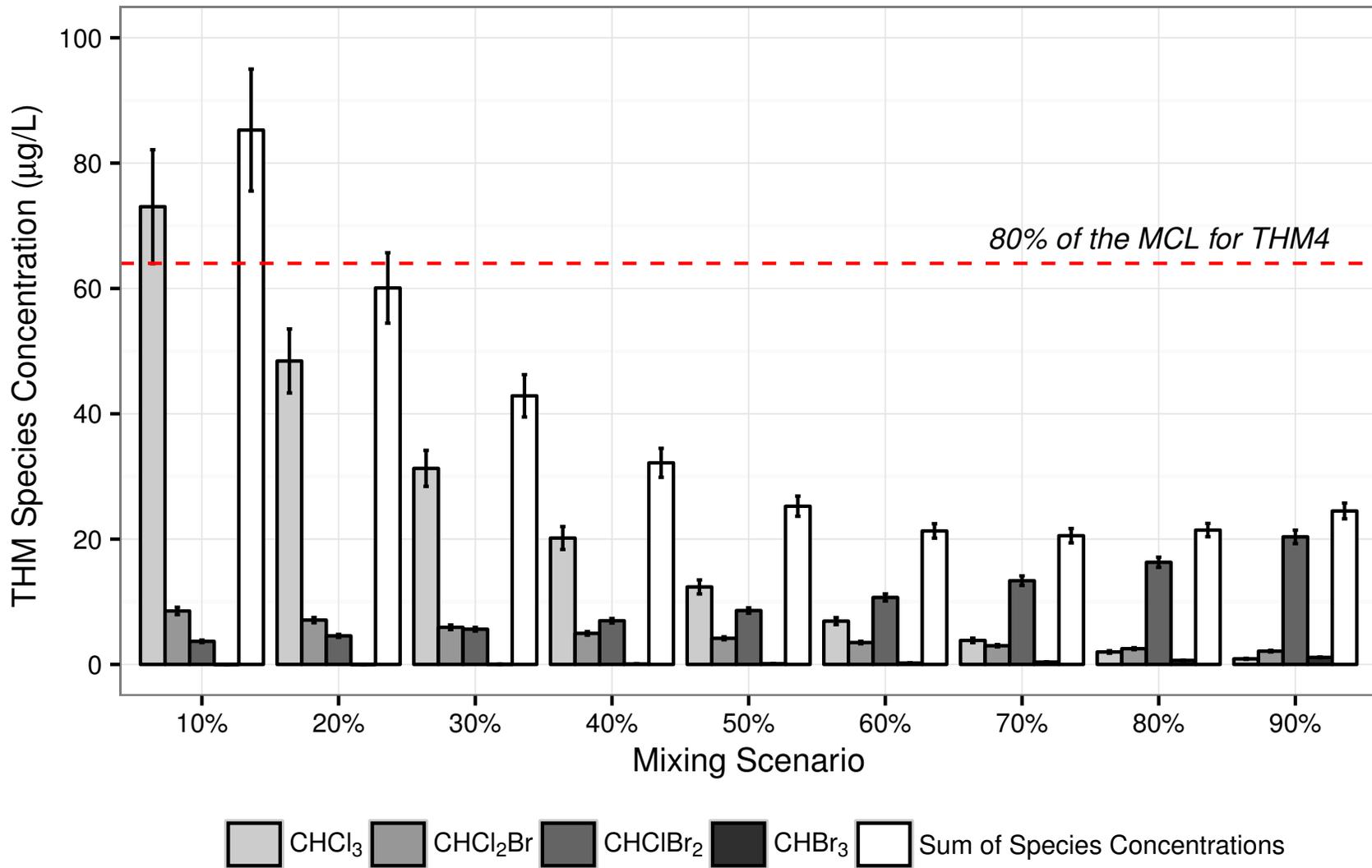


Figure 3.8: Simulated THM species concentrations for the groundwater/ surface water mixing scenarios with the 3 mg/L TOC scenario for surface water and 2% seawater mixing scenario for groundwater; the mixing scenario describes the fraction of groundwater mixed with the surface water source; dashed line shows 80% of the maximum contaminant level (MCL) for THM₄.

The increase in bromination with higher groundwater mixing leads to increased finished water risk. Figures 3.9 and 3.10 show the effects on finished water risk for the two mixing scenarios described above. As a higher proportion of groundwater is used, finished water risk increases. For the baseline surface water scenario, mixing with high source water bromide groundwater will reduce finished water risk for the 30 and 40% groundwater mixing scenarios, but the cumulative risk remains above an excess cancer risk of 1 in 100,000 in all cases. Similarly, in source waters with high TOC, mixing with high-bromide groundwater leads to a mean cumulative THM risk above the threshold for all mixing scenarios, as shown in Figure 3.10. In both scenarios, mixing surface waters with 30-40% ground water will reduce risk but not below desired threshold values. Mixing with higher percentages of groundwater, or with groundwater that is elevated in bromide due to sea level rise, will increase the risk associated with brominated DBP formation.

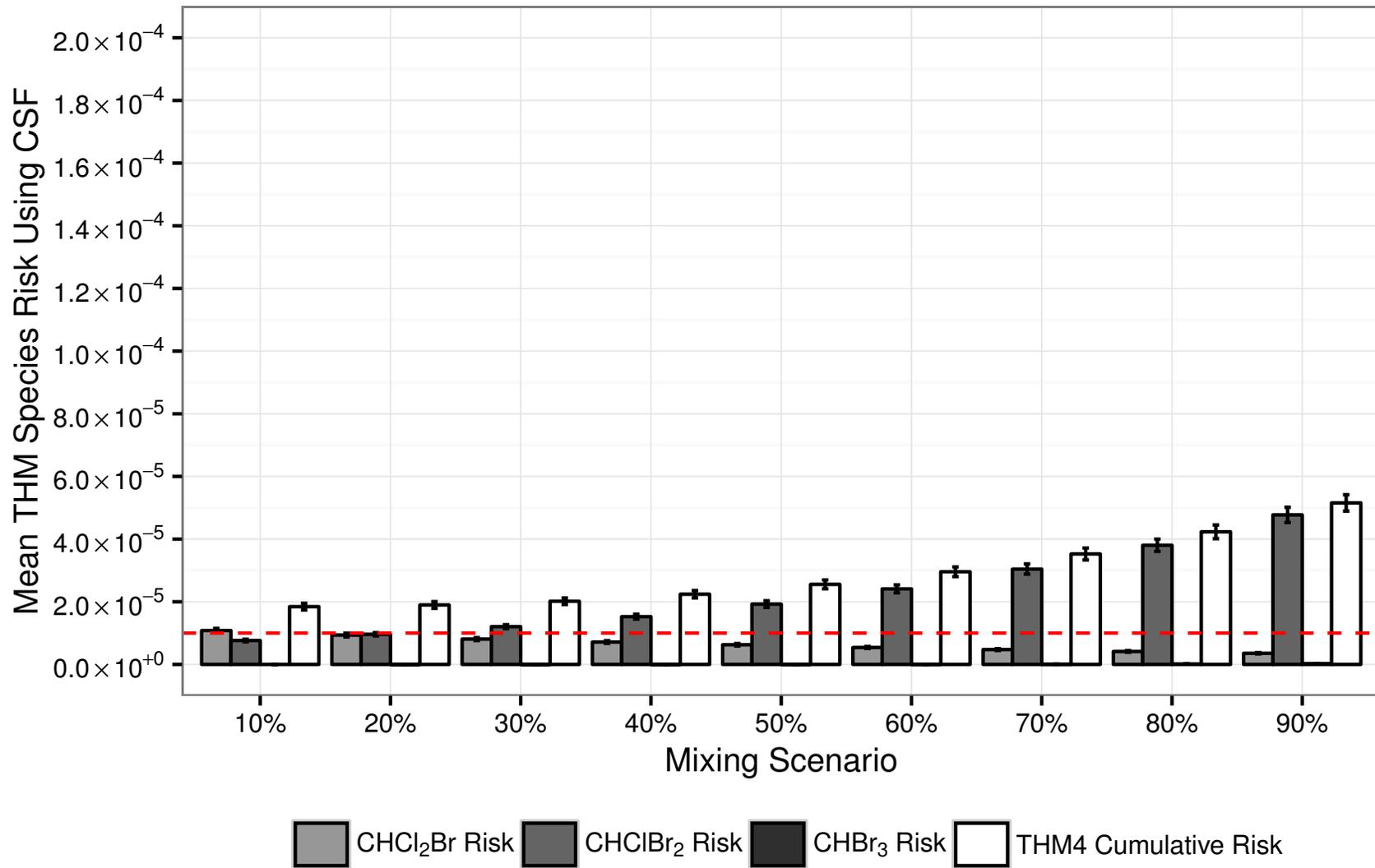


Figure 3.9: Simulated brominated THM species risk using cancer slope factors for the groundwater/surface water mixing scenarios with the baseline surface water and 2% seawater mixing scenario; the mixing scenario describes the fraction of groundwater mixed with the surface water source; dashed line shows the threshold of one additional cancer case per 100,000 people exposed.

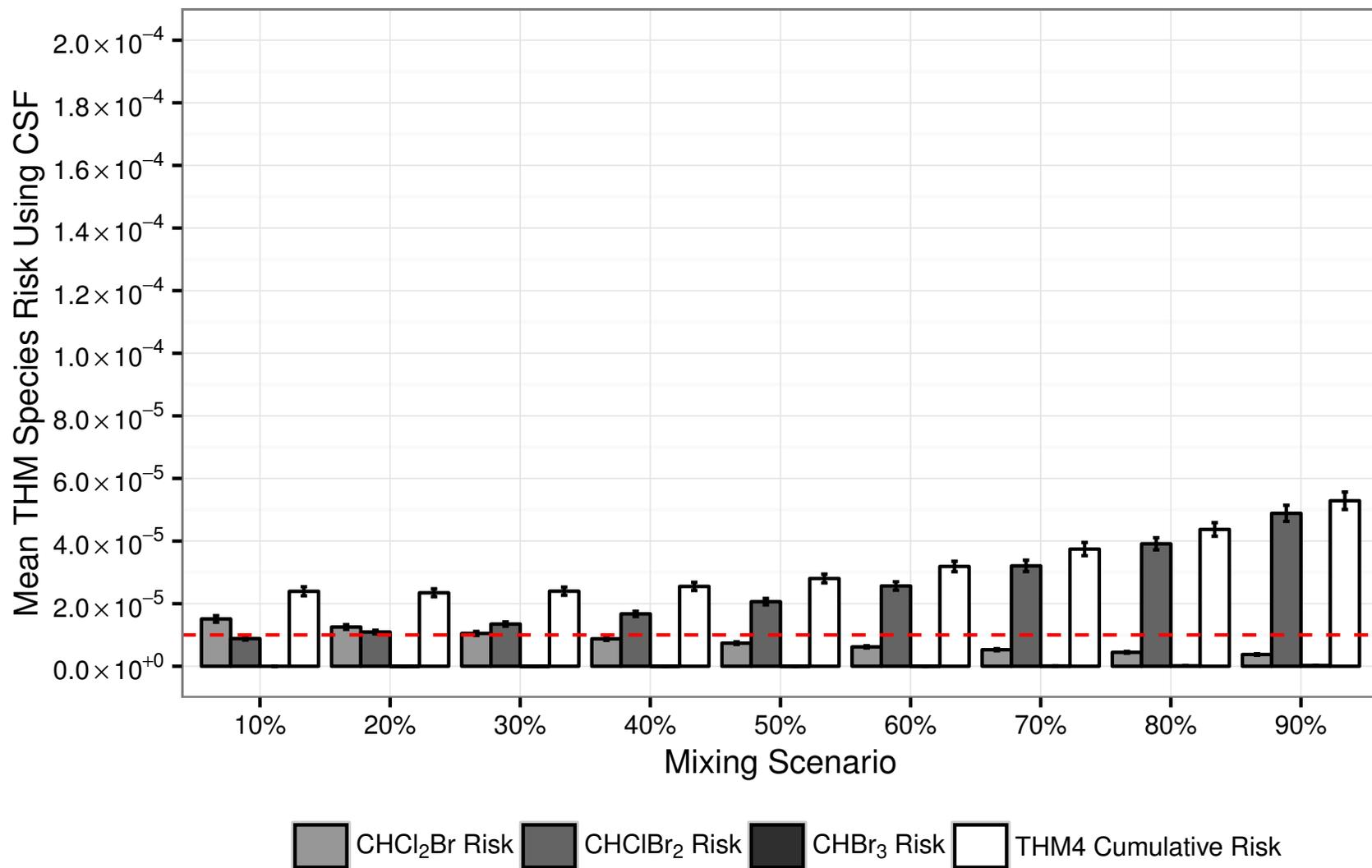


Figure 3.10: Simulated brominated THM species risk for the groundwater/ surface water mixing scenarios with the 3 mg=L TOC scenario for surface water and 2% seawater mixing scenario for groundwater; the mixing scenario describes the fraction of groundwater mixed with the surface water source; dashed line shows the threshold of one additional cancer case per 100,000 people exposed.

3.4 Conclusions

The present analysis assessed the impact of climate change-induced increases in source water bromide concentrations and temperature as a result of saltwater intrusion for a coastal aquifer in New Jersey. Monte Carlo techniques were used to capture uncertainties in source water quality parameters, which were then incorporated into DBP statistical models for THM₄ species concentrations to evaluate finished water quality. The BSF and percent bromination by mass were calculated to determine the relative contribution of brominated THMs. Intrusion of ocean water into coastal aquifers due to sea level rise is expected to increase bromide in source waters for utilities using estuaries and coastal groundwater. Although this problem depends on the specific geology of the location, many regions have experienced saltwater intrusion (Motz et al., 2014; Chen et al., 2010; Barlow and Reichard, 2010; DRBC, 2008), and other analyses suggest sea level rise could result in increased saltwater intrusion in many regions (Sawyer et al., 2016; Badaruddin et al., 2015). In coastal areas with high groundwater utilization, saltwater intrusion could be exacerbated by groundwater withdrawal rates. The present work indicates even small changes in saltwater intrusion can have significant effects on finished water THM₄ and the extent of bromination in the THM. Despite finished water THM₄ concentrations remaining, for the most part, below the regulatory limit of 80 $\mu\text{g}/\text{L}$, increased bromination of the THM could increase the risk to consumers above an acceptable threshold. Drinking water utilities using coastal groundwater or estuaries should consider the long-term potential impacts of saltwater intrusion as a result of rising sea levels on treatability of source water. As a result of climate change, coastal utilities may need to consider long-term capital investments to improve their capacity to handle high-bromide source waters. Additionally, extra consideration should be taken for surface water utilities considering mixing with groundwater sources as elevated source water bromide could pose additional challenges for health risk, despite meeting regulatory requirements for THM.

Acknowledgments

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Chapter 4

Estimated coal-fired power plant bromide contributions to disinfection by-product risk in the Monongahela River Basin¹

¹Kolb, C., Good, K. D., and VanBriesen, J. M. (2018). "Estimated coal-fired power plant bromide contributions to disinfection byproduct risk in the Monongahela River Basin." *In preparation*.

Abstract

Increasing source water bromide concentrations are a problem for drinking water utilities where bromide contributes to the formation of toxic and carcinogenic disinfection byproducts (DBPs). The present work evaluates the role of coal-fired power plant wet flue-gas desulfurization (FGD)-associated bromide loads on in-stream bromide concentration changes in the Monongahela River Basin in Water Year 1998 (during a nation-wide study) and over a five year period from Water Years 2013 through 2017 and estimates the associated drinking water DBP risk at an intake downstream of these discharges. Bromide concentration contributions from power plants in the Monongahela River represent a significant portion of observed bromide concentrations at the modeled drinking water intake. Under mean flow conditions, power plants operating wet-FDG represent 45-70% of the median daily observed bromide concentration in the river near the modeled intake for the period of interest. Seasonal concentration effects are observed due to changes in the dilution capacity of the river. During low flow months (e.g., September), bromide concentration contributions increase (with assumed stable loads). The effect of elevated bromide concentrations on bromine incorporation into DBPs and DBP-associated risk are estimated for the modeled drinking water utility. Power plant-associated bromide loads lead to increased bromine incorporation into trihalomethanes (THM) and elevated THM-associated risk, particularly during low-flow conditions. Flow-weighted bromide concentration monitoring of wet FGD wastewater discharges, as well as routine monitoring at drinking water intake locations, will improve estimates of the effect of power plant bromide concentration contributions on drinking water sources, DBP speciation, and associated risk.

4.1 Introduction

Anthropogenic bromide loads entering surface waters can increase bromide concentrations at drinking water intakes. Elevated bromide in water subject to disinfection increases the rate and extent of formation of disinfection by products (DBPs) (Heeb et al., 2014; Westerhoff et al., 2004), which have been associated with increased cancer and birth defects in epidemiological studies (Kogevinas and Villanueva, 2011; Salas et al., 2013; Villanueva et al., 2007, 2015). Brominated DBPs, which form only when bromide is present, are more toxic than their chlorinated analogs (Cortes and Marcos, 2018; Sawade et al., 2016; Yang et al., 2014), and regions with elevated source water bromide report stronger correlations of measured DBPs with negative health outcomes (Chisholm et al., 2008; Nieuwenhuijsen et al., 2009; Villanueva et al., 2007). Thus, the presence of bromide in source waters, which increases the formation of brominated DBPs, also increases the risk associated with the use of chlorinated drinking water (Hong et al., 2007; Regli et al., 2015).

Naturally-occurring surface water bromide concentrations are generally quite low (Bowen, 1976, 1979); however, anthropogenic loads can cause significant increases (Soltermann et al., 2016). Fossil-fuel associated wastewaters are elevated in salts, including bromide (Ferrar et al., 2013; Wilson and VanBriesen, 2012), and the discharge of these wastewaters has been reported to increase bromide at drinking water intakes (Landis et al., 2016; Wilson and VanBriesen, 2013), especially when river flow conditions result in insufficient dilution (Weaver et al., 2016; Wilson and VanBriesen, 2013).

In Southwestern Pennsylvania, elevated bromide concentrations have been reported (Handke, 2009; States et al., 2013; Wilson and VanBriesen, 2013). Initial reports implicated oil and gas produced water treatment facilities (Hladik et al., 2014; States et al., 2013) that were accepting increased volumes of bromide-containing wastewater associated with shale gas development. In response to these reports, the Pennsylvania Department of Environmental

Protection (PADEP) called for oil and gas production companies to voluntarily cease sending shale gas-associated produced water to surface discharging plants in mid-2011 (Kraner, 2011). Despite the elimination of these discharges in the Monongahela River, bromide concentrations remained elevated compared with background levels in the region, especially under low flow conditions, suggesting additional bromide loads (Wilson and VanBriesen, 2013). Recently, discharges from coal-fired power plants operating wet flue-gas desulfurization (FGD) have been linked to elevated source water bromide in the region (Good and VanBriesen, 2016, 2017). The effects of these changing source water bromide concentrations on DBPs in finished drinking water in Southwestern Pennsylvania has been reported by multiple researchers (Cadwallader and VanBriesen, 2018; States et al., 2013; Wang et al., 2017; Weaver et al., 2016). However, prior work has not explicitly considered the contribution of these increased bromide loads to risk for affected drinking water system consumers.

The present work evaluates the role of power plant FGD-associated bromide loads on in-stream bromide concentration changes in the Monongahela River over a five year period (October 2012-September 2017, or U.S. Geological Survey Water Years 2013 through 2017) after oil and gas produced water discharges were reduced. Water Year 1998 is also considered for comparison, when wet FGD-associated wastewater discharges were much lower. Concentration contributions for each power plant are modeled and the sum is compared with observed in-stream concentrations in the Lower Monongahela River near Elizabeth, PA. The effect of these concentrations on drinking water DBP bromine incorporation and associated risk are estimated.

4.2 Materials and Methods

4.2.1 Study area: Monongahela River Basin

The Monongahela River is 206 km (128 miles) in length, flowing north from the Tygart Valley River, West Virginia, into Pennsylvania where its confluence with the Allegheny River in Pittsburgh, PA forms the Ohio River. The Monongahela River Basin is 19,010 square kilometers (7,340 square miles) and has a mean annual discharge of 359 m³/sec at river kilometer 18 (mile 11; USGS gage 03085000) for the period of record (WY1939 to WY2017). Figure 4.1 shows the geographic extent of the basin, the locations of power plants operating wet FGD, the locations of oil and gas produced water centralized waste treatment (CWT) facilities, bromide sampling locations, and USGS gage stations. The present work focuses on modeling bromide concentration at a single drinking water intake, located approximately 40 km (25 miles) upstream from the confluence in Pittsburgh. This site was selected due to multiple sources of bromide sampling data from this region of the river; Figure 4.1B shows the locations of the sampling sites. The United States Geological Survey (USGS) gage at Elizabeth, PA (USGS03075070) at river kilometer 39 (mile 24) is just downstream of the intake location and just upstream of the river sampling sites.

There are five coal power plants that have operated wet FGD treatment systems upstream of the drinking water intake during the period of interest (WY1998, WY2013-WY2017) (see Figure 4.1, Table B.1). First Energy Mitchell Power Station in Union, PA (river km 47) and Hatfields Ferry Power Station in Masontown, PA (river km 127) were retired in October 2013 (EIA, 2018a). First Energy Fort Martin Power Station in Maidsville, WV (river km 148), Longview Power in Maidsville, WV (discharges to Dunkard Creek, confluence at Monongahela River km 149), and First Energy Harrison Power Station in Haywood, WV (discharges to West Fork River, confluence with Tygart River forms Monongahela River) continue in operation. Additional coal-fired power plants have operated in the past in the

region, including Elrama Power Plant, which operated wet FGD and retired in 2012, but these discharges were downstream of the bromide sampling sites, thus are not relevant to the analysis period. The power plants discharge through National Pollution Discharge Elimination System (NPDES) permits into the Monongahela River or its tributaries. Locations of these discharges were acquired from the United States Environmental Protection Agency (USEPA) Effluent Limitation Guidelines Questionnaire (USEPA, 2013).

Although bromide source apportionment is out of the scope of the present analysis, considering the previously documented impacts of oil and gas wastewater on bromide levels in the region, facilities accepting conventional and unconventional oil and gas wastewater in Pennsylvania and West Virginia were identified. To do this, current waste facilities as reported by the PADEP oil and gas reporting website (PADEP, 2018a) were mapped in ArcGIS (Esri, 2016); a spatial join was used to identify the facilities located in the Monongahela Basin, including centralized waste treatment facilities (CWTs) and publicly owned treatment works (POTWs). Since the focus is on identifying potential surface water point bromide discharges, other waste disposal methods such as deep well injection and road spreading were not considered. PADEP oil and gas waste reports for year 2013 were also reviewed to ensure that the 2017 list reflects the facilities operating over the study period (PADEP, 2018a). The West Virginia Department of Environmental Protection (WVDEP) does not provide similar reports online, so WVDEP was contacted directly to obtain information regarding facilities accepting oil and gas wastewater (Patel, 2018). The relevant facilities are shown in Figure 4.1 and details are provided in Table B.2.

4.2.2 Data sources and statistical analysis

The present analysis evaluates bromide loads and predicted concentration contributions from power plants for Water Year 1998 (October 1997 - September 1998) and Water Year 2013 (October 2012 - September 2013) through Water Year 2017 (October 2016 - September 2017).

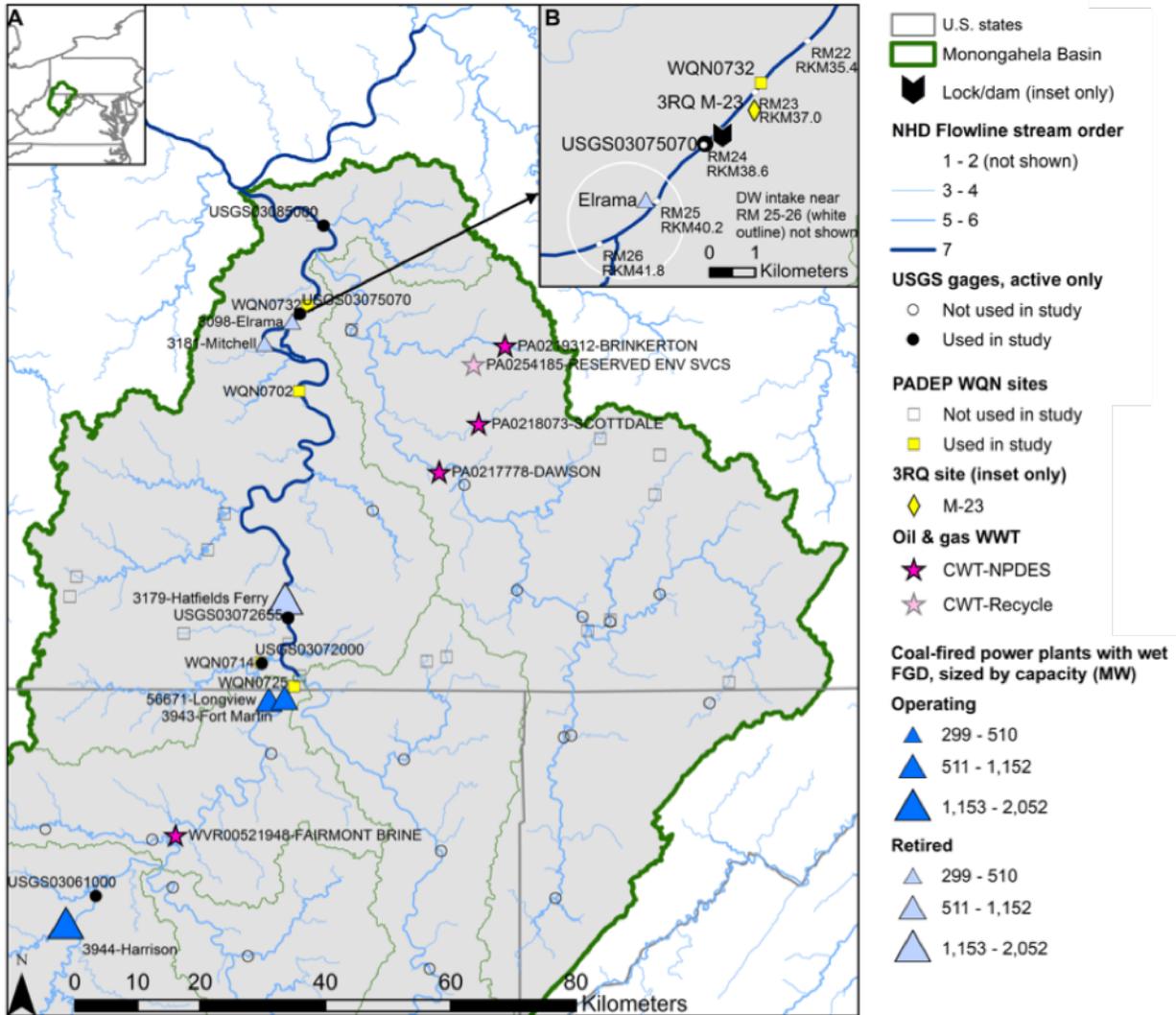


Figure 4.1: Map of the Monongahela River Basin. WQN bromide sampling locations are shown as squares (NWQMC, 2018), and the relevant 3RQ bromide sampling location is shown as a diamond (inset only). USGS gage locations are shown as circles (USGS, 2018c). Coal-fired power plants operating wet FGD are shown as blue triangles (EIA, 2018a); darker indicates active and lighter indicates retired during the modeling period. Inset A shows the location of the basin within the context of the mid Atlantic United States. Inset B shows a more detailed map of the model site. The drinking water intake location (DWTP; within the light circle) is near river kilometers 40-42 (miles 25-26).

This period was selected to compare historical power plant discharges in WY1998 (when few plants were operating wet FGD and bromide concentrations were lower) to more recent power plant discharges following the request for reductions in oil and gas wastewater discharges that were previously identified as causing bromide effects in the Monongahela River between 2009 and 2012 (Wilson and VanBriesen, 2013). Daily water discharge data were retrieved for the gages shown in Figure 4.1 for the period of record (WY1934 to WY2017) (USGS, 2018b). Summary statistics for USGS gage 03075070 are provided in Table B.3, for the period of record, and for each Water Year included in the analysis.

The PADEP operates a statewide sampling network designed to assess water quality (Water Quality Network, WQN) (PADEP, 2018b) with many sites at or near USGS gages. Physical and chemical analyses (including bromide) are conducted on a bimonthly basis. These data are available via the Water Quality Portal (WQP), a data repository maintained by the USGS, the Environmental Protection Agency (EPA), and the National Water Quality Monitoring Council (NWQMC) (NWQMC, 2018). Site WQN0732 is located at Elizabeth, PA, approximately river kilometer 37 (mile 23; see Figure 4.1B) (NWQMC, 2018). Grab sample data for bromide, collected at the Route 51 bridge, downstream of Lock and Dam Number 3, are available at this site from October 2010 to March 2017. The minimum reporting level was 50 $\mu\text{g/L}$ before February 2013 and 25 $\mu\text{g/L}$ after, evaluated using EPA method 300.1 (PADEP, 2018b).

The West Virginia University (WVU) Water Research Institute launched a water quality monitoring and reporting program, Three Rivers Quest (3RQ), in 2009, which involves sampling along the Monongahela, Allegheny, and Ohio Rivers (3RQ, 2017). 3RQ site M-23 is located at river kilometer 37 (mile 23; see Figure 4.1B). Samples were collected at various intervals between July 2009 and September 2017 and processed in a WVU laboratory using EPA method 300.0; the minimum reporting level was 20 $\mu\text{g/L}$ (3RQ 2018). For the present

analysis, these data were acquired manually from the display website (3RQ 2017). Six unusually high values were questioned, and 3RQ corrected three of these values (3RQ, 2018). One unusually high value remained in the subset of data for the Water Years of interest (occurring in October 2012). This value, while unusually high compared with other regional data from the same time period, was not removed from the data set for analysis as 3RQ confirmed its validity.

Additional bromide samples were taken by water treatment plant operators at a drinking water facility located near river kilometer 40 (mile 25; see Figure 4.1B). Samples were collected monthly by plant personnel and analyzed using EPA method 300.1 by the utility's certified laboratory; the minimum reporting level was 20 $\mu\text{g}/\text{L}$. These data were provided by the utility (DWTP, 2017).

Due to the presence of below detection data, summary statistics were computed using regression on order statistics (ROS). ROS is a robust, semi-parametric method used to estimate summary statistics from data with censored values (Helsel, 2005; Shumway et al., 2002). The method is described in detail in prior publications (Francis et al., 2009; Kolb et al., 2017). For visualization purposes, below detection data were imputed from a truncated lognormal distribution using ROS-derived summary statistics and are shown as open symbols in presented figures. Additional statistics were computed based on alternative methods for handling below detection limit data (e.g., replacing below detection data with zero or a value set at the detection limit or at half the detection limit) for comparison. To compare in-river bromide datasets, nonparametric Mann-Whitney tests were used. Results indicate that monitoring locations are not statistically significantly different (Table B.4). All statistical analyses were performed in the R computing language using the NADA package (Lee, 2015) and EnvStats package (Millard, 2018). Summary statistics for each dataset are provided in Table B.5, and Figure B.1 shows the flow and bromide data over time.

Source water bromide data were also extracted from the EPA Information Collection Rule (ICR) database (USEPA, 2000). The ICR database represents a nationwide sampling effort at drinking water plants from July 1997 to December 1998. Bromide samples were collected monthly from plant intakes with a detection limit of 20 $\mu\text{g}/\text{L}$. Two drinking water intake locations on the Monongahela River were reported in the ICR: one located at the model site and one downstream of the model site. The present study incorporates data from the modeled intake location.

The observed in-stream bromide concentrations were compared to modeled concentrations to evaluate the relative contribution of wet FGD associated bromide discharges to concentrations observed in the river near the modeled drinking water intake.

4.2.3 Modeling effects of bromide discharges

The goal of the present analysis was to estimate the extent of bromine incorporation in trihalomethanes (THMs), a dominant class of DBPs, and to estimate associated drinking water risk resulting from wet FGD power plant discharges of bromide upstream of a drinking water intake. To model these effects, several data sources and modeling techniques are used. Figure 4.2 outlines the structure of the model and the flow of data source incorporated into each modeling component. Each of the modeling components - bromide load (Panel A), bromide concentration contribution (Panel B), and THM formation and risk (Panel C) - and the data sources used are discussed in greater detail in the subsequent sections.

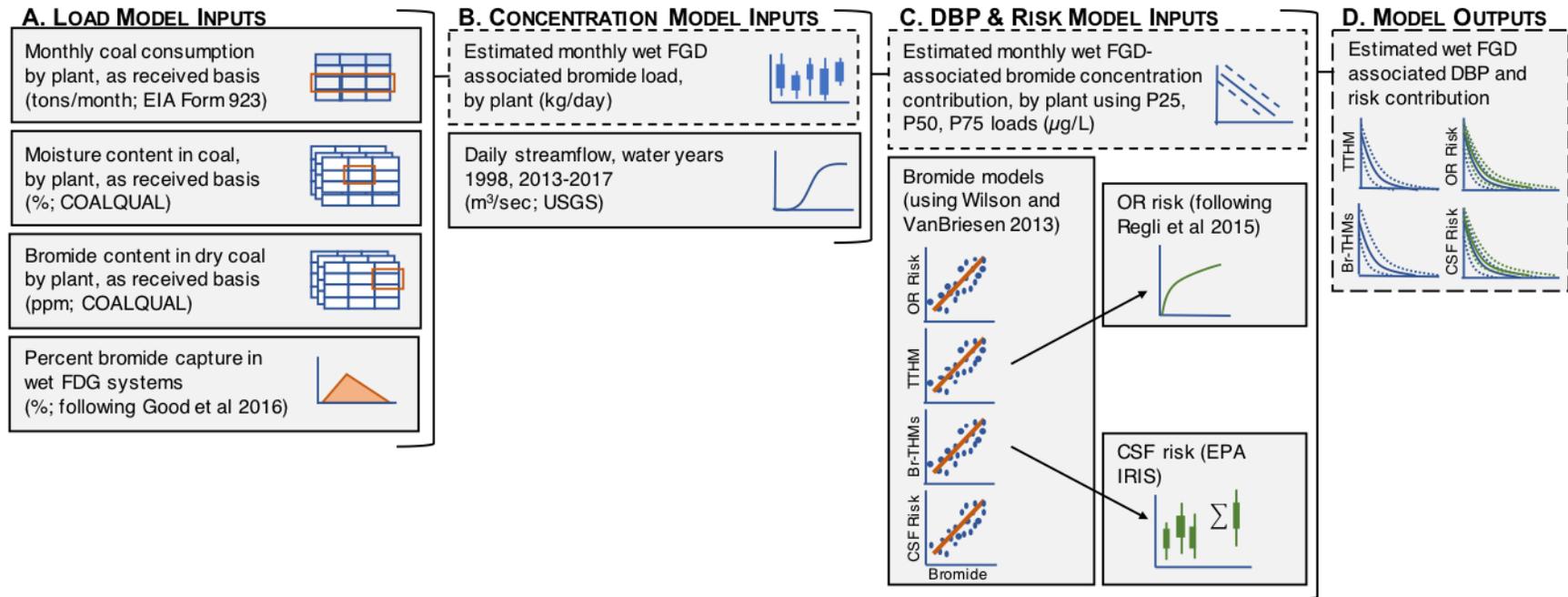


Figure 4.2: Schematic of model components and the associated data flows between components for the wet FGD power plant analysis. The short dashed framing represents intermediate model outputs and the long dash framing represents the final model output.

Estimating bromide loads from coal-fired power plants

Bromide loads discharged by power plants could be estimated with information about the concentration and flow rate of wastewater discharges. However, wastewaters at power plants are rarely monitored for their concentration of bromide. While observed bromide concentrations for wet FGD wastewaters have been reported for some facilities (EPRI, 2004, 2007; USEPA, 2013), these are not associated with flow measurements and thus cannot be used to estimate loads. Further, bromide loads are expected to vary dependent on the source coal burned at a power plant, and thus, observations for wet FGD bromide concentrations show significant variability (EPRI, 2004, 2007).

In the absence of direct monitoring data for specific power plants FGD discharges, Good and VanBriesen (2016, 2017, 2018) developed a method to estimate coal-fired power plant bromide loads using information on coal use (e.g., type and consumption rate). The present work takes this generalized approach and adapts it for individual power plants by linking coal use at each plant to county-level coal bromide data.

The U.S. Energy Information Administration (EIA) provides data for coal consumption and deliveries on a monthly basis for each power plant on Form 923 (EIA923) (EIA, 2018b). Quantity and coal source data were extracted for calendar years 2012 to 2017 for each power plant operating wet FGD systems in the region: Mitchell (EIA ID 3948), Hatfields Ferry (3179), Longview (56671), Harrison (3944), and Fort Martin (3943). Similar data were extracted for calendar years 1997 and 1998 from EIA Form 423, which predates Form 923, to estimate historical bromide load contributions when fewer power plants were operating wet FGD systems.

Consumption data do not include information on the bromide and moisture content specific to the coal being consumed; coal delivery information, however, identifies the county

from which the coal delivery originated and the type and quantity of coal delivered. The United States Geological Survey (USGS) maintains a database of county-level coal quality (COALQUAL) from mines across the United States (USGS, 2018a), which includes information on bromide and moisture content. For each delivery of coal to each plant, rather than using the moisture content and bromide associated with that general coal rank (as in Good and VanBriesen, 2018), data specific to the county of origin for each coal delivery was extracted from COALQUAL. A mass-weighted moisture content and bromide concentration were derived based on the delivery origin information for each month and power plant. When multiple samples in the COALQUAL database were from the same county, equal weight was assigned to each sample. For cases in which COALQUAL data were unavailable (two counties in West Virginia), bromide and moisture data were sampled from the other counties from which the plant received coal. Bromide and moisture content were sampled using a weighted bootstrap such that the counties from which the most coal was delivered for a particular plant would be sampled more frequently than a county with less coal delivered. Bromide capture in wet FGD associated wastewater was modeled from a triangular distribution (min = 77%, most likely = 84%, and max = 100%) following Good and VanBriesen (2016); this incorporates the bromide capture in flue gas and the capture from the flue gas into the FGD wastewater. A summary of these modeling components is shown in Figure 4.2A. For each month, 1000 simulations were carried out for each plant and the total monthly bromide load arriving at the modeled intake location was calculated as the sum of plant-specific discharges to the river. Monthly coal delivery, consumption, and stock information for each plant is provided in Figure B.2. Total coal deliveries and bromide content by county origin are shown in Figure B.3, which demonstrates the variability in bromide content by county (most coal delivered to these plants was the same rank - bituminous). Table B.6 shows the subrank of bituminous samples from each county.

Estimating bromide loads from oil and gas produced water facilities

For the four CWTs with NPDES permits that accept oil and gas wastewater in the Monongahela Basin (shown in Table B.2) discharge monitoring data were reviewed in order to estimate current and potential maximum bromide loads. For the three facilities located in Pennsylvania, these data were obtained through the publicly available PADEP electronic discharge monitoring report (DMR) website (PADEP, 2018a). For the facility located in WV, DMR data were obtained directly from WVDEP (Patel, 2018).

Two of the four CWTs (NPDES PA0218073-Scottdale and WV0116408-Fairmont Brine) reported bromide concentrations; bromide loads were estimated directly using the reported flows (Tables B.7 and B.8). Total dissolved solids (TDS) concentrations were also reported for Scottdale, and Br/TDS ratios were calculated for each reporting month. The mean Br/TDS from Scottdale for all data (0.014) was then applied to the other two PA CWTs (NPDES PA0217778-Dawson, NPDES PA0219312-Brinkerton), which reported TDS concentrations but not bromide concentrations (Tables B.9 and B.10). Bromide loads were then estimated for Dawson and Brinkerton using TDS-derived estimated bromide concentrations (product of the reported TDS and assumed Br/TDS) and reported flows. The Scottdale Br/TDS values were consistent with previously reported Br/TDS for CWTs treating oil and gas wastewater (Wilson et al., 2014).

According to the DMR data, none of the four CWTs have reached their permitted maximum daily flow. Thus, for each facility, an upper bound bromide load was estimated using the maximum permitted flow and the median of the maximum daily reported (or estimated) bromide concentration. For the facilities reporting only TDS, this would be the average value of estimated bromide concentration derived from the Br/TDS ratio and reported TDS concentration.

Estimating bromide concentration contributions

Because bromide is non-reactive under typical environmental conditions, the dilution capacity of the receiving water body controls the concentration contribution of anthropogenic loads. Estimating the bromide load at the power plant discharge point enables prediction of the bromide concentration contribution from individual power plants at any downstream drinking water intake location using information about river flow conditions (Good and Van-Briesen, 2017).

As noted above, the total monthly bromide load from coal-fired power plants in the basin was determined by summing the estimated individual power plant bromide loads for every month in the target time periods (Water Years 1998 and 2013 through 2017). The distribution of these values represents total anthropogenic power plant-associated bromide loads to the watershed upstream of the modeled drinking water intake. Bromide concentrations at the intake were estimated using the median and 25th and 75th percentile load estimates over the range of flow conditions for each Water Year at the USGS gage closest to the intake. A summary of how the bromide load estimates are used to predict concentrations is shown in Figure 4.2B. Concentration distributions were predicted on a monthly and Water Year basis in the simulation period using the median estimated load and the range of flow conditions in that month or Water Year.

Estimating THM and risk associated with coal power plant bromide loads

Predicting DBPs in drinking water is difficult due to the many factors that affect DBP formation, including source water conditions (e.g. temperature, pH, bromide and total organic carbon (TOC) concentrations) and plant operational conditions (e.g. disinfectant type and dose). Many models to predict DBPs have been developed using survey data or plant-specific data (Chowdhury et al., 2009; Ged et al., 2015; Sadiq and Rodriguez, 2004). These models capture the widely observed relationship between higher source water bromide concentra-

tions and increased bromine incorporation in DBPs, focusing primarily on trihalomethanes (THMs). Total THMs (TTHMs) are a regulated class of DBPs defined as the sum of four individual THM species: chloroform (CHCl_3), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (CHBr_3). The net effect on TTHM of elevated source water bromide is typically higher TTHM on a molar and a mass-basis (Bond et al., 2014; Symons et al., 1993). Increased bromine incorporation in unregulated DBPs is also observed from elevated source water bromide (Krasner et al., 2006; Pan and Zhang, 2013; Zhai et al., 2014). Despite this general understanding, most TTHM models were developed based on datasets that focus on THM formation in low bromide, moderate TOC water under chlorination conditions, since these are the dominant characteristics of large drinking water utilities in the United States (Krasner et al., 1989; McGuire et al., 2002). The applicability of these TTHM models to other conditions is generally poor, particularly with respect to assessing the role of bromide (Ged et al., 2015). In addition, few DBP models predict individual THM species, which show the most significant response to increasing bromide concentrations. Risk assessments based on TTHM (such as those used during the Disinfectants/Disinfection Byproducts (D/DBP) rule (USEPA, 2010)) can be applied to modeled TTHM; however, they may under-estimate risk changes associated within increased bromine incorporation caused by source water bromide changes (Cadwallader and VanBriesen, 2018; Francis et al., 2010; Kolb et al., 2017).

Regli et al. (2015) estimated the effect of source water bromide increases on risk estimates based on odds ratios (ORs), following the method described in the D/DBP rule (USEPA, 2010) and summarized in Equation 4.1, where r represents the risk associated with the TTHM concentration of concern. ORs are used to compare the relative odds of negative health outcome for an exposed population compared to a population with little to no exposure. For the present analysis, ORs are used to compare the effect of additional TTHM exposure resulting from coal power plant associated bromide discharges relative to zero exposure to

TTHM (where risk of zero exposure is defined as $r_0 = 0.02047$, following Regli et al. (2015)).

$$OR = \frac{r}{1-r} = 0.02090 \times e^{TTHM_4 \text{ Concentration} \times 0.00427} \quad (4.1)$$

TTHM models cannot be coupled to species-specific risk assessments; however, individual THM species predictions can be assessed using reported species-specific risk values, such as cancer slope factors (CSFs). This approach focuses solely on the THM species and cancer as an outcome and does not consider how TTHM is intended to be an indicator of overall DBP risk or consider risk other than cancer. Thus, this approach may under-estimate risk associated with unmeasured and unregulated DBPs and risk of outcomes other than cancer; these unconsidered risks may change in response to increased source water bromide. Generally, CSFs are used to assess the cancer risk associated with mixtures of chemical species, where total risk is determined by adding the individual species risk (Choudhury et al., 2000). CSF derived risk estimates are calculated following Equation 4.2 (Theodore and Dupont, 2012), where C is the THM species concentration, IR is the intake rate, ED is the exposure duration, CSF is the species-specific cancer slope factor, BW is body weight, and LT is lifetime. The intake rate is estimated to be 2 liters per day, exposure duration as 70 years, the average adult body weight to be 70 kg, and a lifetime to be 70 years (Asante-Duah, 2002; USEPA, 2012). The U.S. EPA Integrated Risk Information System (IRIS) provides CSFs for the three brominated THM, which are provided in Table B.7 (USEPA, 2016).

$$Drinking \ water \ cancer \ risk = \frac{C \times IR \times ED}{BW \times LT} \times CSF_{oral} \quad (4.2)$$

In order to use these risk estimate methods, it is necessary to predict the effect of the bromide concentration contribution change at the intake on THM formation. As noted above, this type of prediction is challenging because models developed for individual drinking water systems or regions are not always suitable for other locations or systems (Ged et al., 2015). The present work uses the prior work by Wilson and VanBriesen (2013) who conducted a 3-

year field study of source water and finished water at multiple drinking water plants using the Monongahela River as a source. Modeled relationships between source water bromide and finished water TTHM, THM species, OR-derived risk, and CSF-derived risk were developed from the field study data (see Equations 4.3 through 4.9). Additionally, the modeled TTHM (Equation 4.3) and species-specific THM (Equations 4.4 through 4.7) concentrations were used to calculate OR and CSF risk following Equations 4.1 and 4.2, and these results were compared to the direct bromide concentration to risk estimates (Equations 4.8 and 4.9). All modeled results are based on the bromide concentration contribution distribution for power plants produced by considering the median estimated bromide load over the range of flow conditions for the Water Years considered. A summary of the methods used here are presented in Figure 4.2C and 4.2D.

$$[TTHM] = 72.35 \times e^{0.2796 \times [Br^-]} \quad (4.3)$$

$$[Chloroform] = 11.22 \times e^{-0.1005 \times [Br^-]} \quad (4.4)$$

$$[BDCM] = 33.21 \times e^{0.516 \times [Br^-]} \quad (4.5)$$

$$[DBCM] = 124.8 \times e^{1.483 \times [Br^-]} \quad (4.6)$$

$$[Bromoform] = 38.21 \times e^{1.490 \times [Br^-]} \quad (4.7)$$

$$\text{OR risk} = 0.007333 \times e^{0.3036 \times [Br^-]} \quad (4.8)$$

$$\text{CSF risk} = 0.0002170 \times e^{0.7751 \times [\text{Br}^-]} \quad (4.9)$$

4.3 Results and discussion

4.3.1 Power plant bromide loads

The five coal power plants operating wet FGD treatment systems upstream of the bromide monitoring locations during the period of interest (WY1998, WY2013-WY2017) used a total of between six million (WY1998 and WY2017) and 15 million (WY2013) tons coal/year. The retirements of Hatfields Ferry and Mitchell power plants (October 2013) significantly reduced the power plant coal usage in the Monongahela River Basin, with concomitant declines in bromide loads associated with FGD systems. Harrison and Fort Martin power plants continue to be major bromide contributors. Harrison Power Station (2052 MW capacity) uses significantly more coal (4.4 million tons/year on average for the study period) than the other power plants in the basin. Harrison power plant greatly reduced its coal consumption in September 2017, leading to further reduction in bromide loading in the basin. Figure B.2 provides additional details regarding coal consumption, deliveries, and stocks for these power plants.

The type of coal used at the facilities within the study period did not vary; all facilities burned predominately bituminous coal mined in counties from Kentucky, Ohio, Pennsylvania, and West Virginia. Figure B.3 shows the range of bromide content for bituminous coal from these counties and the total amount of coal delivered during the study period; bromide concentrations associated with these coals fall within the expected concentrations associated with bituminous coal throughout the United States, shown on the far left of Figure B.3 (Good and VanBriesen, 2018). Table B.6 summarizes the bituminous coal subtype sampled in each county. It is notable that Harrison uses coal almost exclusively from one county in

WV (Marion, county code 49) and the median bromide concentration from that county is 20 ppm. This value is similar to the median U.S. value for bituminous coal (18 ppm), but the variability within this county is significantly lower than the national variability. This may be due to more similar bromide levels within counties than among many counties nationally, or it may be due simply to the smaller sample size for the county-level data.

Figure 4.3 shows the modeled bromide loads for each power plant for Water Year 1998 and Water Years 2013 to 2017 as well as the total from all plants (far right panel). Only two power plants were operating wet FGD systems in 1998 (Harrison and Mitchell) and thus the total bromide load discharged to the river from wet FGD was significantly lower (median 185 kg/day), compared with 2013, when all five power plants were operating wet FGD systems (median 659 kg/day). Subsequently, when Hatfields Ferry and Mitchell closed, loads declined slightly (median 358 kg/day in 2014-2016). And, when Mitchell closed in 2017, loads dropped significantly (median 264 kg/day in 2017).

As expected based on these operational changes, the cumulative bromide load estimate across all plants also indicated a statistically significant difference ($p < 0.05$) between all Water Years except 2014-2016 ($p = 0.1$). For individual plants, the results indicate statistically significant differences ($p < 0.05$) between all Water Years except 2013-2014 ($p = 0.7$) at the Harrison power plant and 2014-2017 at the Longview power plant ($p = 0.5$). These differences correspond to statistically significant differences in power generation (and, consequently, coal consumption), as shown in Table B.8.

The loads in this work are lower than loads estimated for these specific power plants in Good and VanBriesen (2017), while they are consistent with estimates in Good and VanBriesen (2018). The lower prediction in Good and VanBriesen (2018) and the present work is due to the range of bromide concentrations assumed for coal in Good and VanBriesen (2017), as

that work was completed prior to revisions to the COALQUAL database that make direct use of bromide data possible. Good and VanBriesen (2017) predicted bromide loads using a minimum, maximum and median estimated bromide concentration for the general rank of coal used at these plants (bituminous), while Good and VanBriesen (2018) used bromide concentration data from COALQUAL associated with sub-rank (eastern Bituminous). Figures B.4, B.5, B.6 compare the predicted loads for Harrison, Fort Martin, and Longview between the previous work and the present results. Good and VanBriesen (2017) predicted median bromide loads for these power plants as 396, 207, and 157 kg/day, respectively. In the present work, using bromide data specific for coal deliveries to the facilities on the Monongahela River, the estimates for median bromide loads in 2016 at these plants are 150, 131, and 83 kg/day, respectively, similar to the values predicted by Good and VanBriesen (2018). The current predictions show a more narrow range since they are based on samples from coals in only a few counties, which show lower inter-sample variability (see Figure B.3).

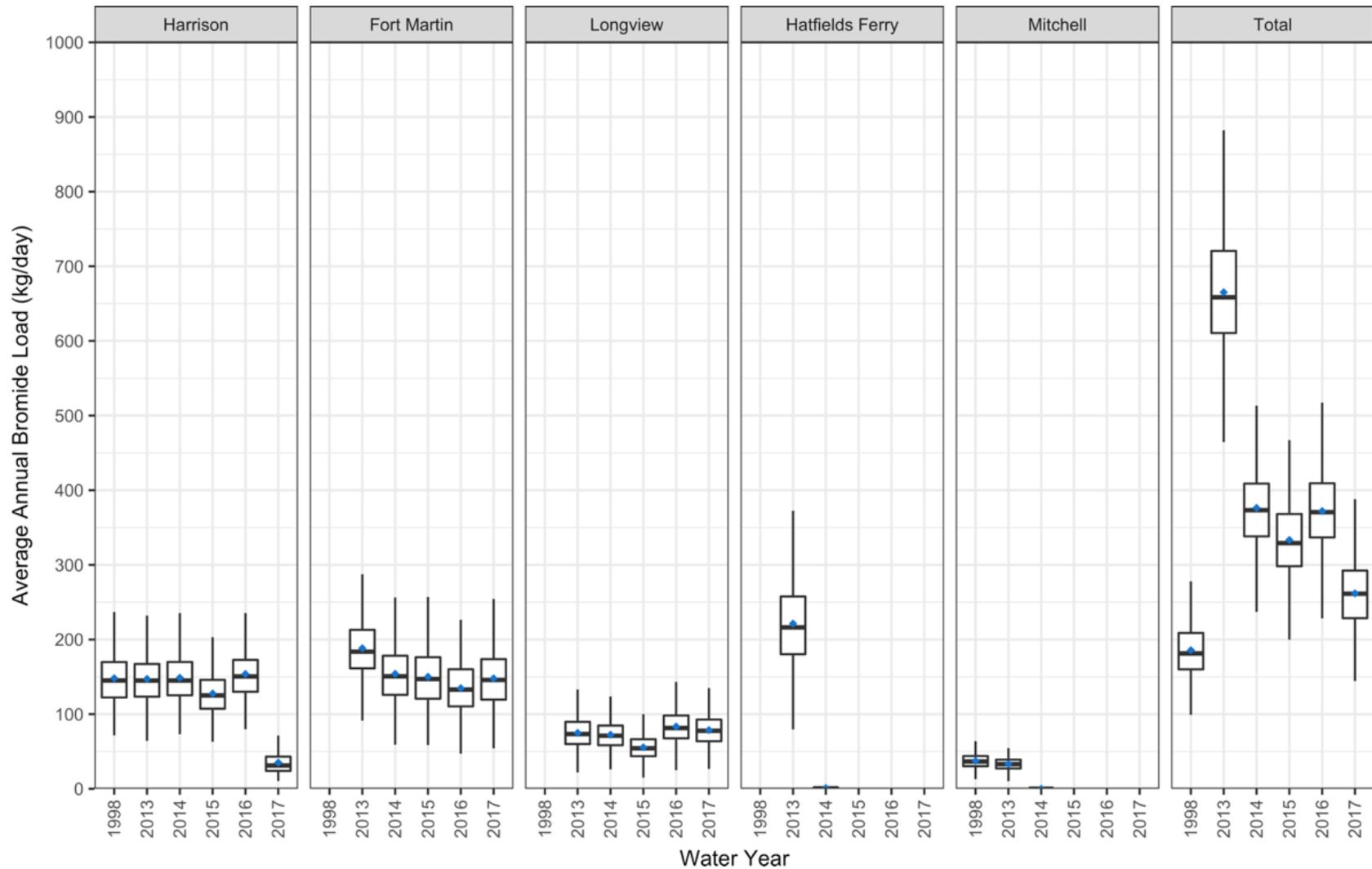


Figure 4.3: Estimated bromide load by power plant for the Water Years of interest. The box denotes the median, 25th and 75th percentiles; the whiskers extend to 1.5 times the interquartile range; the blue diamond denotes the mean. The top of each panel identifies the power plant and the rightmost panel shows the total bromide load from all power plants.

4.3.2 Oil and gas wastewater discharge bromide loads

This analysis identified 4 centralized waste treatment facilities (CWTs) with NPDES permits (3 in PA, 1 in WV), 1 CWT treating for recycle (zero liquid discharge, PA), and no POTWs that accept oil and gas wastewater in the Monongahela Basin (see Figure 4.1 for locations). A list of the four CWTs with NPDES permits is provided in Table A2. Only one discharging CWT (WVR00521948-Fairmont Brine Processing) is located in a subbasin that could be potentially affecting the modeled site evaluated in this study; the other three discharging CWTs are located in the Youghiogheny River subbasin; the confluence of this river with the Monongahela River is downstream of the modeled site. None of the CWTs are expected to be currently contributing significantly to in-stream bromide concentrations. Under mean flow conditions, Fairmont Brine Processing contributed 11 kg/day in November 2016, 1.8 kg/day in December 2016, and 1.9 kg/day January 2017, but less than 0.5 kg/day for all other months during the study period (see Tables B.9 - B.12). A summary of the estimated bromide loads from the four CWT facilities is also provided in Table B.2.

4.3.3 Bromide concentration contributions

The bromide concentration at the drinking water intake controls the effect of bromide on the rate of DBP formation and the extent of bromine incorporation in the formed DBPs. Bromide load estimates can be used to estimate the concentration contribution from these loads under various flow conditions. Figure 4.4 shows the concentration discharge curves for each Water Year, with flow for the period of record on the x-axis (14-2,600 m³/sec). The solid black line represents the cumulative (i.e., all power plants) median bromide load predicted. The dashed black lines represent the 25th and 75th percentile for the cumulative load estimates, while the grey shading shows the full range of load estimates. These load lines extend to the minimum and maximum flow conditions observed for the Water Year shown. The mean flow for each Water Year is shown by the vertical blue dashed line near the middle of each plot. The 7Q10 flow is the lowest 7-day flow over the course of 10 years and is shown

by the vertical blue dashed line near the far left of each plot; 7Q10 low flow conditions represent a worst-case scenario that could be used in setting discharge limits to control the effects of bromide discharges on downstream drinking water intakes. The concentration-discharge curves enable estimates of in-stream bromide concentration contributions at the intake under any flow condition. For example, the predicted bromide concentration contribution from the median estimated bromide load under 7Q10 flow conditions is $103 \mu\text{g/L}$ in Water Year 2016, which had the lowest flow conditions of the Water Years studied. The predicted bromide concentration contribution for median load estimates at mean flow ranged from $3.7 \mu\text{g/L}$ (Water Year 2013) to $6.8 \mu\text{g/L}$ (Water Year 2016).

As river flow increases (moving to the right in Figure 4.4), coal-fired power plants loads are diluted in higher water volumes and contribute smaller concentrations to the intake location. For Water Years 2014 - 2016 (when loads were most stable) the cumulative contribution to the bromide concentration at the intake from all the power plants based on the median load predictions was between $0.71 \mu\text{g/L}$ at the highest flow and $32 \mu\text{g/L}$ at the lowest flow in 2014, $0.51 - 82 \mu\text{g/L}$ in 2015, and $1.2 - 110 \mu\text{g/L}$ in 2016; these ranges are shown as light yellow banding across each of these panels in Figure 4.4. In 2014 - 2016, flows above the 75th percentile (300, 362, and 287 m^3/sec , respectively) were associated with median bromide concentration contributions of 3.6, 3.4, and $5.2 \mu\text{g/L}$, based on the median load estimates. Flows below the 25th percentile (68.8, 62.3, and 62.1 m^3/sec , respectively) were associated with median bromide concentration contributions of 15.7, 19.7, and $24.0 \mu\text{g/L}$. In Water Year 2016, the 25th - 75th percentile loads led to concentration contributions that ranged from 0.5 - 2.4 under minimum flow conditions to 45 - 223 $\mu\text{g/L}$ under maximum flow conditions, respectively.

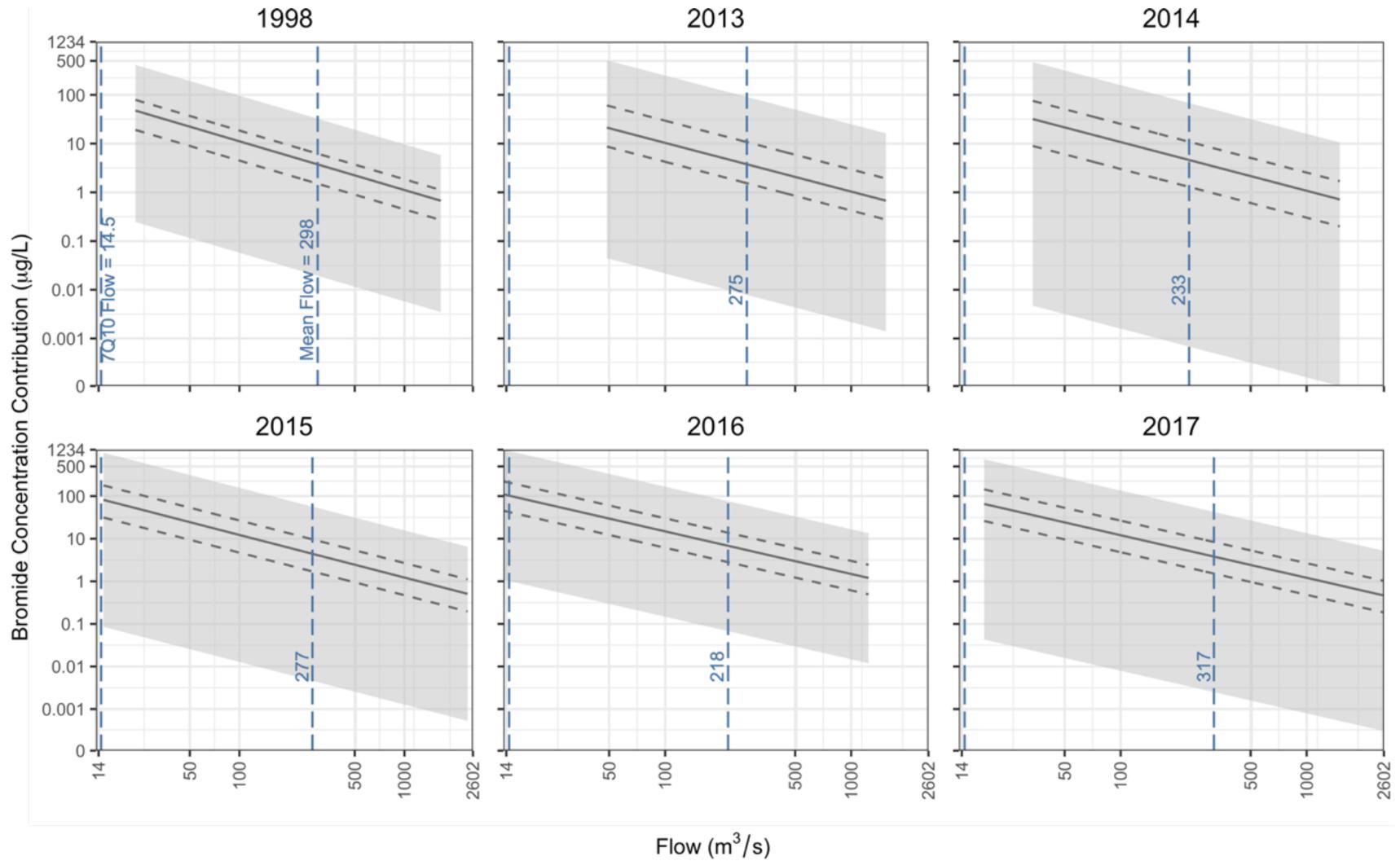


Figure 4.4: Concentration-river discharge relationships for Water Years studied. The solid black line shows the median estimated bromide load, the dashed black lines show the 25th and 75th percentile estimated loads for each Water Year, and the grey shading shows the full range of estimated bromide loads. The mean flow for each Water Year and the 7Q10 for the period of record (14.5 m³/s) are denoted by the vertical blue lines.

Figure 4.5 shows the total estimated bromide concentration contribution from the power plants at the model site for Water Years 2013 through 2017 along with observed bromide concentrations in the river. The predicted concentration contribution distribution is based on the estimated 25th, median, and 75th percentile loads, and the range of flow conditions for the days when observed concentrations were measured; these are shown in the boxplots at the right of each panel (no fill). The observed bromide concentrations are shown in a box plot at the left of each panel (grey fill). In all cases, the box extends to the 25th and 75th percentile of the distribution and the whiskers extend to 1.5 times the interquartile range.

These results indicate that the median bromide load estimate would lead to the power plants representing between 25% (for 25th percentile load in 2015) and 100% (for 75th percentile load in 2016) of the median observed bromide concentrations at the modeled site. The median load estimate predicts the power plants contribute from 38% to 78% of observed river bromide concentrations in 2015 and 2016, respectively. Thus, power plants in the basin contribute a significant portion of the observed bromide concentration at the downstream drinking water intake. As expected, seasonal flow conditions affect the contribution of bromide discharges to downstream drinking water plant intake concentrations, with their effect being more significant during low flow, observed in summer and fall in this region. This trend is also shown in the monthly estimated bromide concentration contributions in Figure B.7, where elevated values are observed in August and September of most years.

Although estimated power plants bromide loads can account for the majority of bromide observed at the modeled site, additional sources of bromide may be present in the basin, which might include road-applied brines (Granato 1996, Dailey, Welch et al. 2014, Tasker et al. 2018) and active or abandoned mine discharges (Cravotta 2008, Cravotta and Brady 2015). These non-point source contributions are difficult to estimate due to lack of monitoring and reporting data. Additional monitoring of bromide discharges to narrow the range of load

estimates for the point sources (e.g., power plants) would facilitate more detailed analyses to determine whether additional sources are contributing bromide to the river.

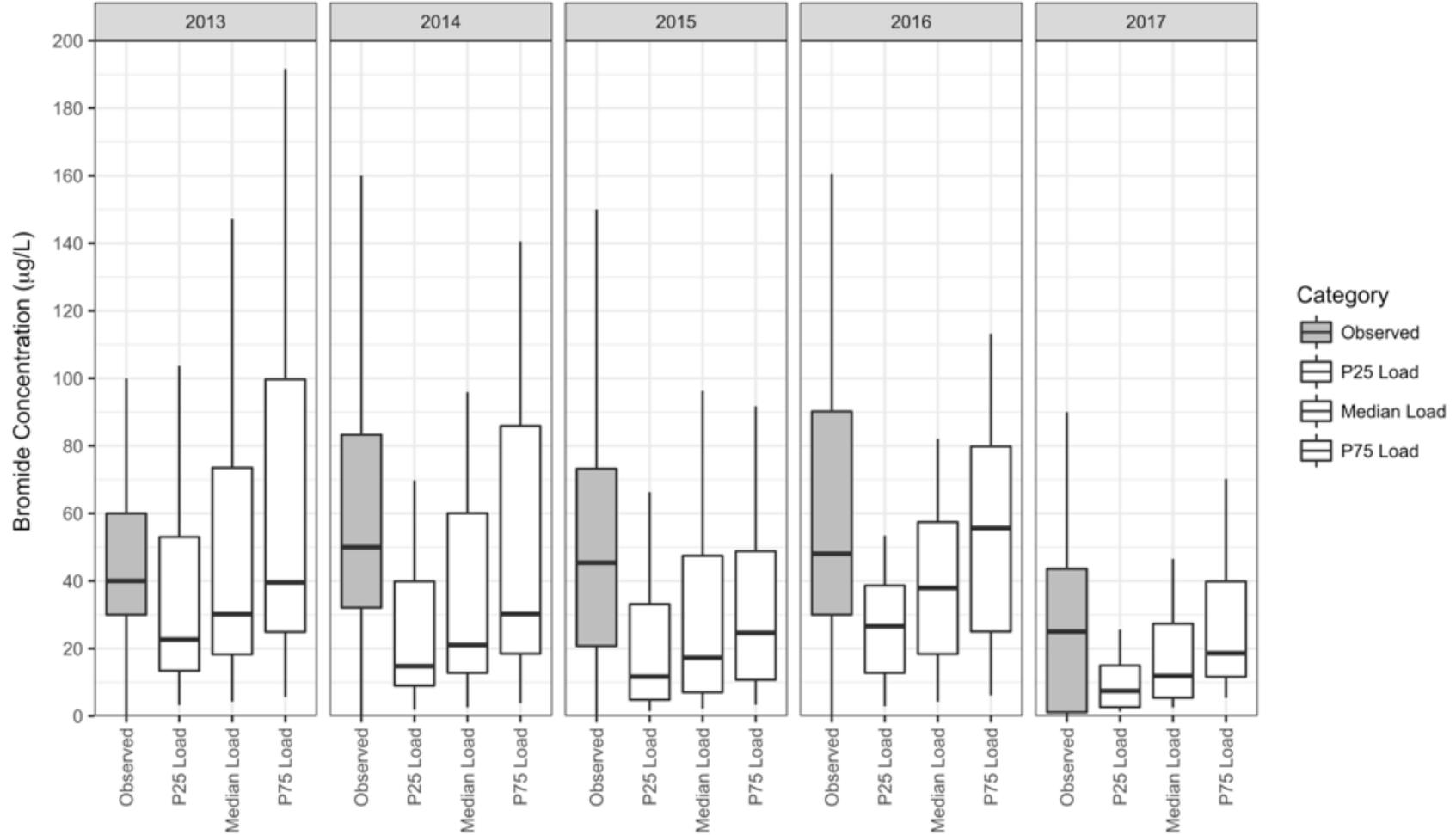


Figure 4.5: Predicted bromide concentration contributions at the model site for Water Years 2013 through 2017. Concentrations were estimated using the 25th, median, and 75th percentile predicted loads and the flow conditions for the selected year. These predictions (white fill) are compared to the observed concentrations (grey fill) at the model site for each year (left-most box plot in each panel). The boxplot shows the median, 25th, and 75th percentiles; the whiskers extent to 1.5 times the interquartile range.

Figure 4.6 shows the predicted bromide concentration contribution as an exceedance curve predicted from the estimated median, 25th, and 75th percentile bromide load for Water Year 2016 across all flow conditions that occurred in Water Year 2016. The black lines show the results for WY2016 and the grey lines for WY1998. The horizontal dashed lines represent the median observed concentration in the river in each of those years. As can be seen in the figure, the median observed concentration in the river did not vary between WY2016 and WY1998, but the power plant bromide concentration contribution between these two years increased significantly. The exceedance probability for the power plant bromide concentration contribution at the median concentration in 1998 was only 3%. In 2016, the exceedance probability for the median concentration was 35%.

4.3.4 TTHM and risk

Figure 4.7 shows the predicted TTHM concentration contribution as an exceedance curve based on bromide concentration contributions (predicted from the estimated median, 25th, and 75th percentile bromide load for Water Year 2016 across all flow conditions observed in 2016). The solid line indicates the median predicted TTHM concentration leaving the treatment plant and the dashed lines show the estimated 25th and 75th percentile TTHM concentration contributions. The blue dashed horizontal lines indicate the maximum contaminant level (MCL) for TTHM, which is the regulatory value of 80 $\mu\text{g/L}$, and 80% of the MCL (64 $\mu\text{g/L}$), which is commonly used as a goal by utilities for TTHM at the end of treatment (prior to the water entering the distribution system where additional TTHM will form as the water travels to the consumers).

The exceedance curve shows that power plants contributed between 23 and 30 $\mu\text{g/L}$ (with median of 25 $\mu\text{g/L}$) TTHM at the drinking water utility downstream at least 50% of the time in Water Year 2016 and can account for up to 40-50 $\mu\text{g/L}$ (with median of 45 $\mu\text{g/L}$)

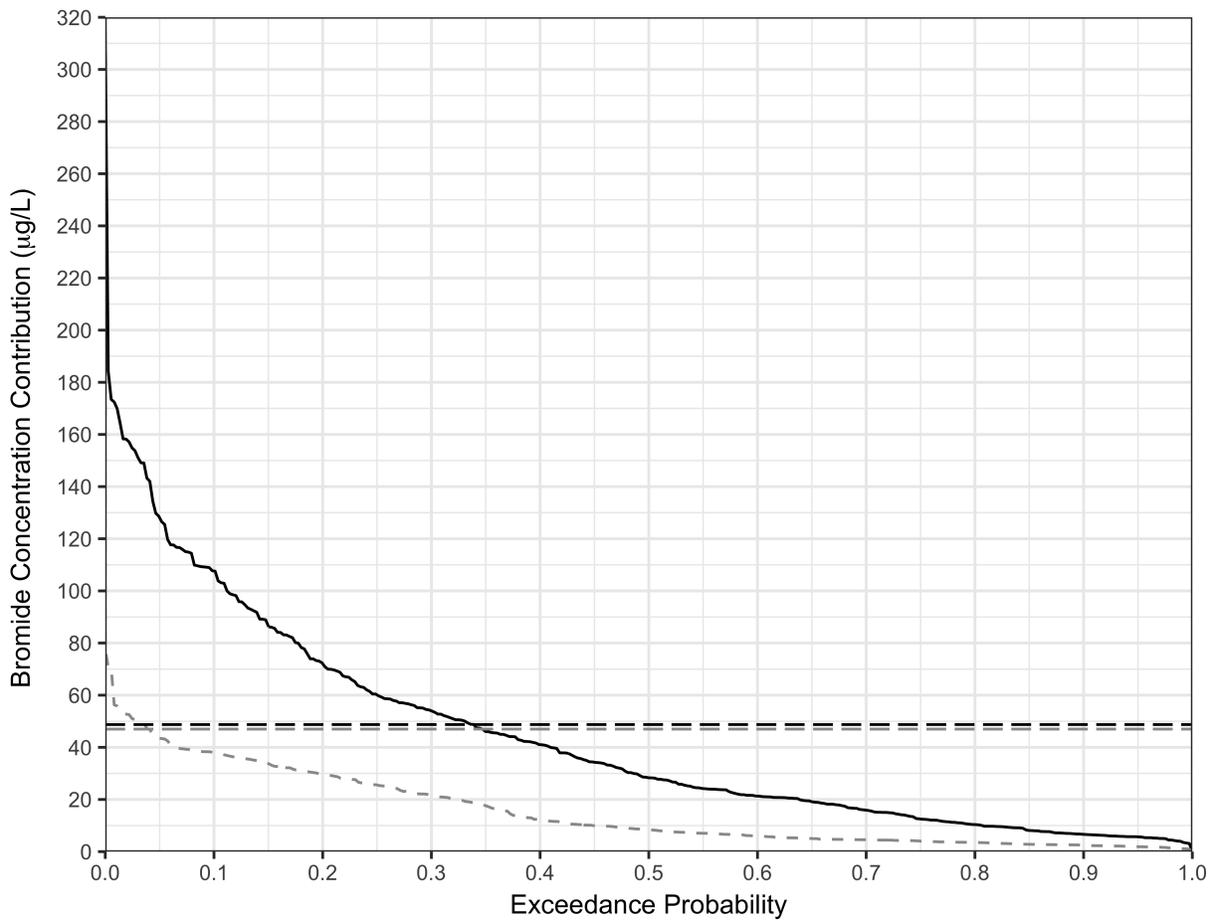


Figure 4.6: Bromide concentration contribution exceedance curve for Water Year 2016 and Water Year 1998. The black lines show the results for WY2016 and the grey lines for WY1998. The horizontal dashed lines represent the median observed concentration in the river in each of those years.

at some times (far left of the plot). Although these concentrations do not exceed the MCL or the 80% of the MCL target, these concentrations represent only the TTHM contribution from power plants in the basin. TTHM will form at the water utility due to the presence of other precursors (most notably organic carbon) and will be higher in summer months (due to higher temperature and more applied chlorine). These concentration contributions could cause a plant to shift from compliance with the TTHM standard to non-compliance even when TTHM concentration contributions caused by other precursors or treatment choices are relatively low.

Although TTHM is the relevant regulatory metric, increased bromine incorporation into THM is associated with increased risk, even if TTHM does not change. Figure 4.8 shows the exceedance probabilities for risk estimated using the CSF method for the median estimated bromide loads across all flow conditions observed in 2016. The 50% exceedance probability, which indicates the likelihood of exceeding a given value 50% of the time is 9.1×10^{-6} , calculated from the THM predictions. The 25% exceedance probability (which represents higher risk) is 1.5×10^{-5} . In other words, there is a 25% likelihood of exceeding this concentration at the median bromide load estimate.

The effect of power plant bromide discharges in the Monongahela River on the downstream intake are significant. Not only do these discharges influence the formation of TTHM, but they shift the speciation of THMs to more brominated forms, which carry a higher risk. The higher risk contribution resulting from these discharges suggests a need to improve treatment operations or reduce bromide discharges to ensure finished water DBP-associated risk does not remain elevated in this basin.

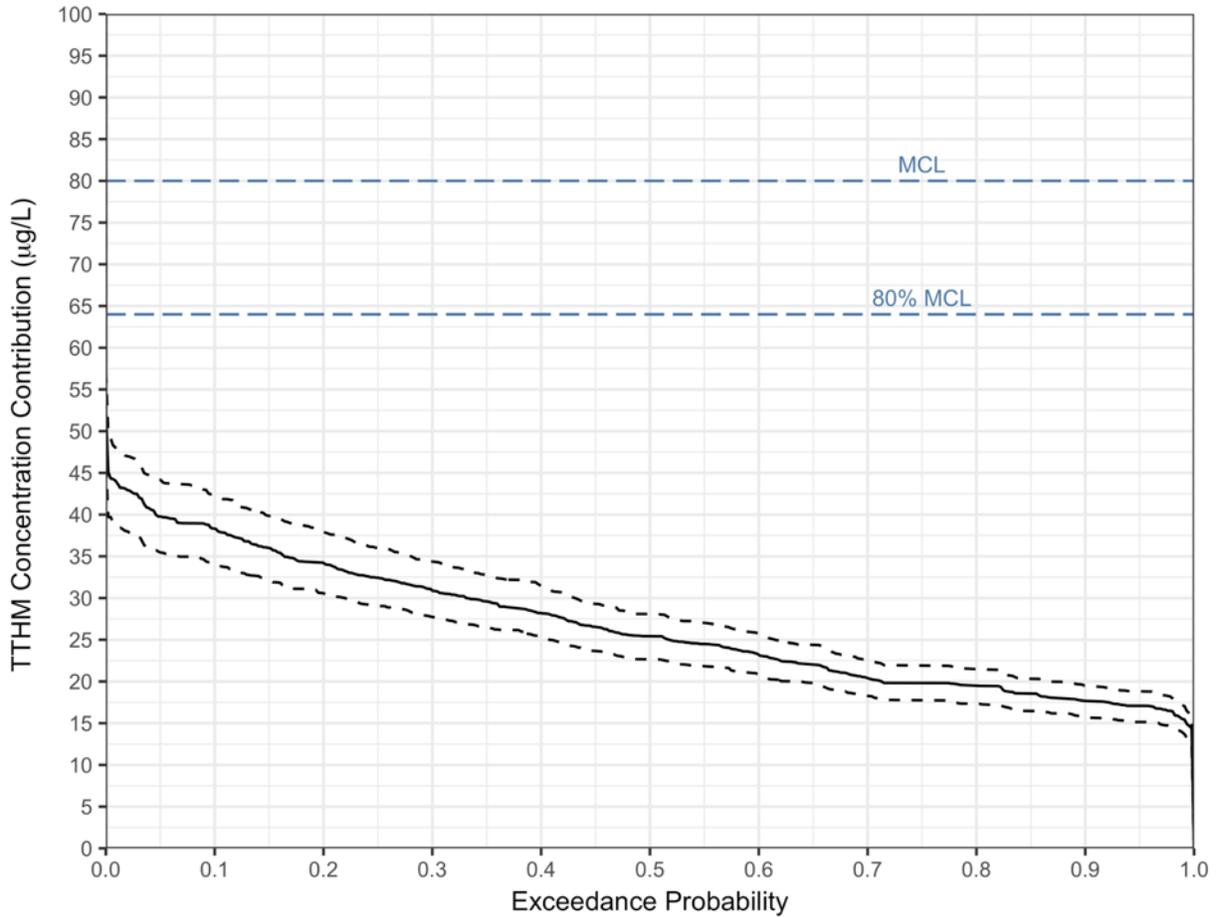


Figure 4.7: TTHM concentration contribution exceedance curve for Water Year 2016. The grey line shows the reported compliance data, measured in the distribution system, and the black line shows the predicted TTHM concentration leaving the treatment plant based on the model results for median estimated load from the power plants. The blue dashed lines indicate the maximum contaminant level for TTHM ($80 \mu\text{g/L}$) and 80% of the MCL ($64 \mu\text{g/L}$).

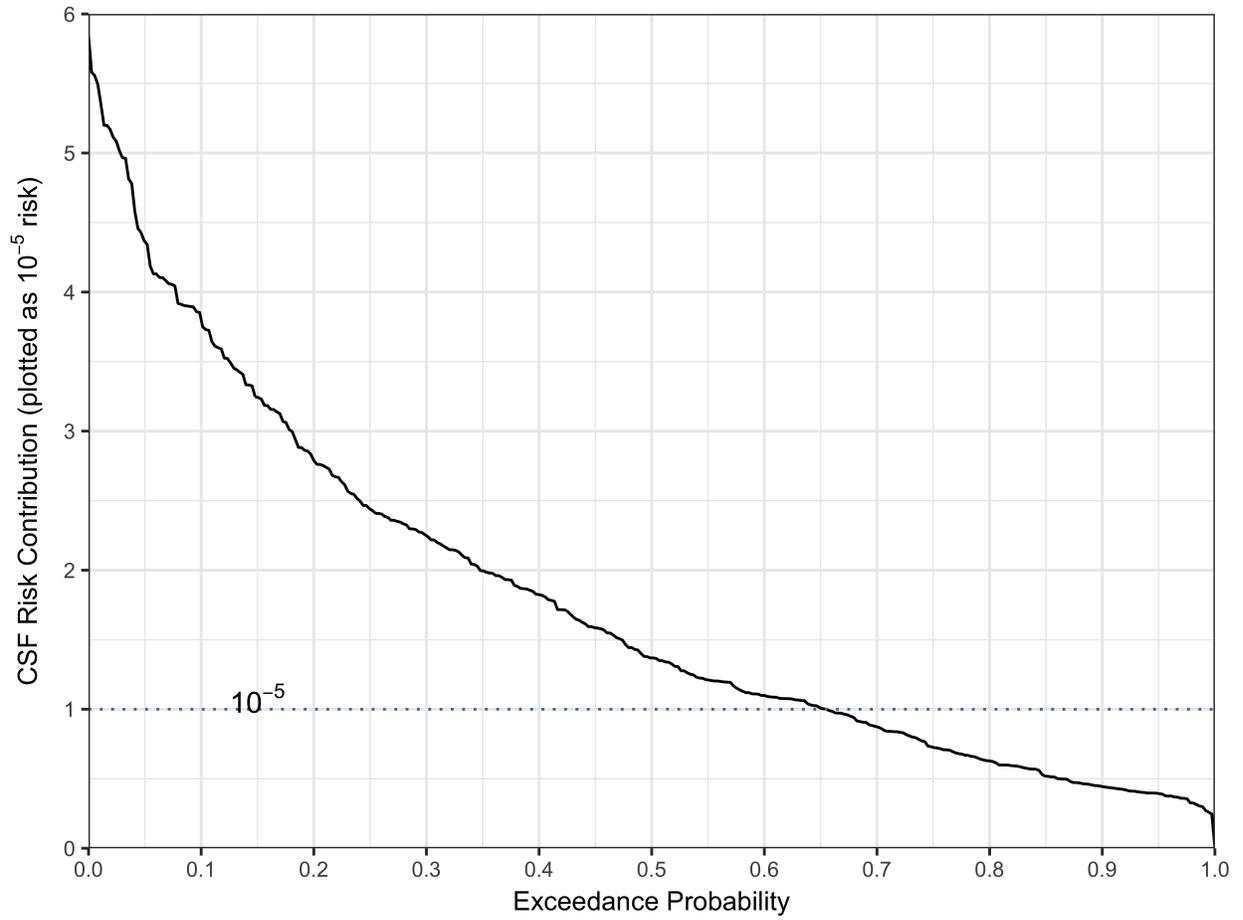


Figure 4.8: CSF risk contribution exceedance curve for Water Year 2016.

4.4 Conclusion

This work demonstrates the effect of elevated source water bromide for the Monongahela River Basin in Southwestern PA on drinking water DBPs and associated risk. In this region, fossil fuel associated wastewaters have been implicated in elevated concentrations of bromide. The present work evaluated the effect of bromide discharges from coal-fired power plants operating wet FGD systems on an intake downstream of the discharge points. Coal power plants with wet FGD were found to contribute between 55-98% of the total observed bromide concentrations at the intake in WY2016. Additionally, the effect of these discharges on THM formation and risk was assessed. For the median modeled bromide load, coal power plant discharges contribute an additional 23 - 30 $\mu\text{g}/\text{L}$ TTHM 50% of the time in WY2016. At annual exposure levels, this results in an increase in CSF risk of 10^{-5} risk, or 1 additional cancer case in 10,000 people exposed.

This work demonstrates that the contribution of coal power plant associated bromide discharges may significantly affect THM formation and risk at downstream drinking water intakes. Reducing the effect of elevated bromide on DBP risk for consumers may require limiting bromide discharges from power plants or modifying drinking water treatment plants to remove bromide or to reduce DBP formation. Additionally, bromide source attribution enables regulators to identify major contributors and consider discharge regulations to reduce effects on drinking water plants and associated human health risk from DBPs.

Significant uncertainty remains in the present analysis, with most related to the wide range of estimated bromide loads from the power plants. Variability of flow conditions produces wide ranges of concentrations, but these are directly predictable from the routinely measured river flow.

Thus, the key component of the analysis that would benefit from improved specificity is the

bromide load model. This model is based on the best available information on the type and amount of coal being used by the power plants and the capture of this bromide in FGD wastewater, which is presumed to be discharged to the river. A better approach to estimating wet FGD associated power plant bromide loads would be to measure the flow and concentration of bromide from each power plant on a regular basis. This would allow an estimate of bromide loads from these facilities based on observations rather than dependent on historical characteristics of different types of coal.

Drinking water plants routinely measure constituents of concern for drinking water treatability; however, few include bromide measurements. The lack of source water bromide data makes interpretation of the role of bromide in DBP formation at specific plants difficult and complicates attempts to identify when changing bromide concentrations are the driver for DBP compliance problems. Thus, drinking water utilities should consider routine bromide monitoring in their source waters.

In combination, improved monitoring of bromide from discharge points and at drinking water intakes will improve estimates of the effect of anthropogenic bromide discharges on drinking water sources, DBP speciation, and associated risk. This information will allow regulators to assess the need for limits on bromide discharges in specific rivers where drinking water could be negatively affected.

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Chapter 5

Conclusion and Future Work

The control of disinfection byproducts remains a priority for drinking water utilities. As the potential sources of contamination to water supplies continually evolves, drinking water utilities are faced with new challenges in the need to balance microbial control while limiting the formation of toxic DBPs. This work evaluated the effects of increased source water bromide resulting from saltwater intrusion into coastal groundwater and anthropogenic discharges from coal-fired power plants to surface waters on DBP formation, speciation, and risk.

The following sections highlight the major contributions of this work and address the limitations of the present studies. Additionally, potential future work to expand on this work is suggested.

5.1 Conclusions

Chapter 2 evaluated the suitability of TTHM as a surrogate measure for risk at elevated source water bromide concentrations, to frame this issue within the regulatory context. TTHM was developed as a surrogate measure for DBP risk because it was the dominant group of DBPs in chlorinated waters. Epidemiological work based on measuring TTHM suggested it was an adequate indicator of risk. However, most work supporting this asser-

tion was completed in regions where chlorinated THM dominated. Since the implementation of the D/DBP Rule, additional studies have been conducted that suggest the regulation of brominated DBPs would better protect human health (Villanueva et al., 2012). Thus, when change in source water bromide alter DBP speciation toward more toxic brominated forms ensuring low TTHM may not adequately protect human health. New regulatory strategies must consider the projected increases in source water constituents negatively affecting the formation of toxic DBPs and the feasibility of implementing new metrics.

Several alternative regulatory metrics, including THM_3 and BSF, were identified as viable alternatives. THM_3 represents the sum of the three brominated THM species, each of which has been associated with toxicity and carcinogenicity. The individual brominated THM species are were included in the most recent the Unregulated Contaminant Monitoring Rule (UCMR) list (USEPA, 2018), suggesting EPA may be considering regulating them individually under BSF represents another alternative, which could be used in addition to the existing TTHM standard. BSF represents the relative contribution of bromine-containing DBPs to the total. If used in conjunction with the mass-based TTHM standard, it could ensure the bromine-containing DBPs remain at lower concentrations than the chlorine-containing THM to protect against their higher relative risk.

Chapter 3 introduced a case study to assess the effect of increased bromide due to saltwater intrusion for drinking water utilities utilizing groundwater sources along the New Jersey coast. Climate change induced sea level rise is expected to increase saltwater intrusion into coastal aquifers. Because sea water contains elevated levels of bromide, when groundwater wells near the coast become more saline, they will contain higher concentrations of bromide. This effect can be exacerbated in areas with high groundwater utilization rates or where land subsidence is occurring. Results of this analysis demonstrate that drinking water utilities may exceed acceptable risk thresholds for THMs despite meeting current regulatory limits.

Under the 2.0% saltwater intrusion scenario, which corresponds to the upper limit of the secondary drinking water standard for chloride in drinking water supplies, the TTHM concentration exceeded the regulatory threshold and the 10^{-4} risk threshold. At the much lower 0.1% intrusion scenario, the 10^{-5} risk threshold was exceeded despite the water meeting the MCL for TTHM. Thus, elevated risk from brominated DBPs may result even while the utility complies with drinking water standards.

This reinforces the importance of reassessing the current regulatory framework to ensure that drinking water quality is safe for consumption when source water bromide varies. Utilities using estuary or groundwater sources in regions subject to saltwater intrusion may need to consider alternative treatment strategies to reduce the formation of toxic DBPs. Regulatory strategies requiring limits on brominated DBP formation could aid in risk reductions for consumers of coastal groundwater supplies. To achieve these reductions, utilities may need to consider long-term capital investments to develop alternative supplies or to reduce bromide in source waters.

Chapter 4 demonstrates the effect of elevated source water bromide for the Monongahela River Basin in Southwestern PA. In this region, fossil fuel associated wastewaters have been implicated in elevated concentrations of bromide. This work evaluated the effect of bromide discharges from coal-fired power plants operating wet FGD systems on an intake downstream of the discharge points. Coal power plants with wet FGD were found to contribute between 55-98% of the total observed bromide concentrations at the intake during the period evaluated. Additionally, the effect of these discharges on THM formation, speciation, and risk was assessed. For the median modeled bromide load, coal power plant discharges contribute an additional 24 $\mu\text{g/L}$ TTHM 50% during the low-flow year of 2016. At annual exposure levels, this results in an increase in CSF risk of 10^{-5} risk, or 1 additional cancer case in 10,000 people exposed.

This work demonstrates that the contribution of coal power plant associated bromide discharges can significantly affect THM formation and risk at downstream drinking water intakes. Reducing the effect of elevated bromide on DBP risk for consumers may require limiting bromide discharges or modifying drinking water treatment plants to remove bromide or to reduce DBP formation.

The effects of increased brominated DBPs associated with elevated source water bromide concentrations from seawater intrusion and anthropogenic activities are of concern for drinking water utilities and consumers. Improved understanding of bromide sources allows drinking water utilities to plan for changing source water quality conditions. Additionally, bromide source attribution enables regulators to identify major contributors and consider discharge regulations to reduce effects on drinking water plants and associated human health risk from DBPs.

5.2 Future work

This work evaluated two specific scenarios of increasing bromide concentrations on DBP formation and risk. Additional bromide sources must also be considered as cumulative effects may be important in some locations (Solterman et al., 2016). As noted in the Monongahela River study and prior related work (Wilson and VanBriesen, 2014; Wilson et al., 2013; Wilson and VanBriesen, 2012), oil and gas produced water discharges can contain significant bromide. Co-occurrence of this source along with power plant discharges has been previously identified (Good and VanBriesen 2016) as a cause of changes in DBPs in drinking water (States et al., 2013). Road application of these brines as well as other deicing agents may also contribute bromide to watersheds (Tasker et al., 2018). Other anthropogenic sources may include historical use of methyl bromide as a soil fumigant (Taylor, 1994, Wegman et

al., 1983) and ethylene di-bromide as a gasoline additive (Sollars et al., 1982) as well as bromide used in flame retardants (de Wit, 2002), and dyes and pharmaceuticals. Attention to watershed level cumulative bromide effects will be important as regulators decide about discharge limitations for these industries.

Bromide is one of several DBP precursors, and the formation and speciation of the produced DBPs depends on the interactions among precursors. For example, iodide also affects DBP formation (). Organic carbon content (both the concentration and type) is also important for DBP formation (Hua and Reckhow, 2007; Singer et al., 2002; Reckhow and Singer, 1990). Additional work should incorporate improved monitoring studies of all DBP precursors from multiple sources. Source attribution is an important step in identify potential regulatory strategies to reduce discharges and the potential to affect downstream drinking water plants.

Precursor concentrations may also be affected by changes in river conditions, especially flow variability, which may be affected by non-stationary climate. Increased rainfall could cause increased runoff to surface water bodies, leading to more organic carbon loading (Delpla et al., 2015; Sawade et al., 2015; Li et al., 2014; Ritson et al., 2014; Skjelkvale et al., 2005) or increased dilution of bromide and iodide. Warmer temperatures may also change natural organic matter concentrations and nature in surface waters (Lepisto et al., 2014; Ritson et al., 2014; Tranvik et al., 2009; Evans et al., 2005; Arvola et al., 2004). These climate-derived effects should be evaluated in conjunction with changes in loading of halogens from anthropogenic sources to determine how drinking water DBP formation and risk might change in the future.

Additional work could work to expand our current understanding of DBP formation with the use of alternative disinfectants (e.g., chloramine or ozone) under varying source water quality conditions. Prior work has primarily focused on the formation of THMs and HAAs

at drinking water plants utilizing chlorine as the primary disinfectant. Different disinfectants produce distinctive byproducts with different risk profiles. As source water conditions change, the use of alternative disinfectants may increase. For example, shifting from chlorine to chloramine is often a choice that enables a utility to reduce the regulated species (TTHM and HAA₅). However, the role of bromide (and iodide) in DBP formation with alternative disinfectants is not well studied.

Climate change and an uncertain regulatory future complicate drinking water utility planning decisions. Climate change is expected to influence river flow conditions, which could lead to increased dilution of bromide discharges, and thus a reduced effect on THM formation and risk downstream. Alternatively, more flow variability (i.e., lower low flows and higher high flows) could create more seasonally-specific issues for DBP formation resulting from bromide discharges. To address source water protection challenges and reduce finished water risk, models are needed to estimate the effect of these changes on tradeoffs between microbial protection and DBP exposure for consumers.

Finally, additional work could evaluate the costs and benefits of implementing new treatment technologies and regulatory strategies to address many of these issues. This involves studying the feasibility of implementing improved drinking water treatment technologies and comparing this with the feasibility of implementing technologies to reduce discharges of precursors from sources. Incorporating new treatment strategies could aid drinking water utilities in meeting new regulatory standards, adapt to changing source water conditions, and reduce consumer risk. This benefit, however, comes at a financial cost, which could be significantly higher than the cost of removal of bromide (and other precursors) from point discharges like power plants. Further, the feasibility of new technologies in both industries must be evaluated with respect to the associated risk-reduction benefit for the drinking water consumers.

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Appendix A:

Climate change impacts on bromide, trihalomethane formation, and health risks at coastal groundwater utilities

A.1 Additional information on data processing

As described in the primary text, several source water quality parameters influence the formation and speciation of DBPs. The parameters evaluated in this analysis include: pH, temperature, total organic carbon (TOC) concentration, ultraviolet absorbance at 254 nm (UV_{254}), bromide concentration (Br^-), chlorine dose (Cl_2), and chlorine contact time. The data used for the analysis included both below detection and missing data. To ensure an adequate sample size for model validation and to accurately characterize the source water quality data, a lognormal distribution was fit to the observed data (Obolensky 2007; Travis and Land, 1990) and used to impute the missing values.

The robust semiparametric regression on order statistics (ROS) method for multiple imputation (Helsel 2005; Helsel and Cohn, 1988) was used to determine summary statistics for the source water quality parameters. Using the NADA package in the R computing language (Lee 2015), missing data were imputed from a truncated lognormal distribution based on the ROS-derived estimates of the means and standard deviations. For data missing at

Table A.1: Observed source water quality and operational parameters.

Parameter	Mean	95% CI of the mean	Standard deviation
pH	7.56	7.49 - 7.62	0.302
Temp (°C)	14.6	14.1 - 15.0	2.09
TOC (mg/L)	0.561	0.456 - 0.599	0.310
Br ⁻ (mg/L)	0.0521	0.0352 - 0.0636	0.0665
UV ₂₅₄ (nm/cm)	0.0121	0.0109 - 0.0130	0.00479
Cl ₂ (mg/L)	1.56	1.47 - 1.73	0.592
Time (h)	3.25	2.86 - 3.60	1.72

Note: Br⁻ = bromide concentration; Cl₂ = chlorine dose; Temp = source water temperature; Time = chlorine contact time; TOC = total organic carbon concentration; UV₂₅₄ = ultraviolet absorbance at 254 nm.

random, samples were generated for each missing value from the entire distribution. This was performed using a multivariate lognormal distribution, where the correlation between parameters was considered. Table A.1 expands on Table 3.2 and shows the confidence intervals for the estimated mean values for each influent water quality parameter. Confidence intervals were determined using a t-test, and all values were statistically significant (with $p < 0.05$).

A.2 Effects of saltwater intrusion on TDS, chloride, and sulfate

As described in the primary text, at intrusion levels below 1%, TDS, chloride, and sulfate are all below their secondary drinking water standards, confirming the results of Ged and Boyer (2014). These results are shown in Figure A.1. The secondary standards for TDS and

chloride (shown as the dashed red lines) are exceeded in the 2.0% intrusion scenario, but concentrations are below the secondary standard in all other scenarios. The sulfate standard is not exceeded in any scenarios.

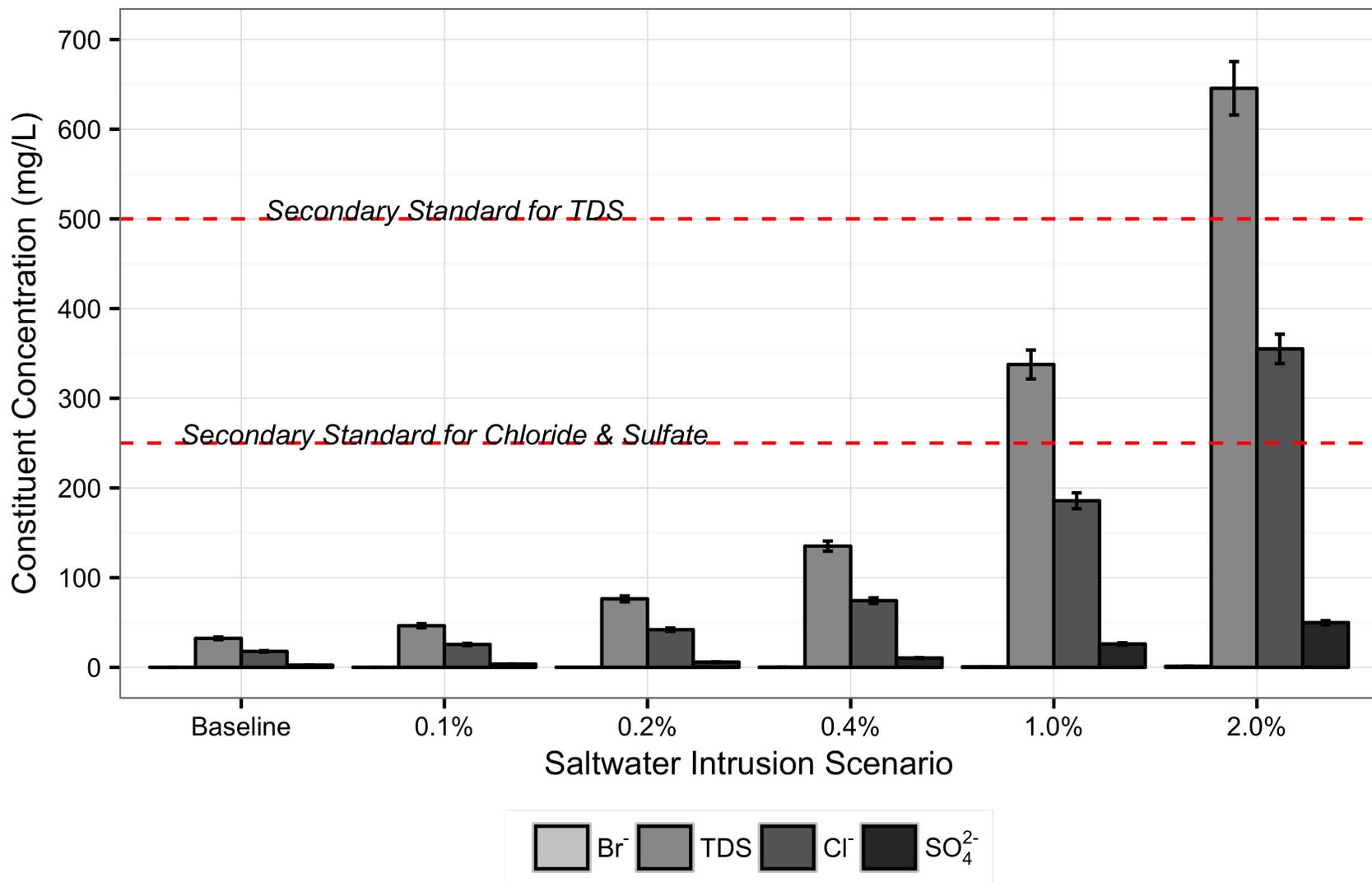


Figure A.1: Mean bromide, TDS, chloride, and sulfate concentrations for each saltwater intrusion scenario; dashed lines show the secondary standard for TDS (500 mg/L) and the secondary standard for chloride and sulfate (250 mg/L).

A.3 Effects of temperature on bromine incorporation and risk

The effect of temperature on bromine incorporation and risk was lower than the corresponding effect of increased bromide. The effect of a 2°C change in temperature on BSF, percent bromination by mass, and risk are shown in Figure A.2 through Figure A.5.

Figure A.2 shows the effect of a 2°C change in temperature on BSF and Figure A.3 on percent bromination by mass. In the 2.0% saltwater intrusion scenario, the BSF increases to nearly 0.7 and the percent bromination by mass is 100%, indicating that almost all of the TTHM present in the finished water contains brominated THMs.

Figure A.4 and Figure A.5 show the effect of a 2°C change in temperature on risk. Figure A.4 shows risk calculated using Cancer Slope Factors. The 10^{-5} risk threshold is exceeded in the 0.1% saltwater intrusion scenario, similar to the effects seen with no change in temperature. Figure A.5 shows risk calculated using Odds Ratios. The 10^{-4} risk threshold in all scenarios, including the baseline saltwater intrusion scenario and the 10^{-2} risk threshold is exceeded in the 2.0% saltwater intrusion scenario.

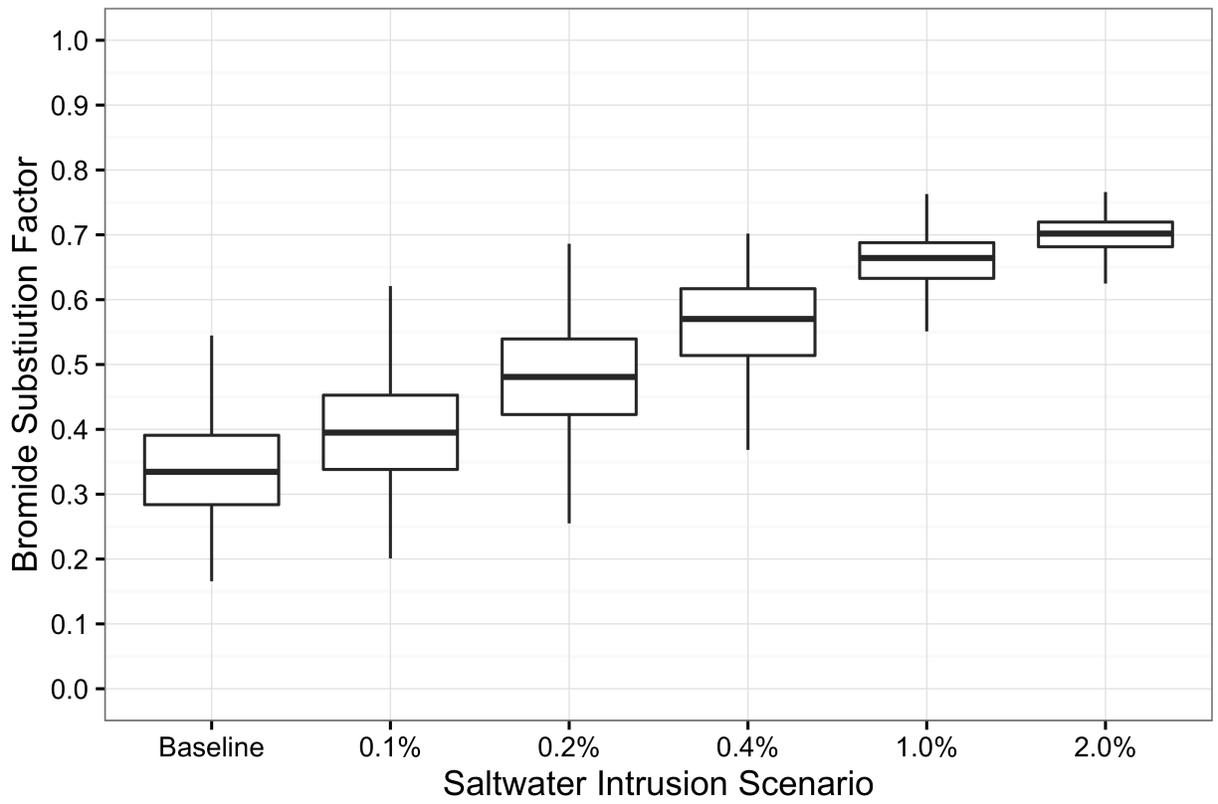


Figure A.2: Boxplot of the BSF for the baseline and saltwater intrusion scenarios with a 2°C change in temperature.

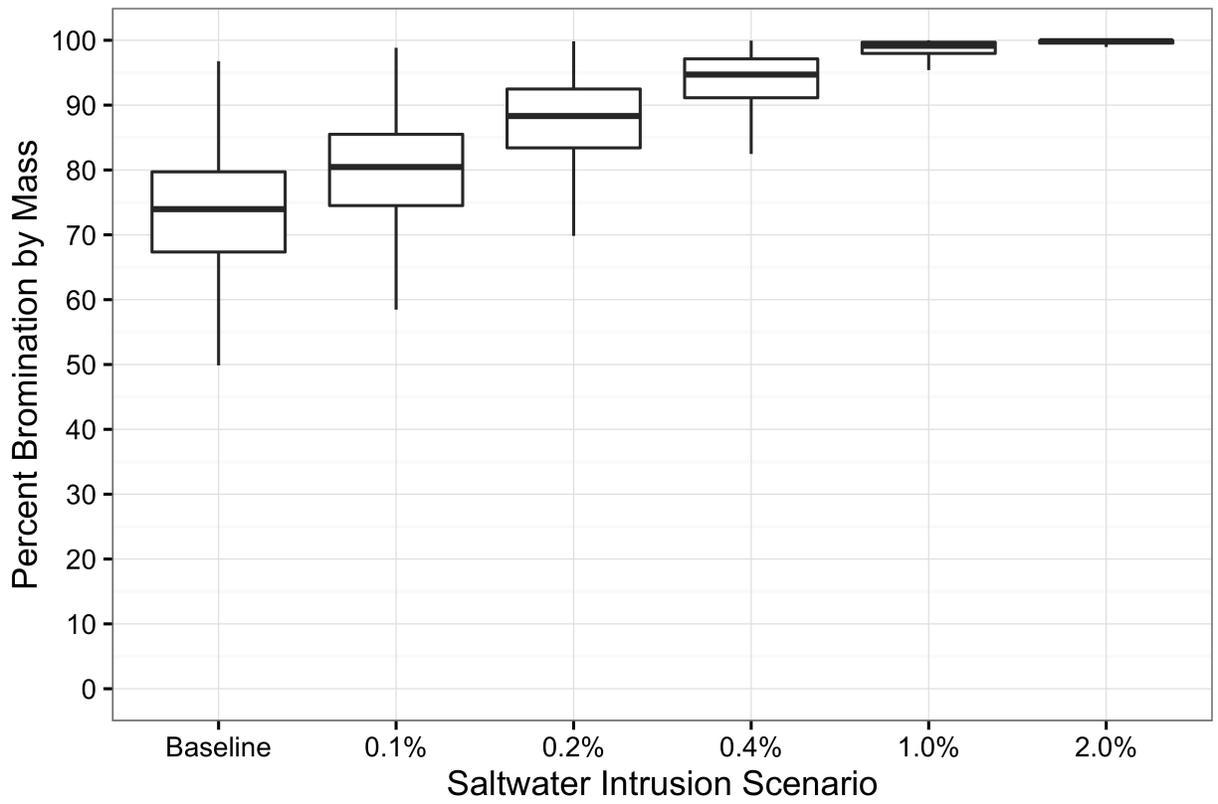


Figure A.3: Boxplot of the percent bromination for the baseline and saltwater intrusion scenarios with a 2°C change in temperature.

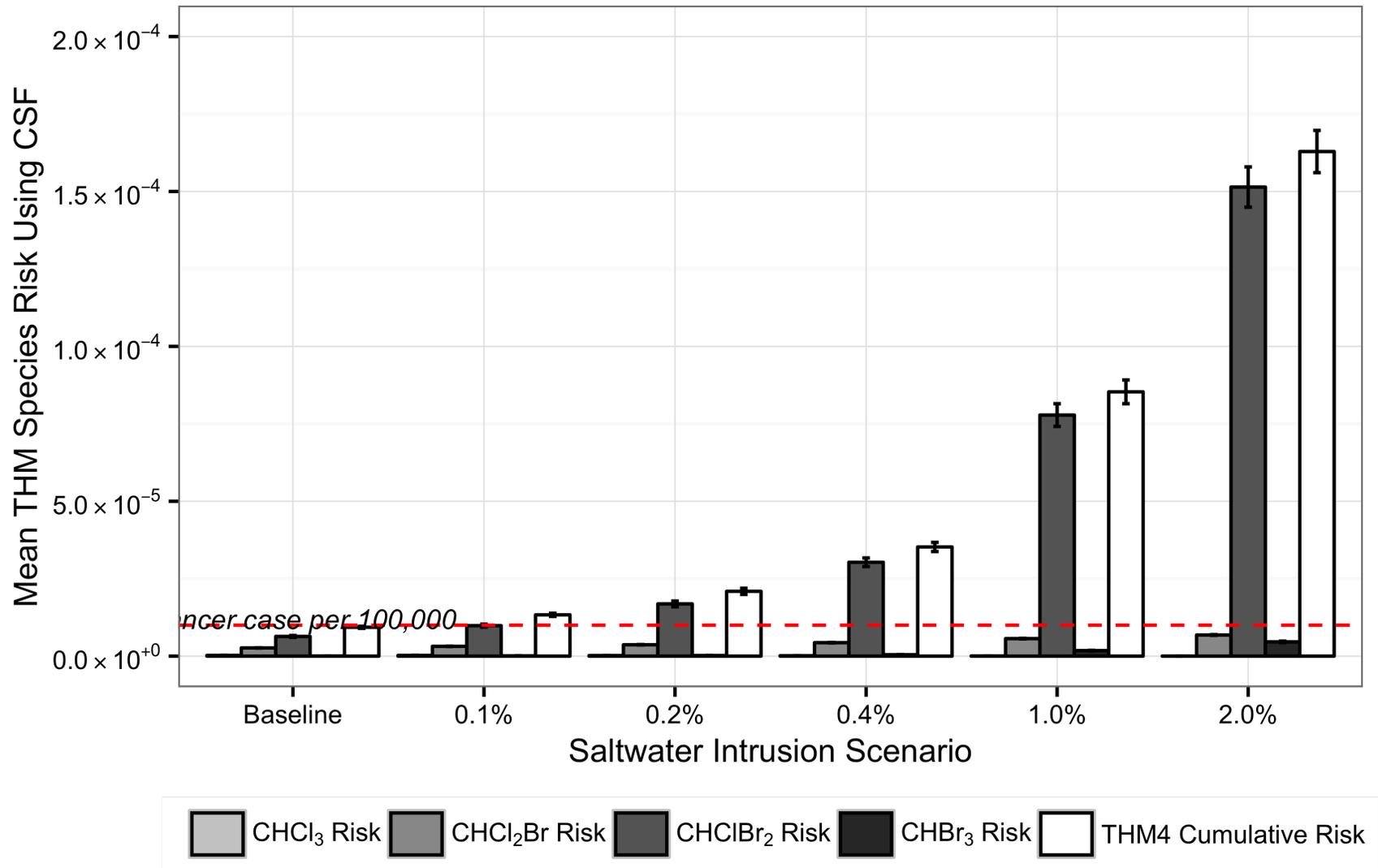


Figure A.4: Mean THM species risk calculated using CSFs for the baseline and climate scenarios with a 2°C change in temperature; dashed line shows the 10^{-5} risk threshold, or 1 additional cancer case per 100,000 people exposed.

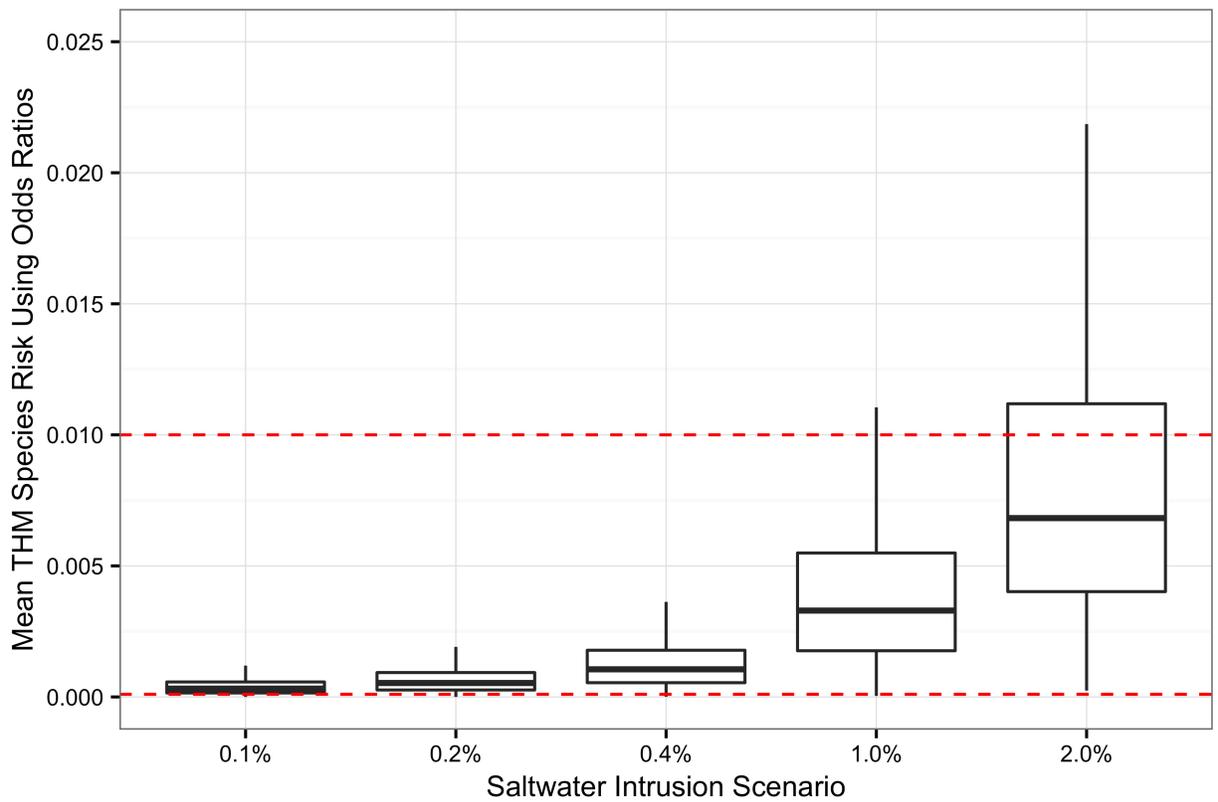


Figure A.5: Boxplot of TTHM risk calculated using ORs for the baseline and climate scenarios with a 2°C change in temperature; dashed lines show the 10^{-2} and 10^{-4} risk thresholds, or 1 additional cancer case per 100 and 10,000 people exposed, respectively.

Appendix B:

Estimated coal-fired power plant bromide contributions to disinfection by-product risk in the Monongahela River Basin

B.1 Summary of power plants and oil and gas wastewater treatment facilities in the Monongahela River Basin

Table B.1 summarizes the history of coal-fired power plants operating wet FGD and Table B.2 summarizes the centralized waste treatment facilities with NPDES permits accepting oil and gas wastewater in the Monongahela River Basin.

Table B.1: Historical Monongahela Basin coal-fired power plants (with NAICS Code 22) operating wet FGD (EIA, 2018).

EIA plant name	EIA plant code	State	First generating unit in service	Wet FGD units in service	Other SO ₂ control in service	Status as of 2016	Nameplate capacity (wet scrubbed), MW	Primary energy source
Harrison	3944	WV	12/1972	12/1994; 12/1994; 12/1994	None	Operational (no planned retirement listed)	2052 (2052)	Bituminous
Hatfields Ferry	3179	PA	11/1969	6/2009; 10/2009; 10/2009	None	Retired 10/2013	1728 (1728)	Bituminous
Fort Martin	3943	WV	10/1967	11/2009; 12/2009	None	Operational (no planned retirement listed)	1152 (1152)	Bituminous
Longview	56671	WV	12/2011	12/2011	None	Operational (no planned retirement listed)	808 (808)	Bituminous
Mitchell	3181	PA	8/1963	8/1982	None	Retired 10/2013	299 (299)	Bituminous

Table B.2: Centralized waste treatment facilities with NPDES permits accepting oil and gas wastewater in the Monongahela River Basin (PADEP, 2018).

Permit	Facility	Type	Estimated current Br load using DMR data (reported TDS, reported flow, assumed Br/TDS = 0.01)	Estimated Br load at maximum permitted flow and average Br concentration
WVR00521948	Fairmont Brine Processing, LLC	CWT with NPDES	< 5 kg/day	1 kg/day (0.6 mg/L Br and 0.288 mgd)
PA0218073	Scottdale Treatment Facility	CWT with NPDES	< 5 kg/day	20 kg/day (28.8 mg/L Br and 0.16 mgd)
PA0217778	Dawson Treatment Plant	CWT with NPDES	< 5 kg/day	50 kg/day (190 mg/L Br 13,800 mg/L TDS assuming Br/TDS=0.014; 0.06 mgd)
PA0219312	Brinkerton Treatment Facility	CWT with NPDES	< 5 kg/day	80 kg/day (110 mg/L Br for 8150 mg/L TDS assuming Br/TDS=0.014; 0.2 mgd)
PA0254185	Reserved Env Svcs Treatment Facility	CWT with recycle (zero discharge)	–	–

B.2 Summary of flow and bromide data in the Monongahela River Basin

Table B.3 summarizes the flow conditions in the Monongahela River at USGS gage 03075070 at Elizabeth, PA for the period of record and water years of interest. Table B.4 shows the correlation between bromide monitoring locations, calculated using Mann-Whitney tests.

Table B.3: Summary statistics of daily flow for USGS gage 03075070 at Elizabeth, PA for the period of record and the water years studied (USGS, 2018). Statistics are reported to three significant figures in m³/sec.

Water Year	Minimum	Median	Mean	Maximum
1998	23.4	217	298	1660
2013	48.7	216	275	1540
2014	33.7	138	233	1510
2015	15.0	161	277	2410
2016	13.5	137	218	1240
2017	18.5	231	317	2600
Period of Record	5.83	152	163	4470

Table B.4: Mann-Whitney tests comparing bromide monitoring location data.

	DWTP	WQN	3RQ
DWTP	1	-	-
WQN	0.811	1	-
3RQ	0.012	0.048	1

Table B.5: Site information and summary statistics by monitoring site for water years 2013-2017.

Site Name	Sampling Frequency	# Obs	# BDL observations (%) Censored)	DL ($\mu\text{g/L}$)	Data Censoring Method ($\mu\text{g/L}$)			
					Zero	$\frac{1}{2}$ DL	DL	ROS
WQN	Monthly	83	27 (32.5)	25/50	41.4 <i>53.5</i> (46.7)	41.4 <i>54.7</i> (45.3)	41.4 <i>55.9</i> (44.1)	41.4 <i>56.6</i> (43.4)
DWTP	Monthly	82	2 (2.4)	20	50.0 <i>61.3</i> (43.8)	50.0 <i>61.5</i> (43.6)	50.0 <i>61.7</i> (43.4)	50.0 <i>61.7</i> (43.3)
3RQ	Weekly (2009-2016) Monthly (2016-2017)	171	69 (40.4)	20	40.0 <i>55.5</i> (65.3)	40.0 <i>56.5</i> (64.3)	40.0 <i>57.7</i> (63.4)	40.0 <i>58.7</i> (62.7)
All	Variable	336	98 (29.2)	-	42.1 <i>56.5</i> (54.7)	42.1 <i>57.4</i> (53.8)	42.1 <i>53.0</i> (43.4)	42.1 <i>58.9</i> (52.5)

The median is the top value, the mean in *italics*, and the standard deviation in parenthesis.

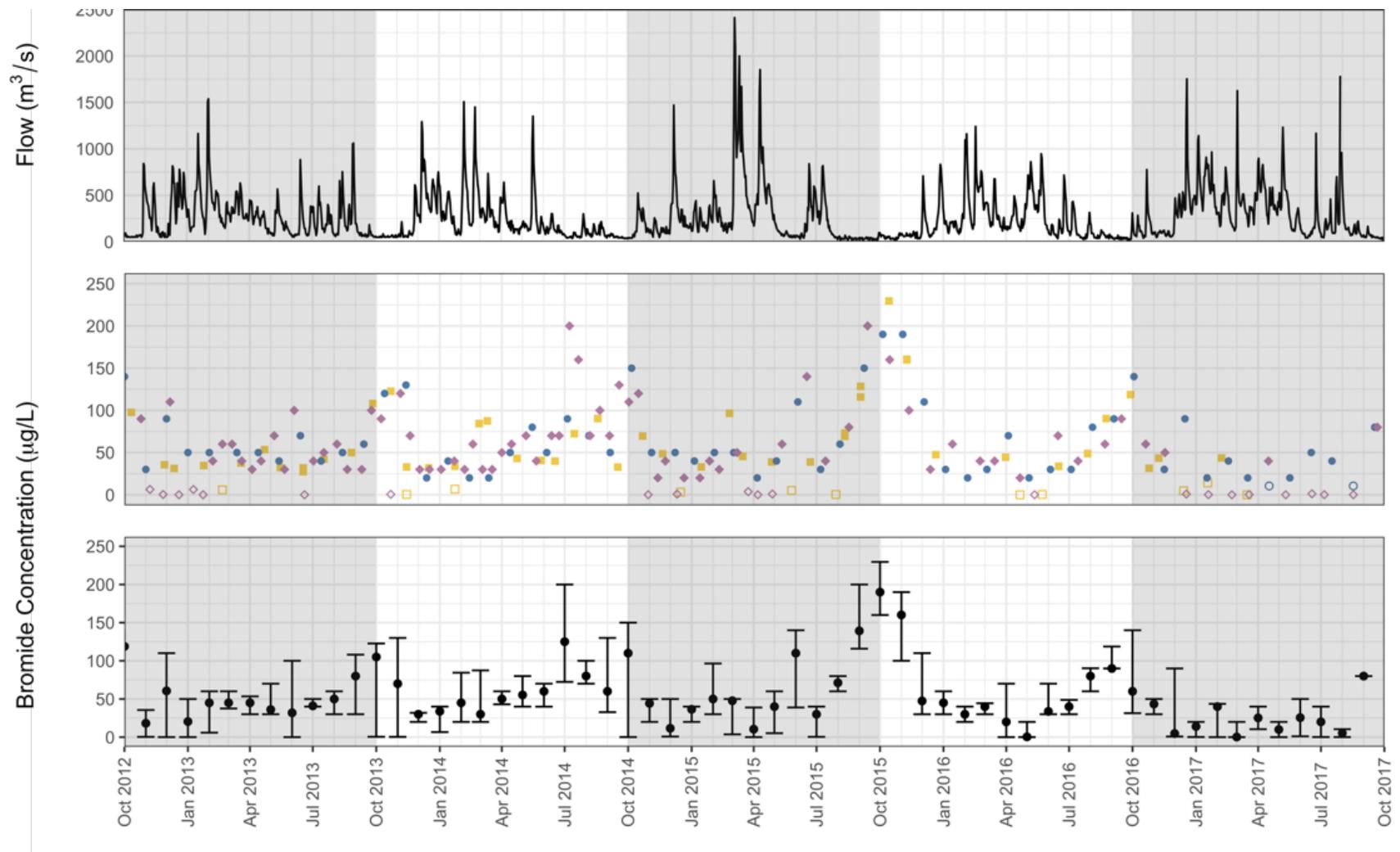


Figure B.1: Daily flow at Elizabeth, PA (USGS gage 03075070; top panel); bromide observations (middle panel) at the observation sites; minimum, median, and maximum observed monthly bromide concentrations across all sites (bottom panel); 3RQ data are shown as yellow squares, WQN data as purple triangles, and the drinking water treatment plant data as blue circles. Imputed below detection bromide data are shown as open symbols. The shaded regions denote water years. One elevated 3RQ value from October 15, 2012 is not shown ($500 \mu\text{g/L}$) to avoid compression of the rest of the data.

B.3 Summary of coal, bromide, and THM risk calculations

Figure B.2 summarizes coal consumption, delivery, and stocks for each plant in the analysis for Water Years 2013-2017. Figure B.3 shows the bromide content and total bituminous coal deliveries by county for each plant in the analysis. Subbituminous coal burned at these plants is minimal (see Figure B.2), thus are not shown. Table B.6 summarizes the rank and number of samples in COALQUAL for the counties from which plants in the Monongahela River Basin received bituminous coal deliveries.

Tables B.9 through B.12 summarize the bromide load estimates for the four CWTs in the Monongahela River Basin. Italicized data were not used in the analysis due to likely data entry errors.

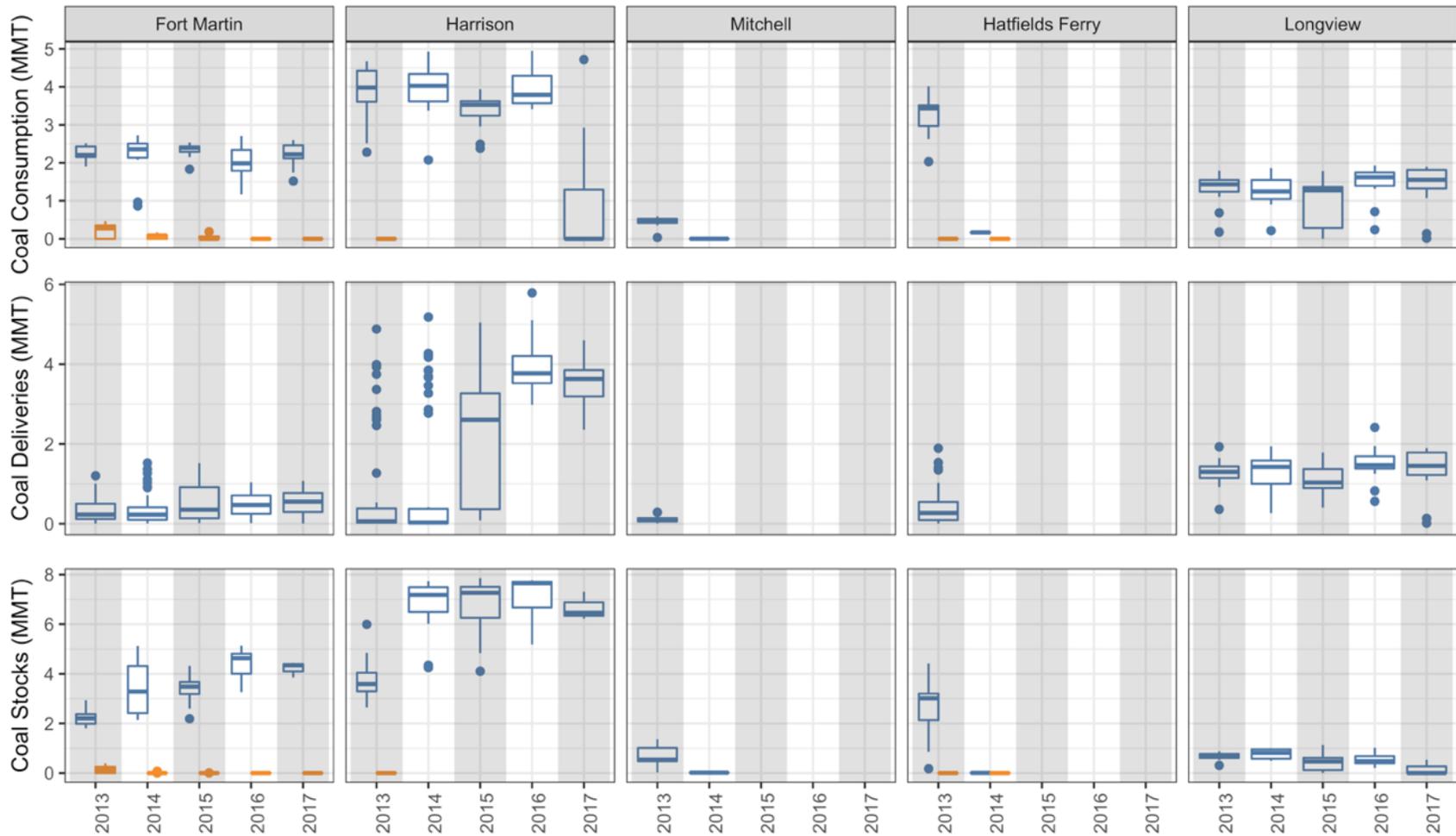


Figure B.2: Boxplots describing coal consumption (top), delivery (center), and stocks (bottom) by water year 2013-2017 and plant. The boxplot shows the median, 25th, and 75th percentiles and the whiskers extend to 1.5 times the interquartile range. Plant names are noted at the top of each panel. Blue boxplots show bituminous coal and orange subbituminous coal.

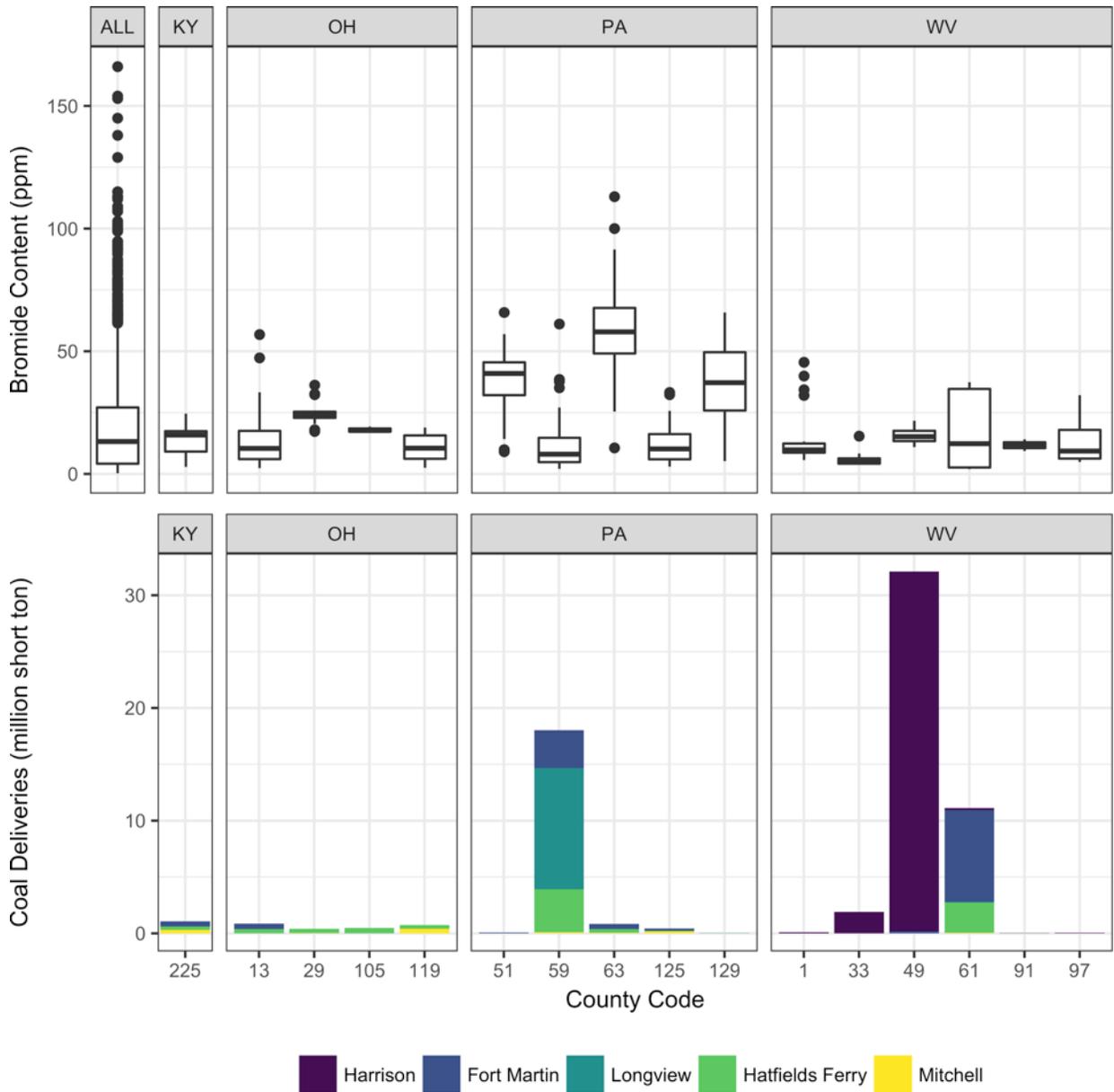


Figure B.3: Bromide content (top) and total bituminous coal deliveries (bottom) by county origin for each plant. The color indicates the plant.

Table B.6: Summary of bituminous coal samples by county.

State	County	County Code	Bituminous Coal Subrank	# Samples
Kentucky	Union	225	High Volatile A	1
			High Volatile B	10
			High Volatile C	7
Ohio	Belmont	13	High Volatile A	75
			High Volatile B	20
	Columbiana	29	High Volatile A	18
			High Volatile B	4
	Meigs	105	High Volatile B	3
	Muskingum	119	High Volatile B	20
			High Volatile C	1
Medium Volatile			26	
Pennsylvania	Fayette	51	High Volatile A	24
			High Volatile C	2
			Low Volatile	2
	Greene	59	High Volatile A	45
			High Volatile B	1
			Medium Volatile	31
	Indiana	63	High Volatile A	15
			High Volatile B	1
			High Volatile A	55
	Washington	125	High Volatile C	1
			Medium Volatile	8
Westmoreland	129	High Volatile A	11	
West Virginia	Barbour	1	High Volatile A	28
	Harrison	33	High Volatile A	8
	Marion	49	High Volatile A	4
	Monongalia	61	High Volatile A	8
	Taylor	91	High Volatile A	2
	Upshur	97	High Volatile A	7

Table B.7: THM species-specific cancer slope factors.

	CSF (per mg/kg-day)	Reference
BDCM	6.2×10^{-2}	(USEPA, 1987)
DBCM	8.4×10^{-2}	(USEPA, 1990)
CHBr ₃	7.9×10^{-3}	(USEPA, 1993)

Table B.8: Mann-Whitney tests comparing bromide load estimates and coal consumption data.

	Year	Water	Bromide load					Coal consumption				
		1998	2013	2014	2015	2016	1998	2013	2014	2015	2016	
Harrison	2013	0.008	-	-	-	-	0.887	-	-	-	-	
	2014	0.032	0.703	-	-	-	0.799	0.887	-	-	-	
	2015	0.000	0.000	0.000	-	-	0.039	0.028	0.014	-	-	
	2016	0.038	0.000	0.000	0.000	0.887	0.977	0.977	0.028	-	-	
	2017	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.000	
Fort Martin	2013	-	-	-	-	-	-	-	-	-	-	
	2014	-	0.000	-	-	-	-	0.556	-	-	-	
	2015	-	0.000	0.000	-	-	-	0.715	0.732	-	-	
	2016	-	0.000	0.000	0.000	-	-	0.118	0.139	0.192	-	
	2017	-	0.000	0.000	0.000	0.000	-	0.270	0.244	0.302	0.636	
Longview	2013	-	-	-	-	-	-	-	-	-	-	
	2014	-	0.001	-	-	-	-	0.630	-	-	-	
	2015	-	0.000	0.000	-	-	-	0.112	0.506	-	-	
	2016	-	0.000	0.000	0.000	-	-	0.143	0.128	0.026	-	
	2017	-	0.031	0.515	0.000	0.000	-	0.347	0.266	0.035	0.843	
Hatfields Ferry	2013	-	-	-	-	-	-	-	-	-	-	
	2014	-	0.000	-	-	-	-	0.572	-	-	-	
	2015	-	-	-	-	-	-	-	-	-	-	
	2016	-	-	-	-	-	-	-	-	-	-	
	2017	-	-	-	-	-	-	-	-	-	-	
Mitchell	2013	0.000	-	-	-	0.052	-	-	-	-	-	
	2014	0.000	0.000	-	-	-	0.154	0.154	-	-	-	
	2015	-	-	-	-	-	-	-	-	-	-	
	2016	-	-	-	-	-	-	-	-	-	-	
	2017	-	-	-	-	-	-	-	-	-	-	
Total	2013	0.000	-	-	-	-	0.000	-	-	-	-	
	2014	0.000	0.000	-	-	-	0.000	0.000	-	-	-	
	2015	0.000	0.000	0.000	-	-	0.000	0.000	0.089	-	-	
	2016	0.000	0.000	0.149	0.000	-	0.000	0.000	0.887	0.114	-	
	2017	0.000	0.000	0.000	0.000	0.000	0.478	0.000	0.000	0.005	0.000	

Table B.9: Discharge monitoring data for NPDES WV0116408-Fairmont Brine (Patel, 2018).

Reporting month	Br as 24-hr composite, 1/month (mg/L)	Average monthly flow (mgd)	Max daily flow (mgd)	Estimated Br load at average flow (kg/d)	Estimated Br load at maximum flow (kg/d)
Limit	–	–	0.288	–	–
07/2014	Not reported	0.063	0.063	–	–
08/2014	Not reported	0.063	0.063	–	–
09/2014	Not reported	0.21	0.21	–	–
10/2014	Not reported	0.09975	0.126	–	–
11/2014	Not reported	0.2225	0.235	–	–
12/2014	Not reported	0.25	0.25	–	–
01/2015	Not reported	0.275	0.275	–	–
02/2015	Not reported	0.15	0.15	–	–
03/2015	Not reported	0.25	0.25	–	–
04/2015	Not reported	0.021	0.021	–	–
05/2015	< 0.05	0.042	0.042	< 0.01	< 0.01
06/2015	< 0.05	0.06	0.06	< 0.01	< 0.01
07/2015	< 0.05	0.15	0.15	0.03	0.03
08/2015	0.33	0.02	0.02	0.02	0.02
09/2015	0.29	0.14	0.2	0.15	0.2
10/2015	0.05	0.042	0.042	0.0079	0.01
11/2015	2.59	0.0225	0.03	0.221	0.3
12/2015	1.24	0.035	0.05	0.16	0.2
01/2016	Not reported	No flow	No flow	–	–
02/2016	< 0.05	0.06	0.08	< 0.01	< 0.02
03/2016	2.35	0.03	0.03	0.3	0.3
04/2016	0.89	0.044	0.046	0.15	0.15
11/2016	57.3	0.05	0.05	11	11
12/2016	13	0.0365	0.038	1.8	1.9
01/2017	8.93	0.0546	0.0546	1.85	1.85
Summary for 5/2015-1/2017, including < values at reporting limit:					
Average	6	0.056	0.064	1.11	1.13
Median	0.6	0.043	0.048	0.151	0.187

Table B.10: Discharge monitoring data for NPDES PA0218073-Scottsdale (PADEP, 2018). Italicized data are excluded from analysis due to likely entry error.

Reporting month	Average monthly					Maximum daily				
	Flow (mgd)	Br (mg/L)	TDS (mg/L)	Br/TDS	Estimated Br load (kg/day)	Flow (mgd)	Br (mg/L)	TDS (mg/L)	Br/TDS	Estimated Br load (kg/day)
Limit	–	–	–	–	–	0.16	–	–	–	–
09/2017	0.005	27.8	3,580	0.0171	0.526	0.01	28.1	3,600	0.00781	1.06
10/2017	0.005	34.8	3,695	0.0207	0.659	0.02	36.8	3,960	0.00929	2.79
<i>11/2017</i>	<i>0.0046</i>	<i>45.4</i>	<i>132</i>	<i>0.756</i>	<i>0.790</i>	<i>0.009</i>	<i>65.6</i>	<i>262</i>	<i>0.250</i>	<i>2.23</i>
12/2017	0.006	23.1	3,350	0.0152	0.525	0.012	31.4	3,420	0.00918	1.43
01/2018	0.006	15.3	2,360	0.0143	0.347	0.01	21.7	3,400	0.00638	0.821
02/2018	0.01	13.7	1,501	0.0200	0.517	0.02	23.3	2,620	0.00889	1.76
03/2018	0.012	26.5	3,045	0.0191	1.20	0.021	27.1	3,330	0.00814	2.15
04/2018	0.014	26.7	3,120	0.0188	1.41	0.025	28.8	3,180	0.00906	2.73
05/2018	0.01	27.3	3,005	0.0200	1.03	0.02	29.4	3,040	0.00967	2.23
06/2018	0.007	37.5	2,990	0.0276	0.992	0.014	39.9	3,020	0.0132	2.11
Average excluding 11/2017	0.008	25.8	2,960	0.0192	0.802	0.02	29.6	3,290	0.00907	1.90
Median excluding 11/2017	0.007	26.7	3,045	0.0191	0.659	0.02	28.8	3,330	0.00906	2.11

Table B.11: Discharge monitoring data for NPDES PA0217778-Dawson (PADEP, 2018). Italicized data are excluded from analysis due to likely entry error.

Reporting month	Average monthly				Maximum daily			
	DMR	DMR	DMR	Estimated	DMR	DMR	DMR	Estimated
	flow	TDS	TDS	Br load	flow	TDS	TDS	Br load
	(mgd)	(mg/L)	(lb/day)	(kg/day)	(mgd)	(mg/L)	(lb/day)	(kg/day)
Limit	–	–	–	–	0.06	–	–	–
09/2017	0.0002	11,300	18.84	0.120	0.0006	12,500	62.55	0.398
10/2017	0.00025	10,540	21.97	0.140	0.005	11,200	467	2.97
<i>11/2017</i>	<i>0.0002</i>	<i>21</i>	<i>12,950</i>	<i>82.4</i>	<i>0.0007</i>	<i>76</i>	<i>13000</i>	<i>82.7</i>
12/2017	0.0003	13,250	33.15	0.211	0.0009	13,800	103.58	0.659
01/2018	0.001	13,275	110	0.700	0.003	18,200	455	2.90
02/2018	0.0014	13,850	161.7	1.03	0.01	15,100	1259	8.01
03/2018	0.0003	6,290	15.73	0.100	0.001	7,240	60.38	0.384
04/2018	0.001	1,270	10.59	0.0674	0.003	1,320	33.02	0.210
05/2018	0.001	13,700	114	0.725	0.002	138,000	230	1.46
06/2018	0.00014	15,550	18	0.115	0.00067	15,700	87	0.554
Average excluding 11/2017	0.0006	11,003	56	0.36	0.0029	25,900	306	1.95
Median excluding 11/2017	0.0003	13,250	22	0.14	0.002	13,800	104	0.660

Table B.12: Discharge monitoring data for NPDES PA0219312-Brinkerton (PADEP, 2018). Italicized data are excluded from analysis due to likely entry error.

Reporting month	DMR flow (mgd)	Maximum daily	
		DMR TDS (mg/L)	Estimated Br load (kg/day)
Limit	0.2	–	–
02/2017	0.014	5,560	4.13
03/2017	0.016	5,740	4.87
<i>04/2017</i>	<i>-0.015</i>	<i>6,890</i>	–
05/2017	0.025	8,080	10.7
06/2017	0.0201	10,600	11.3
07/2017	0.02	9,920	10.5
08/2017	0.02	9,720	10.3
09/2017	0.01	9,800	5.19
10/2017	0.003	9,300	1.48
11/2017	0.009	6,720	3.21
12/2017	0.0035	9,800	1.82
01/2018	0.003	7,720	1.23
02/2018	0.01	8,220	4.36
03/2018	0.003	9,440	1.50
04/2018	0.02	6,070	6.43
05/2018	0.006	5,500	1.75
Average excluding 4/2017	0.01	5,570	1.77
Median excluding 4/2017	0.01	8,150	4.24

B.4 Bromide load comparisons

B.5 Monthly bromide concentration contributions

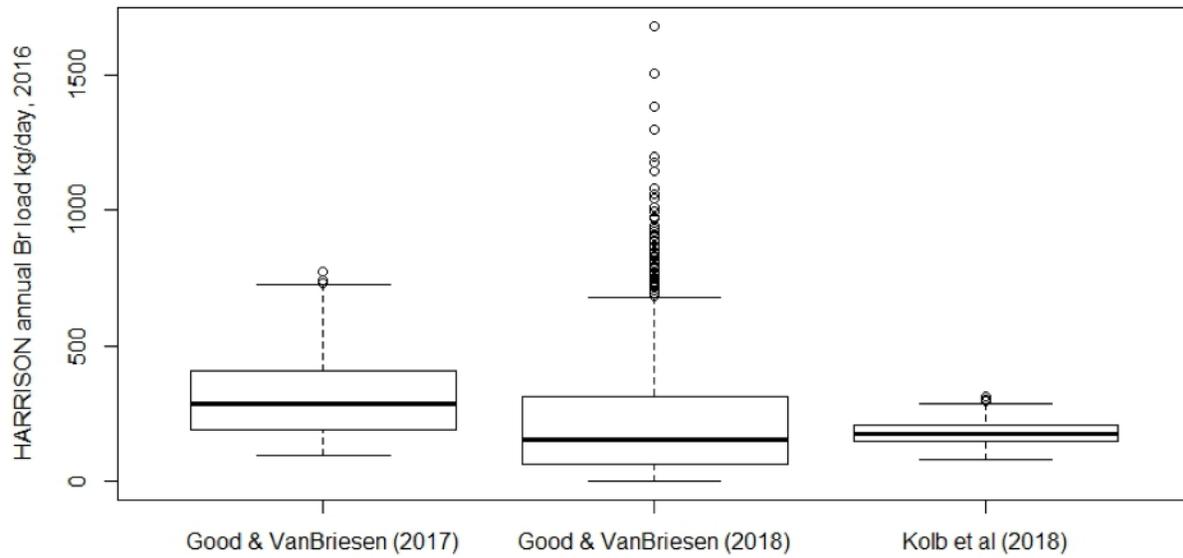


Figure B.4: Comparison of 2016 bromide load for Harrison Power Plant estimates with Good and VanBriesen (2017, 2018).

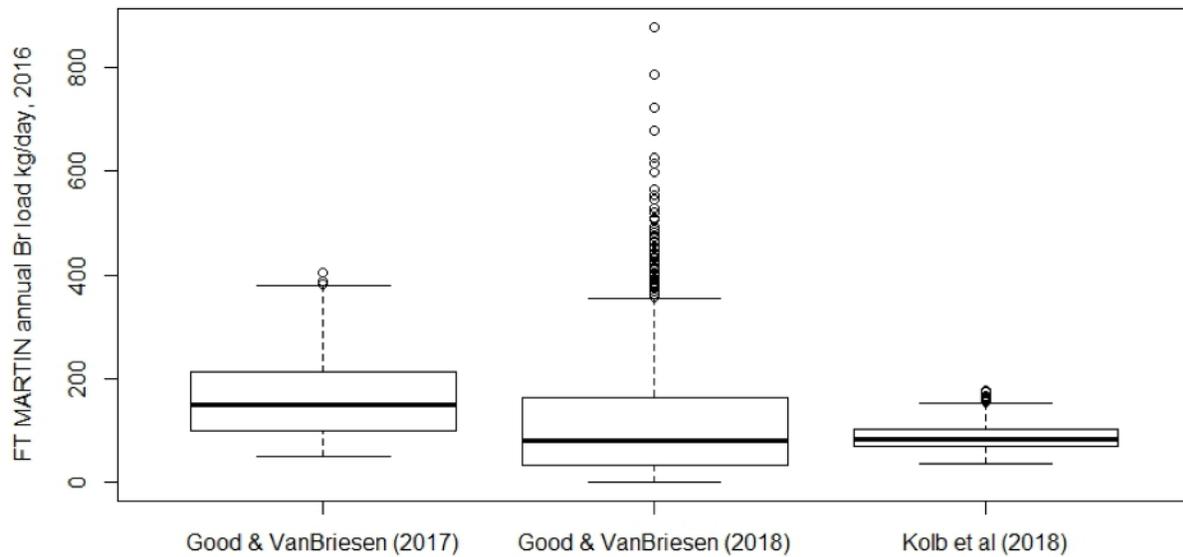


Figure B.5: Comparison of 2016 bromide load for Fort Martin Power Plant estimates with Good and VanBriesen (2017, 2018).

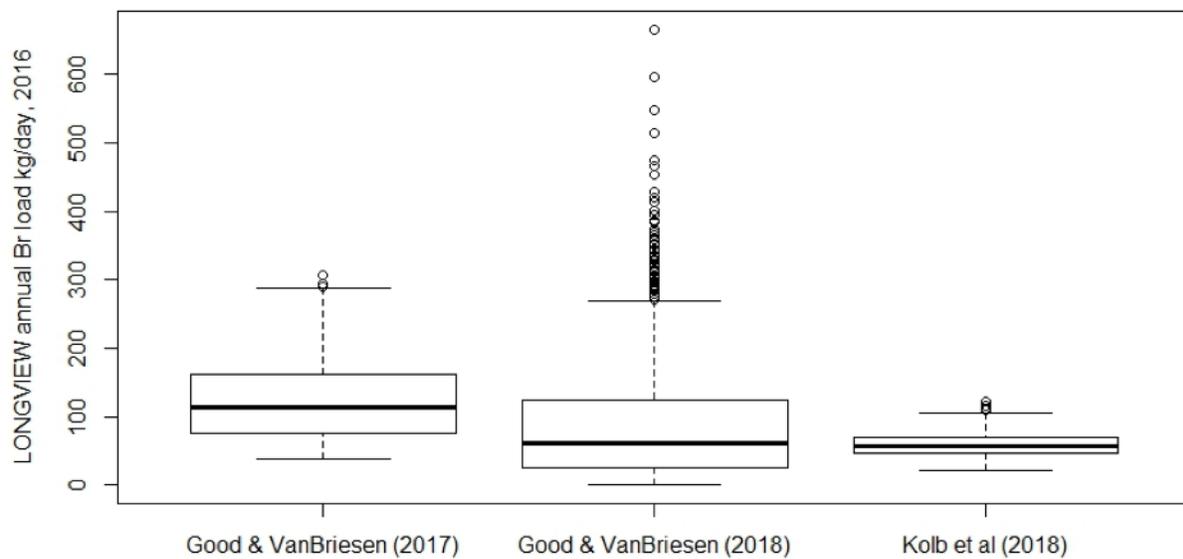


Figure B.6: Comparison of 2016 bromide load for Longview Power Plant estimates with Good and VanBriesen (2017, 2018).

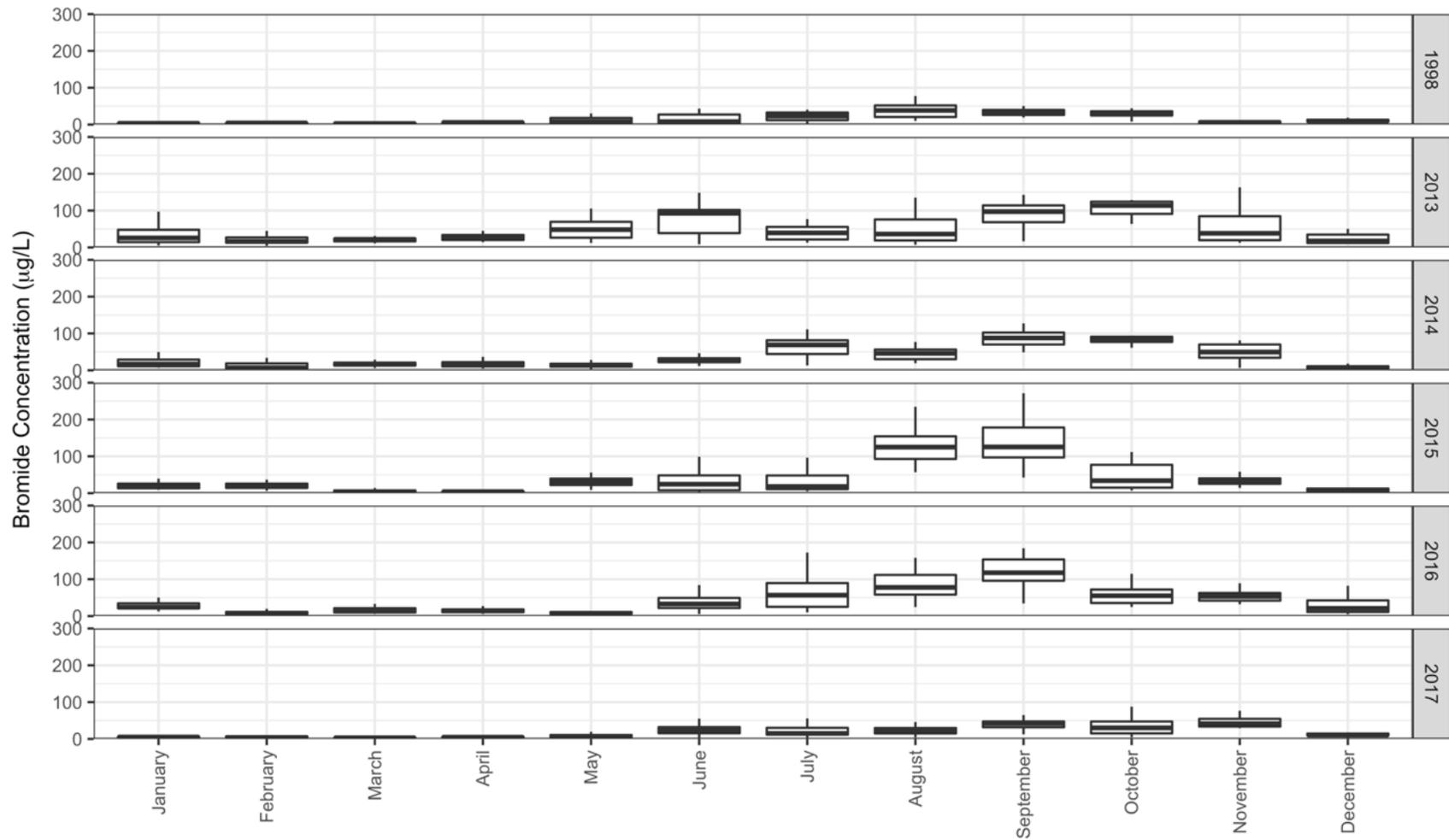


Figure B.7: Boxplots showing the monthly bromide concentration contribution calculated from the median bromide load for the range of flow conditions in the modeled month and water year. Boxplots show the median, 25th, and 75th percentiles; whiskers extent to 1.5 times the interquartile range.