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Source Water Quality Assessment and Source Water Characterization for Drinking Water Protection

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ABSTRACT

Source water quality plays a critical role in maintaining the quality and supply of drinking water, yet it can be negatively affected by human activities. In Pennsylvania, coal mining and treatment of conventional oil and gas drilling produced wastewaters have affected source water quality for over 100 years. The recent unconventional natural gas development in the Marcellus Shale formation produces significant volumes of wastewater containing bromide and has the potential to affect source water quality and downstream drinking water quality. Wastewater from coal-fired power plants also contains bromide that may be released into source water. Increasing source water bromide presents a challenge as even small amounts of bromide in source water can lead to carcinogenic disinfection by-products (DBPs) in chlorinated finished drinking water. However, bromide is not regulated in source water and is not removed by conventional drinking water treatment processes.

The objective of this work is to evaluate the safe bromide concentration in source water to minimize the cancer risk of trihalomethanes - a group of DBPs - in treated drinking water. By evaluating three years of water sampling data from the Monongahela River in Southwestern Pennsylvania, the present analysis reached three conclusions. First, bromide monitoring for source water quality should be taken at drinking water intake points. Water sample types (river water samples vs drinking water intake samples) can lead to different water quality conclusions and thus affect regulatory compliance decision-making. Second, bromide monitoring at drinking water intake points can serve as a predictor for changes in heavily brominated trihalomethanes concentrations in finished water. Increasing bromide in source water can serve as an early warning sign of

increasing formation of heavily brominated trihalomethanes and their associated cancer risks in drinking water. Finally, this work developed a statistical simulation model to evaluate the effect of source water bromide on trihalomethane formation and speciation and to analyze the changing cancer risks in water associated with these changing bromide concentrations in the Monongahela River. The statistical simulation method proposed in this work leads to the conclusion that the bromide concentration in source water must be very low to prevent the adverse health effects associated with brominated trihalomethanes in chlorinated drinking water. This method can be used by water utilities to determine the bromide concentration in their source water that might indicate a need for process changes or by regulatory agencies to evaluate source water bromide issues.

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ABBREVIATIONS AND NOTATIONS

DBPs	Disinfection Byproducts
D/DBP Rule	Disinfectants and Disinfection Byproduct Rule
EPA	Environmental Protection Agency
HAAs	Haloacetic acids
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
PaDEP	Pennsylvania Department of Environmental Protection
TDS	Total Dissolved Solids
THMs	Trihalomethanes
TTHM	Total Trihalomethanes

Chapter 1. Introduction

1.1 Introduction

Large river systems support aquatic life, provide water for drinking and irrigation, enable transportation, and accept and dilute wastewater discharges. Large rivers play a critical role in maintaining the quality and supply of drinking water (USEPA, 2013), yet their water quality can be negatively affected by human activities (Telci et al., 2009). Coal mining and conventional oil and gas drilling activities produce wastewaters that have affected surface water quality in Pennsylvania for over 100 years (PaDEP, 2002). The most recent unconventional natural gas drilling is developing rapidly in the Marcellus and Utica Shale formation and produces significant volumes of high salinity wastewater with potential to negatively affect surface water quality and downstream drinking water quality (Handke, 2008; Wilson and VanBriesen, 2013b). The current challenge for the Monongahela River in Southwestern Pennsylvania is associated with changing surface water quality in response to these changes in watershed activities and variability in large river flow conditions. The changing source water quality directly affects the drinking water quality, as the Monongahela River serves as a drinking water source for 17 drinking water treatment plants in Pennsylvania and West Virginia, and provides drinking water to approximately 1 million people (PaBulletin, 2009).

In 2008, the Pennsylvania Department of Environmental Protection (PaDEP) observed total dissolved solids (TDS) and sulfate concentrations exceeded water quality standards at source water intakes at drinking water facilities along the Monongahela River (Warren,

2010). In addition, significant increases of bromide concentrations have been observed concurrent with expanded unconventional gas development and disposal of bromide-containing produced water (USEPA, 2011b). Surface water bromide concentrations in the United States (US) are typically quite low (14-200 μg/L) (Stanley et al., 2010). Increasing source water bromide presents a unique challenge for large river monitoring as even small amounts of bromide in source water can lead to carcinogenic disinfection by-products (DBPs) in finished water during chlorination; however, bromide is not regulated in the source water and neither removed by conventional drinking water treatment process (Francis et al., 2010).

Elevated bromide concentration in source water leads to increasing total formation of DBPs and more brominated-DBPs speciation in drinking water (Symons et al., 1998; Bond et al., 2014). Brominated-DBPs are well known to be associated with negative human health effects at low concentrations and are more carcinogenetic than chlorinated DBPs (Richardson et al., 2003; Richardsona et al., 2007). However, the effect of changing source water condition together with increasing bromide and their potential to affect DBPs formation and speciation in drinking water has not been evaluated in the Monongahela River basin. The relationship between source water bromide and DBPs in drinking water must be understood to better manage wastewater disposal and minimize human health risk from drinking water. It is also critical to understand the health risk of DBPs contributed by bromide to determine in-stream bromide concentrations that are protective for the health of people using the Monongahela River water as their drinking water source, and for the expanding development of shale gas drilling in other shale

formation areas.

1.2 Problem Identification

Large river systems, such as the Monongahela River, exhibit a high degree of heterogeneity in composition and characteristics in space and time (Sanders et al., 1977; USGS, 1994; Jarvie et al., 2002; Soininen, 2004; Chen et al., 2012). The Monongahela River has historically experienced coal mining, oil and gas extraction, and recently Shale gas development via horizontal drilling and high volume hydraulic fracturing, which make water quality assessment through representative sampling difficult. These energy extraction challenges can threaten ambient surface water quality through landscape changes and wastewater management choices.

To assess surface water quality, water samples are collected, analyzed and compared with water quality criteria (Reinelt et al., 1992; Strobl and Robillard, 2008). Sampling plans for large rivers are often designed based on convenience, experience, expert intuition, and other subjective judgments (Dixon and Chiswell, 1996; Strobl and Robillard, 2008; Khalil and Ouarda, 2009). However, the high degree of heterogeneity of water quality and new water quality challenges imposed by energy extraction activities in the region make accurate assessment of water quality difficult. Further, the source water bromide collected at drinking water treatment plants represents the drinking water intake quality, and also directly links to the THMs formation in the finished water, but these bromide concentrations at the intake points may not represent the overall water quality of the whole Monongahela River. Thus, to evaluate the potential to use drinking water intake

bromide data to inform decisions regarding in-stream safe bromide level first requires the evaluation of the spatial and temporal variability in water quality in the river.

The bromide concentrations in the river were variable over the 3 sampling years from 2009-2012. Drinking water plants on the river do not remove bromide; they do disinfect the water with chlorine, which is necessary to remove bacteria and pathogens from drinking water. Although disinfectant eliminates microbial risk, it reacts with natural organic matter and bromide in the water to form DBPs (USEPA, 2000a). The presence of even small amounts of bromide in source water can lead to the production of DBPs in drinking water plants. Higher level of bromide leads to increasing formation of DBPs and especially increases incorporation of bromide in DBPs. In 2010, the Pittsburgh Water and Sewer Authority observed significant increase of trihalomethanes (THMs) concentration in its finished drinking water, especially brominated-THM species, suggesting a rising bromide level in the Allegheny River (States et al., 2013). Increasing concentrations of TTHMs and brominated THMs were also observed in finished water that used the Monongahela River as source water (Handke, 2008; Wilson, 2013b). However, the effect and potential impact of varying bromide concentrations on DBP formation and speciation in the Monongahela River basin has not previously been evaluated. Prior work indicates that the presence of bromide complicates DBPs control in drinking water due to the complexity of bromine chemistry (Symons et al., 1998). Thus, it is critical to evaluate the rapid changes of source water bromide and their impacts on the formation and speciation of finished water DBPs (especially THMs) at six drinking water treatment plants on the Monongahela River.

The discharge of bromide has been left largely unregulated in the US since bromide has a high human and ecotoxity thresholds (Flury and Papritz, 1993). While direct bromide toxicity is very unlikely (Vanleeuwen et al., 1983; WHO, 2010), formation of brominated-DBPs in drinking water plants is observed at very low bromide levels. The role of source water bromide in the observed increasing bromination of DBPs is clear; however, the significant differences observed in finished water quality associated with different source water bromide levels makes it difficult to determine a source water bromide concentration that would be protective of drinking water consumers. While EPA is considering setting an in-stream water quality criteria for bromide (DiCosmo, 2012), adequate methods for determining such a standard do not exist.

Compliance of DBPs is based on running annual average (RAA), where samples taken at multiple locations are averaged across location and time to determine compliance. In 2006, the Stage 2 D/DBP Rule was promulgated by EPA to provide additional protection from DBPs by stipulating compliance on a locational RAA to ensure the DBP maximum contaminant level (MCL) is met everywhere in the distribution system (USEPA, 2007); only time-averaging continues. In response to the Stage 2 D/DBP rule (which became effective at large surface drinking water plants (population served ≥ 10,000) in January 2012), drinking water plants altered treatment to increase removal of organic carbon, lowering the chlorine demand in the water, and reducing the chlorine dose necessary to achieve disinfection. These process changes often reduce HAA precursors, reducing the risk associated with finished water HAAs; however, they are less effective for THM

precursor removal (Liang and Singer, 2003; USGS, 2013b). Source water bromide concentrations are not significantly removed by any components of conventional drinking water treatment plants, and thus, bromide continues to be a driver for DBP formation and compliance problems regardless of process changes (Francis et al., 2010; Bond et al., 2014). Therefore, there is critical need to understand the link between bromide and risks of DBPs to assess the safe bromide concentration in source water for the protection of drinking water. Further, it is also critical to develop an analysis structure and methods for regulatory decision-making regarding bromide as well as quantifying data needs for bromide criteria development in other basins.

1.3 Research Objects

The research is to evaluate the safe bromide concentrations in source water for the protection of drinking water quality in Southwestern Pennsylvania. To achieve the objective, the dissertation takes the following steps:

1. Evaluate the temporal and spatial difference of water quality, and evaluate the effect of sampling locations and schedules on surface water quality assessment and regulatory decisions in large river systems; thus, proposing suitable sampling locations for determination of relevant bromide concentrations;
2. Explore the seasonality of bromide concentrations in source water and analyze how changing bromide concentrations affect the formation and speciation of DBPs concentrations in finished water in the Monongahela River basin; and

3. Assess the health risks of DBPs in finished water contributed by bromide in source water, and evaluate the safe in-stream bromide concentrations to minimize the human health risk from drinking water.

1.4 Dissertation Structure

Chapter 1 is this introduction. Chapter 2, 3 and 4 address each of the topics in detail. Chapter 5 summarizes the main conclusions from the topics and discusses the potential for future research in this area.

Chapter 2. The Effect of Sampling Strategies on Assessment of Water Quality Criteria Attainment

2.1 Abstract

Sample locations for large river studies affect the representativeness of data, and thus can alter decisions made regarding river conditions and the need for interventions to improve water quality. The present study evaluated three water-quality sampling programs for Total Dissolved Solid (TDS) assessment in the Monongahela River from 2008-2012. The sampling plans cover the same 145 kilometers of river but differ in frequency, sample location and type (e.g., river water sample vs drinking water plant intake sample). Differences resulting from temporal and spatial variability in sampling lead to different conclusions regarding water quality in the river (including regulatory listing decisions), especially when low flow leads to concentrations at or near the water quality criteria. In the Monongahela River considering the full time period of 2008-2012, drinking water sampling indicates the TDS standard (500 mg/L) was exceeded several times. During the same time period river water sampling showed few values above 500 mg/L. Sampling during low-flow conditions indicated TDS values near or exceeding the TDS standard multiple times in 2008-2010, while evaluation of samples taken throughout the year suggest water meeting the criteria.

2.2 Introduction

The Clean Water Act (CWA) was established in 1972 to restore and maintain the chemical, physical, and biological integrity of the Nation's waters, and regulate quality standards of surface waters (USEPA, 2002c). Meeting the water quality expectations

(called criteria) for rivers and streams is intended to protect water uses for humans as well as aquatic and terrestrial plants and animals (Liebetrau, 1979; Said et al., 2004). Increasing human activities in watersheds often adversely affect ambient surface water quality (Cooper, 1993; Hancock, 2002), which is compared with water quality criteria via sampling (Smith et al., 1997; Strobl and Robillard, 2008). Water bodies not meeting criteria are identified as "impaired" waters and listed following Section 303(d) of the CWA (PaDEP, 2009a), Total Maximum Daily Loads (TMDLs) and compliance plans are developed for listed waters to improve their quality (USEPA, 2012b). Inaccurate assessment of water quality can cause loss of value for public use and unnecessary pollution control cost (when pollutants are overestimated), or alternatively, increased risk to human health and the aquatic environment (when pollutants are underestimated) (Nacht, 1983; Dixon and Chiswell, 1996; Smith et al., 2001; Madrid and Zayas, 2007). To ensure accurate assessment of water, significant attention has been paid to analytical method development (Madrid and Zayas, 2007). Similarly, many international studies have focused on developing surface water sampling strategies including selection of sampling locations, frequencies and methods (WFD, 2000; Heald et al., 2009). However, high varying properties in water bodies could make sampling for representative water sample problematic (WFD, 2009), and less attention has focused on ensuring representativeness of water samples used for decision-making (Sanders and Adrian, 1978; Liebetrau, 1979; Madrid and Zayas, 2007; Chen et al., 2012).

Large river systems exhibit a high degree of heterogeneity in composition and characteristics in space and time (Shelton, 1994), making it difficult to collect

representative samples (Keith, 1990; Crain, 2002). Sampling plans for large rivers are often designed based on convenience, experience, expert intuition, and other subjective judgments, which may lead to bias (Dixon and Chiswell, 1996; Madrid and Zayas, 2007; Khalil and Ouarda, 2009). Spatial distribution of sampling sites, sampling frequency, and the number of sampling sites can affect the quality and applicability of the resulting data, and thus can influence the outcome of water quality assessment (Reinelt et al., 1992; McGeoch and Gaston, 2002; Weilhoefer and Pan, 2007). Applications of statistical methods and consideration of cost-effectiveness influence sampling plans as well (Dixon and Chiswell, 1996; Strobl et al., 2006; Strobl and Robillard, 2008; Khalil and Ouarda, 2009).

The significant consequences of the Section 303(d) listing make the collection and evaluation of unbiased, representative water quality sample data critical (Reinelt et al., 1992). However, establishing criteria for water sampling locations to provide representative samples has received relatively little attention from water quality monitoring governmental agencies (Ward and Vanderholm, 1973; Strobl and Robillard, 2008). The guidance for assessment of impaired waters for Section 303(d) listing by the United States Environmental Protection Agency (EPA) to individual states was very general, without specific parameters for data collection to ensure representativeness (Keller and Cavallaro, 2008).

Currently, there are two dominant approaches in the United States (US) for *geographical sampling site selection* in streams and rivers of a large river basin (Magdalene et al.,

2008): the targeted sampling approach of the US Geological Survey (USGS) National Water-Quality Assessment (NAWQA) (Gilliom et al., 1995; USGS, 2001), and the random sampling approach of EPA's Environmental Monitoring and Assessment Program (McDonald et al., 2002; Stevens and Olsen, 2004). These approaches select sampling sites to evaluate the overall water status of a river, which is ideal if the question of interest is related to an in-stream water quality criteria that is protective of aquatic health or human recreational use. However, such sampling approaches may not be ideal for determination of water quality criteria associated with use as a drinking water source due to the significant heterogeneity in large rivers. For example, Total Dissolved Solids (TDS) is a measure of inorganic and organic constituents dissolved in water. The in-stream TDS criteria in Pennsylvania was written for protection of potable water supplies, and thus is relevant only at the point of water supply intake (PaDEP, 2007), and not throughout the river, where samples might be taken to provide representativeness. EPA has not developed specific ambient water quality criteria for drinking water sources (Sklenar and Blake, 2010). However, some states are adopting finished water criteria as in stream ambient water quality criteria to protect source waters that are designated as a drinking water supply, especially when the target pollutant is not removed during drinking water treatment (e.g., TDS, chloride, sulfate) (Sklenar and Blake, 2010). Within Pennsylvania, surface waters used as sources of drinking water supply are considered the highest priority for assessment (PaDEP, 2009a), and the Pennsylvania Department of Environmental Protection (PaDEP) assessments of drinking water supply impairment or attainment is generally based on the review of the intake water quality data provided by voluntary and self-monitoring efforts at drinking water plants (PaDEP, 2009a). However,

the use of drinking water intake sampling locations is uncommon in large river assessment, and it is unknown if this sampling method will lead to different results than other sampling approaches.

Temporal sampling plans are also highly variable in large river systems. Sampling at high frequency with long duration is generally not feasible, and such datasets will not be available for impaired waters in most TMDL studies (Richards, 2004). An extremely useful sampling method in the TMDL process is synoptic survey, which is generally done under low flow conditions with a large number of samples taken at the same time at multiple sites along the river (Richards, 2004). Such sampling may produce unbiased results for low flow conditions, but be a poor representation of average conditions (Richards, 2004).

In the present work, we consider several sampling projects undertaken in a single river over a three-year period. These projects each had different goals and therefore different sampling protocols for selection of sites and sampling frequency. One project focused on drinking water source quality and thus sampled only at drinking water plant intakes. Another project focused on characterization of the river at well-mixed locations downstream of navigational control structures. The final project included sampling at both drinking water intakes and well-mixed river sites; however, samples were taken only in response to reports of elevated conductivity, resulting in sampling predominately during low flow conditions (similar to synoptic survey). These distinct sampling protocols provide key comparative data to determine the relative representativeness of

different collection protocols to answer questions related to in-stream criteria for protection of potable water supplies.

2.3 Materials and Methods

Field Study Location

The Monongahela River is 206 kilometers (128 miles) in length; it flows north through West Virginia into Pennsylvania, where it meets the Allegheny River to form the Ohio River at Pittsburgh (Figure A.1). The Monongahela River is navigationally controlled to create a series of pools and maintain adequate water levels for barge traffic and for industrial and drinking water supply withdrawals (Wilson and VanBriesen, 2013a). There are several flow gages on the Monongahela River that operated by USGS, but only two gages report daily discharge. Previous study indicates the gages are correlated (Wilson and VanBriesen, 2013a), thus the daily flow data at just the Elizabeth gage are used in the present study (USGS, 2013a). The Monongahela River serves as drinking water source for 17 drinking water treatment plants, supplying approximately 1 million people. The lower Monongahela River drains 1.92×10^4 km^2, and is fed by five major tributaries, with highly variable pollutant loads (Wilson, 2013a). The significantly different tributary water quality and the navigationally-controlled flows give the river a high degree of spatial and temporal heterogeneity, which makes water quality assessment through representative sampling difficult. In 2008, the PaDEP observed TDS and sulfate concentrations that exceeded water quality standards (500 mg/L TDS standard and 250 mg/L sulfate standard) at all 17 drinking water intakes along the Monongahela River (Warren, 2010; Wozniak, 2011). In response to these reports, the PaDEP and several

research teams in the region increased sampling within the River, leading to the data sets evaluated in this work.

Sampling Sites and Sample Measurement

The sampling sites are located on the main stem of the lower Monongahela River (see Figure A.1), which are identified by river kilometer (KM); KM0 is in Pittsburgh where the Monongahela River meets the Allegheny River to form the Ohio River. Table 2.1 lists the number of sampling locations and the number of samples collected at these locations by each group. Although each group included a variety of different parameters, only TDS is evaluated in the present work.

Table 2.1 Sampling Locations and the Number of TDS Samples at Each Location

	Sample Type	Number of Sampling Sites	Total Number of Samples	Sampling Years[2] Year 1	Year 2	Year 3	Year 4
				Number of samples taken in each year (Number of samples taken in summer[3])			
DEP[1]	River Water	40	221	74 (0)	51 (39)	69 (9)	27 (16)
	Drinking Water Intake	14	217	112 (0)	14 (9)	52 (28)	39 (22)
WV	River Water	4	243	9 (9)	75 (18)	75 (18)	84 (24)
CMU	Drinking Water Intake	6	433	0 (0)	200 (71)	157 (57)	76 (23)

[1] DEP stands for the Pennsylvania Department of Environmental Protection data; WV stands for the West Virginia Water Research Institute data; CMU stands for Carnegie Mellon University data.
[2] Sampling years are defined as follows: Year 1 is 09/01/2008 through 08/31/2009; Year 2 is 09/01/2009 through 08/31/2010; Year 3 is 09/01/2010 through 08/31/2011; Year 4 is 09/01/2011 through 08/31/2012.
[3] Summer in the region is defined by typical low flow conditions that occur from June-August.

Data Set 1 (DEP): The Pennsylvania Department of Environmental Protection collected samples from the Monongahela River to assess water quality between Fall 2008 and Summer 2012, due to suspected high levels of dissolved solids. The data are accessible at

the website of the Community Information page of the Southwest Regional Office of PaDEP (PaDEP, 2013). Data are from two kinds of samples: river water samples and drinking water intake samples. Sampling was not routine, but was responsive to complaints or detections of high conductivity via sensors at drinking water intake locations, leading to more samples during low flow conditions in the river. For laboratory measurements, water samples were collected in 125 or 500 ml plastic bottles, then iced and transported to DEP laboratory for analysis (PaDEP, 2009c). Samples collected after August 2010 were analyzed using Standard Method 2540C (at 180^{o}C) for TDS while samples prior to August 2010 were analyzed at 105°C (PaDEP, 2013). An analysis that the DEP conducted of replicate samples using the two temperatures did not yield significant differences (PennsylvaniaBulletin, 2010).

Data Set 2 (WV): West Virginia Water Research Institute conducted a comprehensive three-year water quality monitoring program in response to the need for chemical data on the Monongahela River following the detection of high TDS levels during the summer of 2008 (Ziemkiewicz et al., 2011). Data are accessible from a water quality GIS map at the 3 River QUEST website (ThreeRiverQuest, 2013). WV sampled at four sites (KM37, KM98, KM132, KM142; see Figure A.1) on the main stem of the lower Monongahela River starting in July 2009. The four sites were chosen downstream of navigational control structures to increase the likelihood of adequate mixing and to align sampling locations with USGS gages in the basin (Ziemkiewicz et al., 2011). Field samples were collected biweekly and analyzed for 19 water quality parameters (including TDS) at

REIC Laboratories Inc; TDS was analyzed using Standard method 2540C (at 180^{o}C) (Ziemkiewicz et al., 2011).

Data Set 3 (CMU): Carnegie Mellon University's Water Quest Center conducted research focused on the role of source water characteristics in finished drinking water quality. Samples were taken at intake points of drinking water treatment plants along the river. Six intakes on the Monongahela River (Figure A.1) were sampled weekly from late spring through late fall, and biweekly or monthly during the winter and early spring from September 2009 to July 2012. These samples represent each navigational pool of the river, except the pool between Braddock Lock and Dam at KM 17.9 and Elizabeth Lock and Dam at KM 38.6, since this pool has no drinking water treatment plant. Samples were collected in 500 mL polypropylene bottles and stored at 4°C in an ice cooler during transport prior to laboratory analysis. Water samples were analyzed in the Hauke Environmental Laboratories at Carnegie Mellon for multiple parameters, including TDS. TDS concentrations in samples were determined by following Standard Method 2540C (at 180^{o}C) (Eaton et al., 2005). For quality control, one blank sample and one standard TDS/conductivity solution (Ricca Chem Company) and one duplicate sample were analyzed for every ten samples (Wilson, 2013a).

Statistical Analysis Methods

Water quality time series data often contain characteristics that do not allow routine application of statistical methods (Hirsch and Slack, 1984; Hipel et al., 1988; Hipel and McLeod, 1994). Characteristics that complicate these data include: (1) missing values, (2)

non-normality, (3) censored data (below detection limit measurements), (4) unequal sampling intervals, (5) presence of outliners, (6) seasonal variation, and (7) periodicity (Hirsch and Slack, 1984; Hipel et al., 1988). Thus, water quality data are often considered "messy" (Hipel and McLeod, 1994; Hipel et al., 1988) which makes classic statistical methods difficult or impossible to implement appropriately (Zetterqvist, 1991). To obtain useful information from the available messy data, statistical approaches specific to time series water quality data must be used (Zetterqvist, 1991; Hipel and McLeod, 1994) and nonparametric methods are required. The upper-tailed Mann-Whitney rank sum test is employed to evaluate statistically significant differences between medians and to determine if one dataset tends to produce higher values compared to the second dataset (Wilson and VanBriesen, 2013b). Notched Box-and-Whisker plots enable evaluation of significance differences between medians (Hipel and McLeod, 1994). If the median line in one box overlaps within the notches in the other, then there are no significantly differences in the median between the two observations at 5% significant level. The Seasonal Kendall test is a nonparametric test, valid for use with seasonal data, evenly or unevenly spaced observations, missing observations, censored data and ties (the same concentration observed more than once) (Hipel and McLeod, 1994). The Seasonal Kendall test was applied in the present work using the DOS program Kendall.exe released by the USGS (Helsel et al., 2006).

Statistical Assessment for Section 303(d) Listing Decision

The EPA listing methodology requires determination of whether the annual mean value exceeds the criteria; in the present case, the secondary drinking water criteria for TDS is

500 mg/L. Individual states may use different methods for identifying the status of water bodies (USEPA, 1991a) and Pennsylvania uses a modified assessment method. The details of the EPA listing methodology and the PaDEP listing methodology are provided in the Appendix A. Statistical analyses were performed in Minitab 16 (Minitab Inc, State College, PA). All data sets were evaluated for normality by Anderson-Darling normality test (see Table A.1 in Appendix A). For EPA listing decisions, the Chen's modified t-test was performed in Excel following EPA guidance (USEPA, 2003b). For PaDEP listing decisions, the normally distributed data were subject to the one-sided t-test, while non-normally distributed data were evaluated with a binomial test following PaDEP guidance (PaDEP, 2009b).

2.4 Results and Discussion

The large data sets available for this comparative work enable a number of data groupings to address the main questions of how sampling frequency and sample type (drinking water intake vs. river water) affect conclusions regarding water quality criteria attainment for drinking water sources. Table 2.1 provides details of the number of samples per sampling year. Table 2.2 provides mean, median, standard deviation and range of the data, as well as the sub-divided data by year and by type (drinking water intake and river water). Also shown is the percentage of samples that exceeded the secondary drinking water standard for TDS of 500 mg/L for each data group.

Table 2.2 Statistical Descriptions of Water Quality Data for TDS

Year	Mean (mg/L)	Median (mg/L)	Standard Deviation (mg/L)	Range (min; max) (mg/L)	Observation exceeds criteria (%)

	Full Data Set	413	378	206	(98; **1090**[1])	27
	09/2008-08/2009 (RW and DW[2])	**516**	**529**	263	(100; **1090**)	55
	09/2008-08/2009 RW	**559**	**606**	237	(104; **1090**)	65
	09/2008-08/2009 DW	487	490	276	(100; **908**)	48
	09/2009-08/2010 (RW and DW[2])	414	426	97	(160; **580**)	20
	09/2009-08/2010 RW	410	424	93	(160; **576**)	18
DEP	09/2009-08/2010 DW	428	435	112	(216; **580**)	29
	09/2010-08/2011 (RW and DW[2])	331	338	78	(98; **730**)	0.82
	09/2010-08/2011 RW	366	370	70	(226; **730**)	1.4
	09/2010-08/2011 DW	285	284	64	(98; 384)	0.0
	09/2011-08/2012 (RW and DW[2])	273	245	90	(152; 466)	0.0
	09/2011-08/2012 RW	301	280	106	(152; 466)	0.0
	09/2011-08/2012 DW	254	238	72	(154; 424)	0.0
WV	Full Data Set	245	219	101	(68.7; **549**)	0.82
	09/2009-08/2010	261	237	117	(68.7; **549**)	2.4
	09/2010-08/2011	235	205	88	(91; 460)	0.0
	09/2011-08/2012	238	213	93	(104; 480)	0.0
CMU	Full Data Set	284	281	115	(46; **608**)	2.5
	09/2009-08/2010	309	316	132	(46; **608**)	5.0
	09/2010-08/2011	270	272	94	(100; **538**)	0.64
	09/2011-08/2012	261	228	99	(102; 494)	0.0

[1] Bold text indicates concentration exceeds the water quality criteria.
[2] RW denotes River Water Samples; DW denotes Drinking Water Intake Samples.

Figure 2.1 shows the data for TDS (values on left axis each panel) and flow (values against right axis, plotted down from the top in each panel) for the period of study from September 2008 to August 2012. Each symbol represents the mean TDS value taken by one of the sampling teams across all of its sites in the river at the same sampling date, with the extensions representing one standard deviation. Figure 2.1 indicates four large time gaps associated with the DEP sampling, which is episodic, and generally confined to expected low flow times (July-November in Southwestern Pennsylvania). As noted

previously, DEP sampling is responsive, rather than scheduled; sampling takes place when monitoring systems (usually for conductivity) indicate concentrations of TDS may be elevated (e.g., sampling occurs when conductivity exceeds 720 μS/cm) (PaDEP, 2012). The effect of this selective sampling will be considered in the statistical analysis as few DEP data exist during the wetter periods of the year, when lower concentrations would be expected (and are observed by the other sampling teams). Figure 2.1(b-d) show that CMU and WV water samples from 2009-2012 are unevenly spaced but with smaller sampling gaps than DEP data. Figure 2.1(b-d) also show clear seasonal patterns, with increasing TDS concentrations in the summer (June to August) and decreasing concentrations in the winter (December to February), again likely due to changing flow conditions affecting dilution of TDS loads in the system.

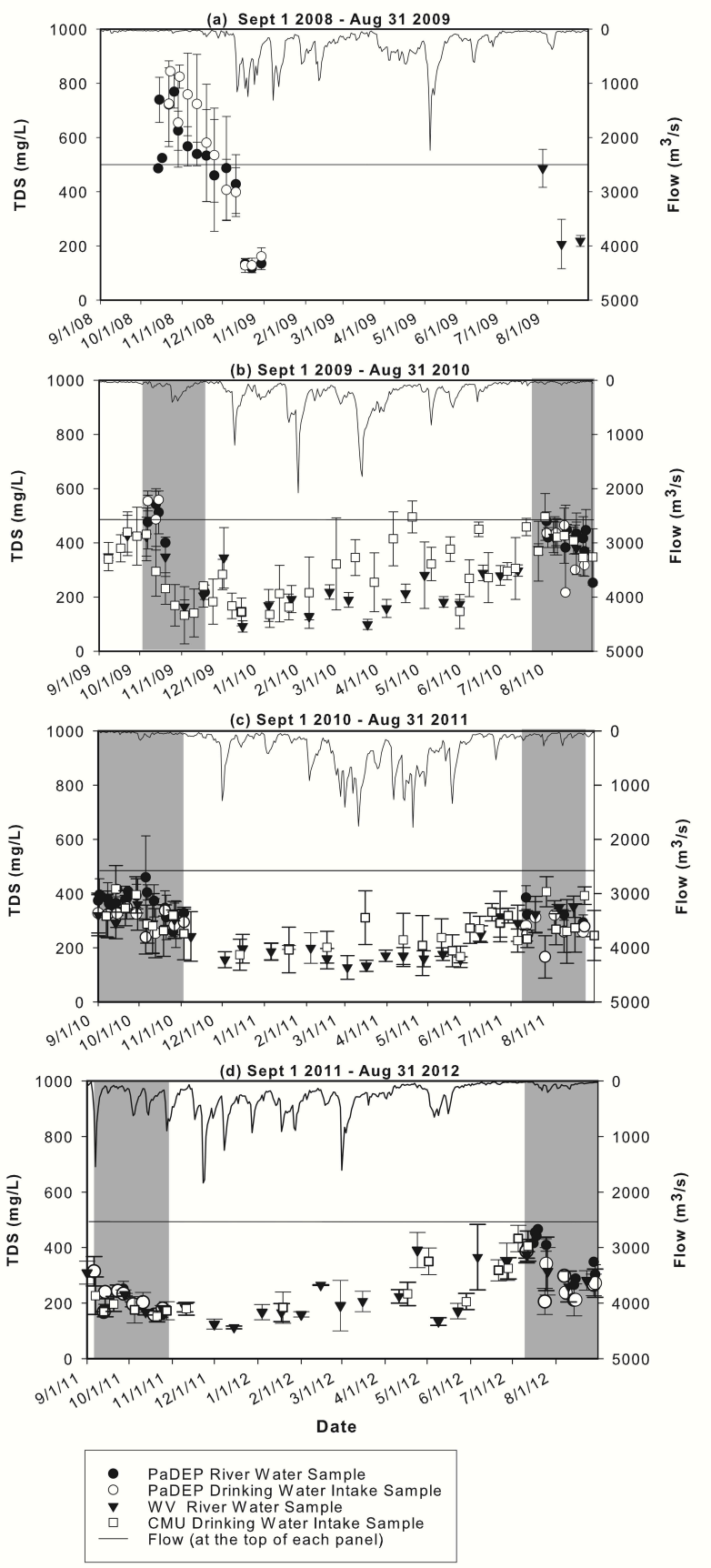
(a) Sept 1 2008 - Aug 31 2009
(b) Sept 1 2009 - Aug 31 2010
(c) Sept 1 2010 - Aug 31 2011
(d) Sept 1 2011 - Aug 31 2012
TDS (mg/L)
Flow (m3/s)
Date
PaDEP River Water Sample
PaDEP Drinking Water Intake Sample
WV River Water Sample
CMU Drinking Water Intake Sample
Flow (at the top of each panel)

Figure 2.1 Time series plot of TDS concentrations of water samples collected by DEP, WV, and CMU research groups from 2009-2012. The straight line across each panel indicates the 500 mg/L TDS secondary drinking water criteria.

Despite the significant gaps in DEP data, in order to conduct comparisons with CMU and WV data, six overlapping sampling periods (shaded gray in Figure 2.1) among the three sampling groups were identified. Table A.2 provides summary statistical analyses for specific overlapping sampling periods among the data sets. The results below first discuss analysis of the full data sets, and then consider analyses by year and by considering these overlapping time periods.

Table 2.2 indicates considering all available data from each group that DEP data show higher values than CMU or WV; more than ¼ of DEP samples exceed the standard. The highest reported TDS by DEP was more than twice the drinking water standard (1090 mg/L); while the mean (516 mg/L) and median (529 mg/L) in 2008-2009 exceed the 500 mg/L secondary drinking water standard. These extremely high TDS values cannot be explained solely based on low flow conditions; the average flow on sampling dates in 2008-2009 (209 m^3/s) was significantly higher than the average flow in 2009-2010 (53.8 m^3/s), 2010-2011 (54.9 m^3/s) and 2011-2012 (105 m^3/s), suggesting that higher TDS concentrations were caused by higher TDS loads entering the basin in 2008-2009 than in subsequent years.

The WV and CMU data indicate mean TDS values during the study period are approximately *half* the secondary drinking water standard (mean 245 mg/L for WV and mean 284 mg/L for CMU); however, both groups detected values above the secondary

drinking water standard occasionally (<1% of WV samples and 2.5% of CMU samples). Interestingly, CMU drinking water sampling data show exceedences of the TDS standard occasionally through Fall 2011 (highest value 538 mg/L) as do DEP data (highest value 730 mg/L), while the well-mixed WV river samples did not detect any exceedence after Fall 2010 (highest value 480 mg/L).

Effect of selective sampling on assessment of water quality

We hypothesize that the differences in assessed TDS values likely reflects the fact that while CMU and WV sampling continued throughout the year, DEP data were collected in response to high conductivity levels detected in the river. This temporal bias in sampling by DEP increases the mean value by neglecting high flow, low concentration sampling times. Rather than being representative of the overall conditions of the drinking water source across the full year, the DEP data represent synoptic sampling, identifying the worst water quality expected in the resource. To evaluate this hypothesis we consider overlapping sampling periods and seasonal analyses.

We consider six overlapping sampling periods (shaded gray in Figure 2.1) among the three sampling groups. No significant difference was observed between DEP *drinking water intake* samples and CMU *drinking water intake* samples in TDS ($p=0.637$) during the overlapping sampling periods, suggesting that sample timing alone likely accounts for differences in mean TDS values for CMU and DEP data sets. However, for *river water samples*, there is significant difference ($p\leq0.001$) between DEP river water TDS and WV river water TDS data during the overlapping sampling periods, with DEP data higher than

WV values. The reason for this is not clear; however, it may be due to the spatial differences in coverage as PaDEP used 40 sampling sites throughout the river, while WV used 4 well-mixed sampling sites.

The clear seasonal pattern of increasing TDS concentrations in the summer and decreasing concentrations in the winter, is seen across all sampling data (Figure 2.1), suggesting this is a true representation of seasonal variability in the river. This is not unexpected as flow shows similar seasonality (low in June-November and higher in November-March). Although TDS concentrations are not significantly correlated with flow (R^2=0.177, 0.0047 and 0.0734 for DEP, WV and CMU data, respectively), the highest TDS values did occur during low flow conditions. Seasonal data can make statistical analysis more difficult. The distribution of data within a season (as well as across the full year as evaluated above) must be considered (McLeod et al., 1991). Box-and-Whisker plots (using the five number summary) (Turkey, 1977) can provide a graphical display of distributed data to visualize the seasonality of the data (McLeod et al., 1991). Box-and-Whisker plots for DEP, WV and CMU seasonal TDS data are shown in Figure A.2 indicates that WV and CMU have sufficient data to demonstrate a seasonal concentration effect, with low TDS concentrations observed in the Fall (September-November), Winter (December-February) and Spring (March-May), and high TDS concentrations observed in the Summer (June-August). DEP data do not indicate a seasonal effect; however, this is due to their limited collection during wetter conditions in winter and spring.

The elevated TDS levels observed in the summer suggests a relevant comparison of the data sets would focus on summer season data, when higher contaminant concentrations are expected and all three research groups have sufficient data for comparison. Summer season data are shown in Box-and-Whisker in Figure A.3. The Monongahela River has experienced much lower average flow in summer 2010 (62.8 m^3/s) and summer 2012 (56.4 m^3/s) than summer 2011 (101 m^3/s). DEP river water TDS is significantly higher ($p=0.0002$) than WV river water TDS in summer 2010. DEP drinking water intake and CMU data are not significantly different for summer 2010. CMU drinking water intake TDS is significantly higher ($p=0.0001$) than DEP drinking water intake TDS in summer 2012; DEP river water and WV data are not significantly different for 2012. During the highest 'low flow' (2011), no significant differences are observed among the three data sets. Figure A.3 also shows that during the low flow summers of 2012, WV river water TDS were significantly lower ($p=0.025$) than CMU drinking water intake TDS. However, DEP drinking water intake TDS is significantly lower than DEP river water TDS in summer 2011 ($p=0.025$) and summer 2012 ($p<0.001$). Thus, these results confirm that water samples collected at different locations and from different sources during low flow condition may be especially likely to represent different conditions and may lead to different water quality decisions.

Effect of sample type on assessment of water quality

As noted previously, CMU samples are all from drinking water plants while WV samples are all from river locations, and DEP data include both drinking water intake and river samples. For DEP data from 2008-2012, the mean TDS reported in river water samples is

significantly higher than the mean TDS reported in drinking water samples ($p=0.0001$). When considering the sub-divided data by year and by type, significant differences are observed in TDS level in 2010-2011, with DEP river water samples showing higher concentration ($p<0.0001$) than its drinking water samples. However, no significant differences are observed between the two types of samples collected by PaDEP in other sampling years. The significant test results are tabulated in Table A.3.

Similarly, significant differences exist between CMU drinking water samples and WV river water samples (see Table A.3). The mean TDS level in CMU drinking water samples for 2008-2012 (284 mg/L) is significantly higher ($p<0.0001$) than the mean TDS in WV river water samples (245 mg/L) during this time period. Within each sampling year, CMU drinking water intake TDS levels are significantly higher ($p\leq0.0027$) than WV river water TDS in the first two sampling years (2009-2010 and 2010-2011). However, there is no difference ($p=0.128$) for the last sampling year 2011-2012, which may be due to gaps in the CMU data set in late August of this final year of sampling. The differences between CMU and WV data suggest that sampling source (river water vs drinking water intake) affects the results of TDS monitoring, likely because the drinking water intake samples are not from well-mixed locations. Incomplete mixing within the river may lead to higher TDS levels at drinking water intakes than are observed at well-mixed river samples. Since the 500 mg/L TDS standard is relevant for drinking water source protection only, these differences suggest sampling for compliance should be at drinking water intake locations rather than at well-mixed river locations that may not represent source water conditions.

While none of the groups sampled at the same location at the same time, CMU and WV were often sampling at very near locations (e.g., KM40 and KM37) the same week in the same year. These paired samples, while not representing duplicates, do provide insight into differences in results based on the sampling locations. Notched Box-and-Whisker plots (McGill et al., 1978) (Figure 2.2) applied using Matlab enable evaluation of the significance differences in paired TDS among different data sets, which detects that the two TDS medians of water quality samples in WV and CMU data at the paired location and sampling dates are statistically significantly different. This is further confirmed by Mann-Whitney rank sum test (p=0.0119). Detailed information on the 3 paired location analyses are provided in Appendix A.

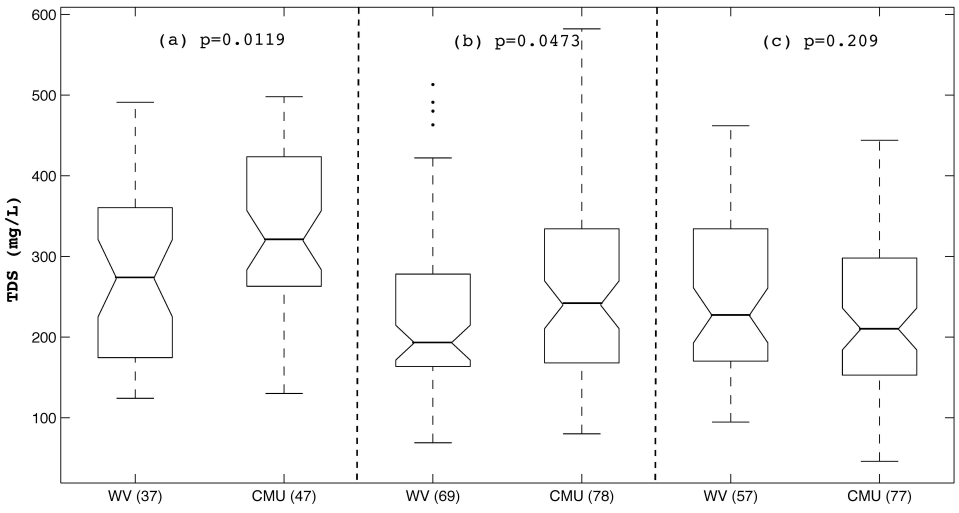

Figure 2.2 Notched Box-and Whisker plots for time and location paired WV and CMU TDS data.

The paired data (Figure 2.2) provide insight into effect of sample types; however, they contain the seasonal variability discussed before. We further consider the seasonal trend at these targeted paired sampling locations by the Seasonal Kendall. A significant decreasing trend in TDS is observed in WV data at KM37 during the sampling years, while no trend was observed from the paired CMU dataset at KM 40. Results of detailed analysis of Seasonal Trend test are provided in the Appendix A. The results again indicate that drinking water intake sampling and river water sampling provide different assessments. In this case, the river water sampling suggests TDS has been declining over the study period, while drinking water intake sampling suggests no change.

Statistical assessment for Section 303(d) listing decision

As noted in the methods section, EPA and PaDEP listing decisions are based on different data analysis methods. Decision analysis results of whole year data sets are shown in Table A.7-A.8 in the Appendix A. DEP river water and drinking water intake samples in the first sampling year (09/2008-08/2009) exceed the 500 mg/L TDS criteria using the EPA method for non-normally distributed data. The results for 2009-2012 indicate that the river was meeting the TDS criteria based on analysis of DEP, WV and CMU data. When comparing *river water samples* only, the upper 1-sided 95% confidence intervals for the mean of DEP samples are 30 to 50% higher than WV samples. When comparing *drinking water samples* only the upper 1-sided 95% confidence interval for year 2009-2010 is 493 mg/L based on DEP data, which is approaching the 500 mg/L criteria, and is 50% higher than that (327 mg/L) based on CMU samples. However, the drinking water

samples collected from 2010-2012 by DEP and CMU are comparable by this measure, and are higher than the river water samples taken by WV.

The PaDEP listing methodology produces similar results; however, PaDEP samples indicate impairment using river water and drinking water samples (Table A.8). Although CMU samples suggest the TDS levels are meeting the criteria in each sampling year, the upper 90% limit of TDS levels are higher compared to WV river water samples, which confirm the result from earlier significance testing indicating that TDS levels in CMU and WV samples are different, likely due to the difference between drinking water source water sampling and river water sampling.

Decision analysis results only based on summer data are shown in Table A.9-A.10. Table A.9-A.10 obtain the same listing decisions as those based on whole year data sets for both EPA and PaDEP listing methodologies, which suggest the synoptic sampling design meets the goal of assessing water quality during low flow conditions.

2.5 Conclusion

Different listing decisions would be made based on use of river water samples and drinking water intake samples. DEP selective sampling leads to presumed higher TDS levels for the river and thus does not represent the typical overall water quality conditions in the Monongahela River; however, the synoptic design meets the goal of assessing during low flow, which likely represents the worst case conditions. Significant differences and different seasonal trends are observed between river water samples and drinking water intake samples, with drinking water samples showing higher TDS

concentrations in this system. Further, water samples collected during low flow conditions are especially likely to show variability due to sample type and location, which suggests sampling for compliance should be at drinking water intake points to represent source water quality. These persistent differences suggest the sampling data sets provide different pictures of water status in the Monongahela River. Using these data sets independently is likely to lead to different conclusions about the status of the river and the need for interventions to improve water quality.

Chapter 3. Disinfection By-Product Speciation in Finished Drinking Water from the Monongahela Basin during changing source water bromide conditions

3.1 Abstract

The present study evaluates the impact of changing bromide concentrations in the Monongahela River Basin (related to fossil-fuel associated wastewater management) on the formation and speciation of finished water disinfection-by products (DBPs) at six drinking water treatment plants from 2009 to 2012. Increasing formation of brominated-trihalomethanes (THMs) in finished water was observed at all plants during higher source water bromide conditions. Quarterly bromide concentrations are significantly correlated with heavily brominated-THMs (dibromochloromethane and bromoform) concentrations and percent brominated-THMs and bromine incorporation factor (BIF). Changes of bromide lead to proportional changes of DBCM formation and BIF value in finished water, and lead to bromoform formation at twice that level. Reductions in source water bromide in 2011 were instrumental in lowering THM levels that same year.

3.2 Introduction

Drinking water disinfection by-products (DBPs) are formed when organic constituents in the source water are oxidized by the applied disinfectant. The formation of DBPs depends on the source water characteristics (e.g., alkalinity, type of organic matter) and the treatment processes within the drinking water plant (e.g., coagulant dose, disinfectant type). For treatment plants employing chlorine as a disinfectant, the most common disinfection by-products formed are trihalomethanes (THMs) and haloacetic acids

(HAAs), and these classes of DBPs are regulated in finished drinking water to protect human health. The predominate forms of THM and HAA are chlorinated, reflecting the incorporation of the applied chlorine into the oxidation products. However, when the source water contains other halogens (e.g., bromide and iodide), these forms are oxidized by the applied chlorine and can then be incorporated into DBPs, leading to mixed chloro-bromo products (e.g., dibromochloromethane, DBCM) as well as fully brominated species (e.g., bromoform).

Surface waters in the United States (US) usually have low bromide concentrations (Flury and Papritz, 1993), ranging from 0.014-0.2 mg/L (Bowen, 1966, 1979), while some ground water systems, especially those near the US shorelines, can have higher bromide levels. Recently, some inland drinking water systems have been experiencing increasing bromide concentrations (Handke, 2009; Fiske et al 2011; States et al 2013), with changes attributed to discharges from oil and gas produced water treatment (Wilson and VanBriesen, 2013) and coal-fired power plants using air pollution control system (Gutierrez 2014). Higher concentrations of bromide in source waters result in increased total concentration of DBPs (Symons et al. 1993) as well as increased incorporation of bromide in the DBPs (Symons et al. 1993, Chang et al. 2001, Clark et al. 2001, Sohn et al, 2006, Sun et al. 2009). Since brominated DPBs are associated with risk at lower concentrations than chlorinated DBPs, DBP bromination is associated with higher risk for drinking water consumers (Rook, 1974; Richardson et al, 2003; Berry et al, 2007).

While different bromide concentrations have been documented at drinking water plants throughout the US (e.g., USEPA 2000; Weinberg et al, 2002), rapid changes in bromide concentrations have been uncommon in the past, and thus, evaluation of source water changes on DBP formation at specific drinking water plants has not been possible. The unique recent experience in southwestern Pennsylvania of rapidly changing bromide concentrations in source water used of drinking water due to changes in river flow as well as changes in discharges of produced water from oil and gas development enables evaluation of at-plant changes. The present study evaluated the finished water THMs speciation at six drinking water plants in a single river basin over a three-year field study during a time of changing source water bromide. The present work documents and quantifies the associated changes in THM speciation in response to bromide concentration changes. Although HAAs are also regulated by EPA, this study focuses on THMs levels as high bromide source waters are more associated with THM concerns (Bond et al., 2014), because coagulation treatment processes generally remove more HAA precursors than THM precursors (Liang and Singer, 2003; USGS, 2013b). Further, THM problems are more widely reported in this basin than are HAA issues.

3.3 Methods and Materials

Sampling Sites, Sample Collection and Measurement

The Monongahela River is 128 miles (206 kilometers) in length, and flows from West Virginia to Pittsburgh, Pennsylvania, where its confluence with the Allegheny River forms the Ohio River. Source and finished water samples were taken approximately biweekly at 6 drinking water treatment plants on the Monongahela River from September

2009 to September 2012. The sampling sites and detailed information about sample collection and laboratory analysis methods were previously described (Wilson and VanBriesen, 2013b). Briefly, source water (500 mL) was collected from the intakes of the drinking water treatment plants in polypropylene bottles and stored in a cooler with ice during transport and in a refrigerator at 4°C prior to analysis. Bromide was determined using an ion chromatograph (Dionex) with an IonPac anion column (4 x 250 mm) and 100 µl sample loop with an eluent of 8 mM Na_2CO_3 and 1 mM $NaHCO_3$ (Fisher Scientific) following a modification of EPA Method 300.1 (USEPA 1997). At least 10% of all water samples were measured in duplicate.

Finished water is the water that has been treated and is ready for distribution to consumers (USEPA, 2004). The finished water samples were collected at the drinking water treatment plants, just prior to entering the distribution system. They do not represent regulatory compliance sampling locations, which would be in the distribution system after some travel time. For finished water analysis, before field sampling, 60 mL amber vials were filled with about 1 g mixture of ammonium chloride (NH_4Cl) combined with phosphate buffer (1% sodium phosphate Na_2HPO_4 and 99% potassium phosphate KH_2PO_4) for sample preservation. This converts free chlorine to monochloramines and stops further formation of trihalomethanes. Finished water samples at the 6 drinking water treatment plants were collected in the prepared 60 mL amber vials and stored in an ice cooler at 4°C before laboratory analysis. All samples were analyzed within 14 days of collection. EPA Standard Method 551.1 was followed to determine the concentrations of the 4 THM species in the finished water samples (USEPA, 1990). A liquid-liquid

extraction using methyl-tertiary-butyl-ether (MTBE) was employed, and THM concentrations were analyzed by gas chromatograph (HP6890) with electron capture detectors detector (ECD), using a 0.25 mm ID x 30 m fused silica capillary column (Restek). Calibration standards were prepared by a series of dilutions of stock standard solution (Fisher Scientific) that contained the each of the four trihalomethanes in methanol (200 μg/mL). The analytical method has detection limits of 0.01 μg/L chloroform, 0.01 μg/L bromodichloromethane, 0.02 μg/L chlorodibromomethane, and 0.05 μg/L bromoform.

During the 3-year field sampling, source water samples and finished drinking water samples were collected at drinking water plants at the same date. However, it usually took 1 or more days for source water to be treated and ready to be distributed to consumers, thus, the finished water samples do not represent the same water as the source water samples on a point-by-point basis.

Other Data Used

Flow data were retrieved from USGS gages located near Sites B and E (USGS, 2014; gage 03075070 and gage 03072655) for the relevant days associated with sampling. Analysis of 74 years of data shows the two gages to be significantly correlated (r^2=0.98; p value =0.001), and thus the river flow is assumed to be constant at all the sites (Wilson and VanBriesen, 2013b). Source water temperature data were retrieved from RAIN (RAIN, 2013) at the same sampling sites.

Data Limitations

Censored data are concentrations not observed because they are below the detection limit (Helsel and Lee, 2006). Censored bromide and THM concentrations were observed at all drinking water plants on some dates. Censored bromide data (33% of samples) were replaced with values from below the detection limit, following the method described in (Wilson and VanBriesen, 2013b). For censored THM data, the EPA method requires they be reported *as zero* for the calculation of annual average (USEPA, 2012a). Thus, censored THM concentrations in this study are replaced with zero for statistical analysis to maintain consistency with reporting requirements.

During the course of the study, to reduce THM formation and meet drinking water regulations, two drinking water treatment plants changed their disinfection practices. The drinking water treatment plants at site B and C switched from free chlorine to chloramine in April 2012 and June 2011, respectively. The DBPs primarily formed when chloramine is used as a disinfectant differ from when free chlorine is used as a disinfectant (Diehl et al. 2000), and thus data collected after the disinfectant changes were excluded from analysis. Therefore, the range of data for site C is from September 2009 through May 2011 and the range of data for site B is from September 2009 through March 2012.

Only two of the drinking water plants (Site E and F) were included in the Information Collection Rule from 1997-1998 (EPA 1996, McGuire et al. 2002); therefore, long-term comparisons to this baseline data set are made only for these plants. The presentation of

results uses Site F for detailed discussion due to the available comparison with the ICR data at this site. Analyses for all plants are included in the Appendix B.

Statistical Analysis and Computational Methods

Quarterly data were analyzed as: quarter 1 (January, February, and March), quarter 2 (April, May, and June), quarter 3 (July, August, and September) and quarter 4 (October, November, and December). Quarterly data are represented by computing the geometric mean based on all available data within the quarter.

Current Maximum Contaminant Level (MCL) limits the sum of four THM species concentration to 80 µg/L (USEPA, 2003c). Total THM (TTHM) in µg/L was calculated as the mass-based concentration sum of the four THM species.

$$TTHM = \sum THM_4 = CHCl_3 + BDCM + DBCM + CHBr_3 \quad \text{(Equation 1)}$$

Percent brominated-THM is used to evaluate the mass percentage of brominated-THM species in the sample. Percent brominated-THM was calculated as

$$Percent\ brominated\ THM = \frac{BDCM+DBCM+CHBr_3}{CHCl_3+BDCM+DBCM+CHBr_3} \quad \text{(Equation 2)}$$

Bromine Incorporation Factor (BIF) is used to evaluate the molar percentage of brominated THM (Krasner et al., 2008). In Equation 3, the parentheses indicate molar concentration, which is equivalent to the fraction of halogen atoms present in THM that

are bromine, with the remainder being chlorine atoms, where in this case BIF ranges from 0 to 1. Some versions of BIF do not include a multiplication of 3 (corresponding to the three halogens in a THM molecule) in the denominator, and as a result range from 0 to 3. The present study applies Equation 3 for BIF calculations.

$$BIF_{THM} = \frac{THM-Br}{THM-X} = \frac{0\times(CHCl_3)+1\times(BDCM)+2\times(DBCM)+3\times(CHBr_3)}{3\times((CHCl_3)+(BDCM)+(DBCM)+(CHBr_3)} \quad \text{(Equation 3)}$$

Correlations among bromide concentration and individual THM species, percent brominated-THM and BIF were computed with Spearman rank correlation analysis in Minitab (Statistical software, State College, PA), assuming the data may not be normally distributed (Obolensky and Singer, 2005; Francis et al., 2009). The Mann-Whitney rank sum test was employed to evaluate the statistical significance at α=0.05, p=0.05 level by using Sigmaplot (Systat Software, San Jose, CA). The Mann-Whitney rank sum test was applied due to the non-normally distributed data as many censored data exist in the dataset (Wilson and VanBriesen, 2013b). Linear regression analysis was employed to evaluate the relationship between source water bromide and each THM species.

3.4 Results and Discussion

Source Water Bromide Concentrations

Figure 3.1 shows the bromide concentrations in source water at Site F from 2009 to 2012 collected in this study as well as data from 1997 from the EPA ICR database; the seasonal pattern in concentration represents the effect of flow conditions. Results for other sites are provided in Figure B.1-B.5 in Appendix B. Flow in the Monongahela

River is usually low during the summer (June, July and August) and fall (September, October and November) seasons but high during winter (December, January and February) and spring (March, April and May). Low flow periods were corresponded to elevated bromide concentrations, as expected. Particularly high bromide concentrations occurred in August 2010 (310μg/L) and August 2011 (240 μg/L). However, during the high flow year including the summer of 2011, bromide was particularly low, with concentrations below the levels reported in the ICR for 1997-1998. Previous study found that although flows in summers 2010 and 2012 were similarly low, the bromide concentrations in 2010 were significantly higher than bromide in 2012 (see Figure 3.1), indicating that flow seasonality alone cannot fully explain the bromide changes in the river (Wilson and VanBriesen, 2013b). Bromide load analysis supports this conclusion with high loads in 2009-2011 and lower loads in 2012-2013 (Wilson and VanBriesen, 2013). Thus, these data support the unique experience in southwestern Pennsylvania of rapidly changing bromide loads and associated changes in bromide concentrations in source waters used for drinking water.

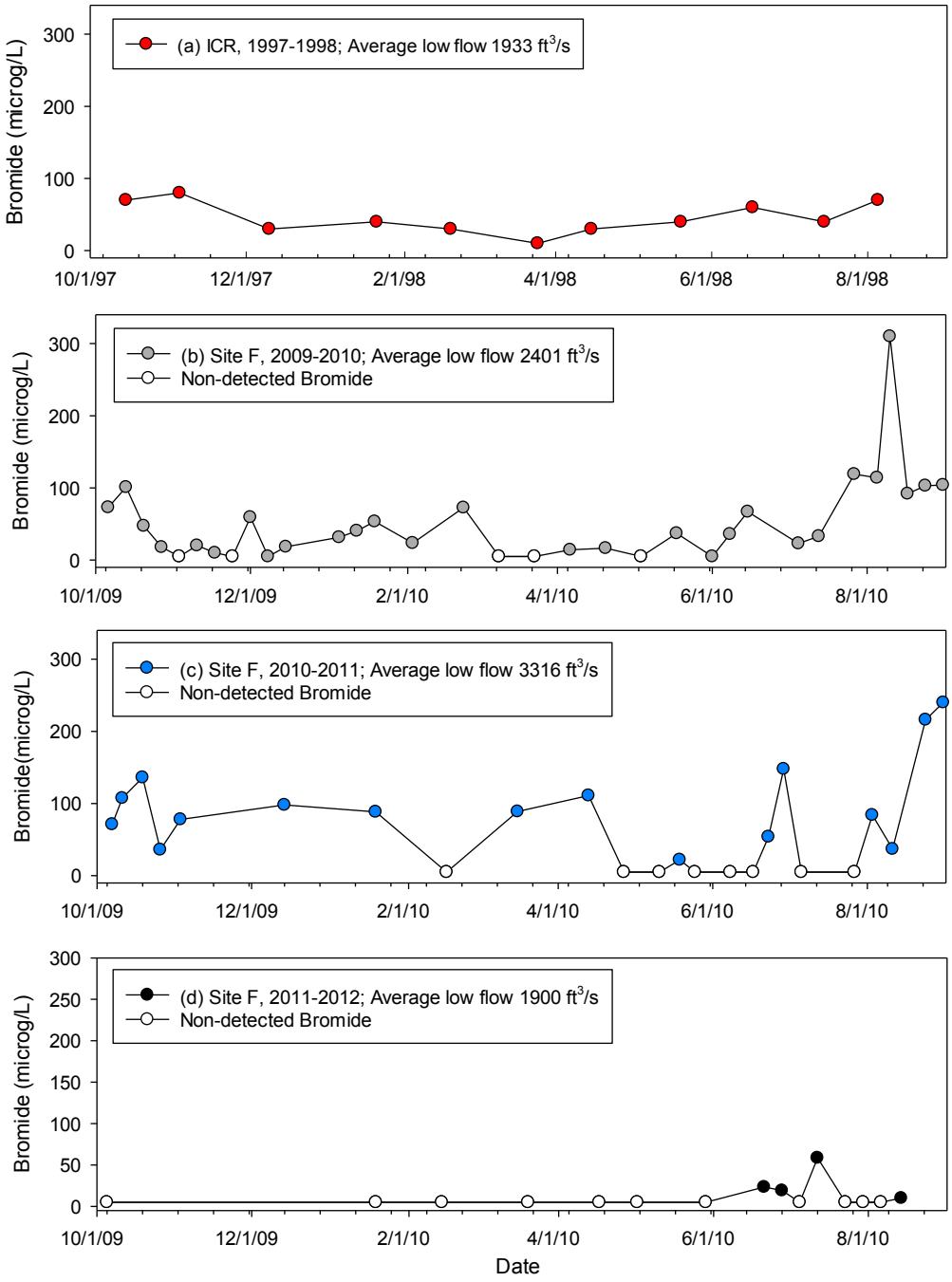

Figure 3.1 Bromide concentrations at Site F on the Monongahela River. Panels show bromide concentrations in 1997-1998, 2009-2010, 2010-2011, 2011-2012, respectively.

Finished Water DBPs at Monongahela River Water Treatment Plants

Although the formation and speciation of THMs are influenced by many conditions (e.g., temperature, reaction time, pH, alkalinity, chlorine dose residual), bromide and TOC

concentrations are well known to have significant impact on the bromination of the formed THMs in finished water (Luong et al., 1982). The chlorine disinfectant can oxidize bromide to bromine, which is a more effective substitution agent than chlorine during THM formation, thus a mixture of chlorine- and brominated-THM species are formed in finished water (Krasner, 2009).

The concentrations of chloroform, BDCM, DBCM, bromoform and TTHM at Site F from 2009-2012 are shown in Figure 3.2. THM concentrations at other sites are plotted in Figure B.1-B.5 in Appendix B. Figure 3.2 shows that chloroform and BDCM were the major formed THM species among the four THMs at this location. The chloroform and BDCM levels in each of the 3 years were similar seasonaly and consistent with increasing chloroform and BDCM levels in the late spring and summer then decreasing levels in the fall and winter. Significance testing (Mann-Whitney rank sum test) results are shown in Table 3.1. The results indicate that although the basin was experiencing rapidly changing bromide concentrations in the source water, the chloroform levels in finished water did not experience significant changes during this period. However, when bromide concentrations were significantly lower in 2011-2012 (Wilson and VanBriesen, 2013b), the BDCM levels were significantly lower ($p=0.037$) than BDCM levels in 2009-2010. Similarly, the DBCM levels were significantly lower ($p=0.002$) than DBCM levels in the previous two years. Bromoform levels were also observed to be significantly lower ($p=0.011$) in 2011-2012 than in 2010-2011. Figure 3.2(c, d) shows these differences, with higher formation of DBCM and bromoform in August 2010 and August 2011, but rare formation of DBCM and bromoform during 2012. These data support the expected

conclusion that elevated source water bromide contributes to the significant increase in the formation and speciation of heavily brominated THMs (DBCM and bromofrom) but does not strongly affect the formation of chloroform in finished water. This is important as the increase in brominated species is not accompanied by a statistically significant decrease in chloroform, thus overall TTHM increases when bromide levels cause an increase in brominated forms without associated decrease in chloroform. Table 3.1 shows that when bromide concentrations were significantly lower in 2011-2012 than 2009-2010 (Wilson and VanBriesen, 2013b), the TTHM levels were significantly lower (p=0.006). Thus, increasing bromide increases bromination as expected and can also increase overall TTHM. Figure 3.2(e) shows that TTHM levels have strong seasonality with elevated during summer in each sampling years and decreased during cold months.

Table 3.1 Significant test on THM species concentrations and TTHM levels in finished water for Site F. Bold values represent significance at significant level α=0.05, p=0.05.

	2009-2010 vs 2010-2011[1]	2010-2011 vs 2011-2012[2]	2009-2010 vs 2011-2012[3]
Chloroform	p=0.436	p=0.324	p=0.097
BDCM	p=0.062	p=0.535	**p=0.037**
DBCM	p=0.133	**p=0.003**	**p=0.002**
Bromoform	p=0.712	**p=0.011**	p=0.117
TTHM	p=0.104	p=0.100	**p=0.006**

[1] Significant test H_o is the median THM level in 2009-2010 is significantly lower than the median THM in 2010-2011; H_1 is the median THM level in 2009-2010 is not significantly lower than the median THM in 2010-2011;
[2] Significant test H_o is the median THM level in 2010-2011 is significantly lower than the median THM in 2011-2012; H_1 is the median THM level in 2010-2011 is not significantly lower than the median THM in 2011-2012;
[3] Significant test H_o is the median THM level in 2009-2010 is significantly lower than the median THM in 2011-2012; H_1 is the median THM level in 2009-2010 is not significantly lower than the median THM in 2011-2012;

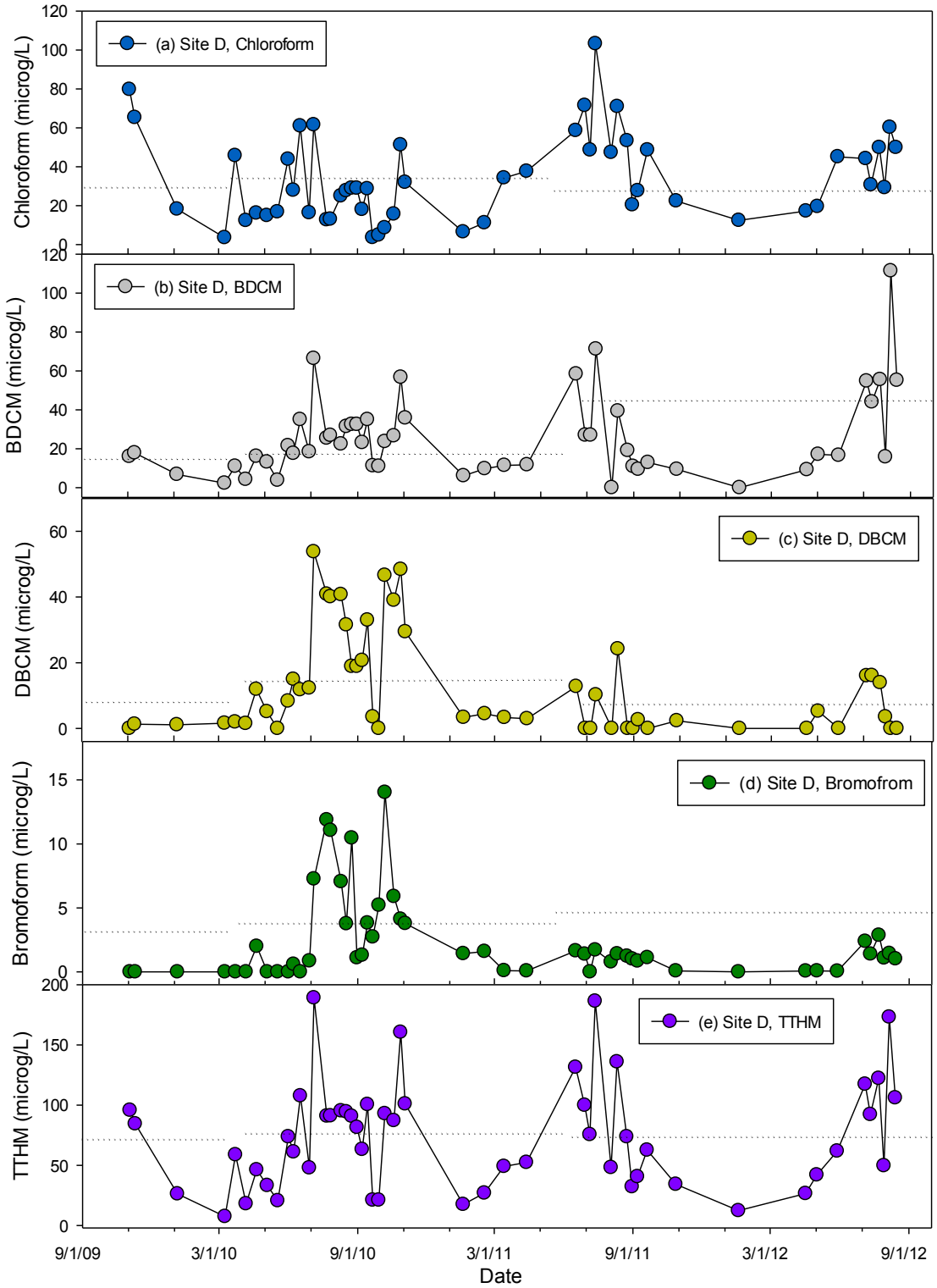

Figure 3.2 Concentrations of each THM species at Site F from 2009-2012. Panels show the concentrations of chloroform, BDCM, DBCM, bromoform and TTHM in finished water.

Drinking water TTHM compliance monitoring is based on quarterly average values following the Stage 2 DBP rule (USEPA, 2003c). Quarterly data of TTHM and individual THM species at 6 drinking water plants were computed from the collected data and are shown in Table B.1. Figure 3.3 shows the quarterly THM levels and bromide concentrations for Site F (similar plots for the other sites are given in Figures S11-S15). TTHM levels in finished water at Site F exceeded the 80 μg/L standard (red dash line) during quarter 2 and 4 in 2010 and quarter 2 in 2011. Figure 3.3 suggests that quarterly increasing formation of bromoform in finished water resulted from high source water bromide. Specifically, although the TTHM level (104 μg/L) in quarter 2 in 2010 was higher than TTHM level (61.7 μg/L) in quarter 3 in 2010, the average bromoform level (0.80 μg/L) in quarter 2 in 2010 was 3 times lower than bromoform (4.63 μg/L) in quarter 3 in 2010, likely resulting from the lower bromide (14.9 μg/L) present in source water in quarter 2 in 2010 than in quarter 3 in 2010 (104 μg/L).

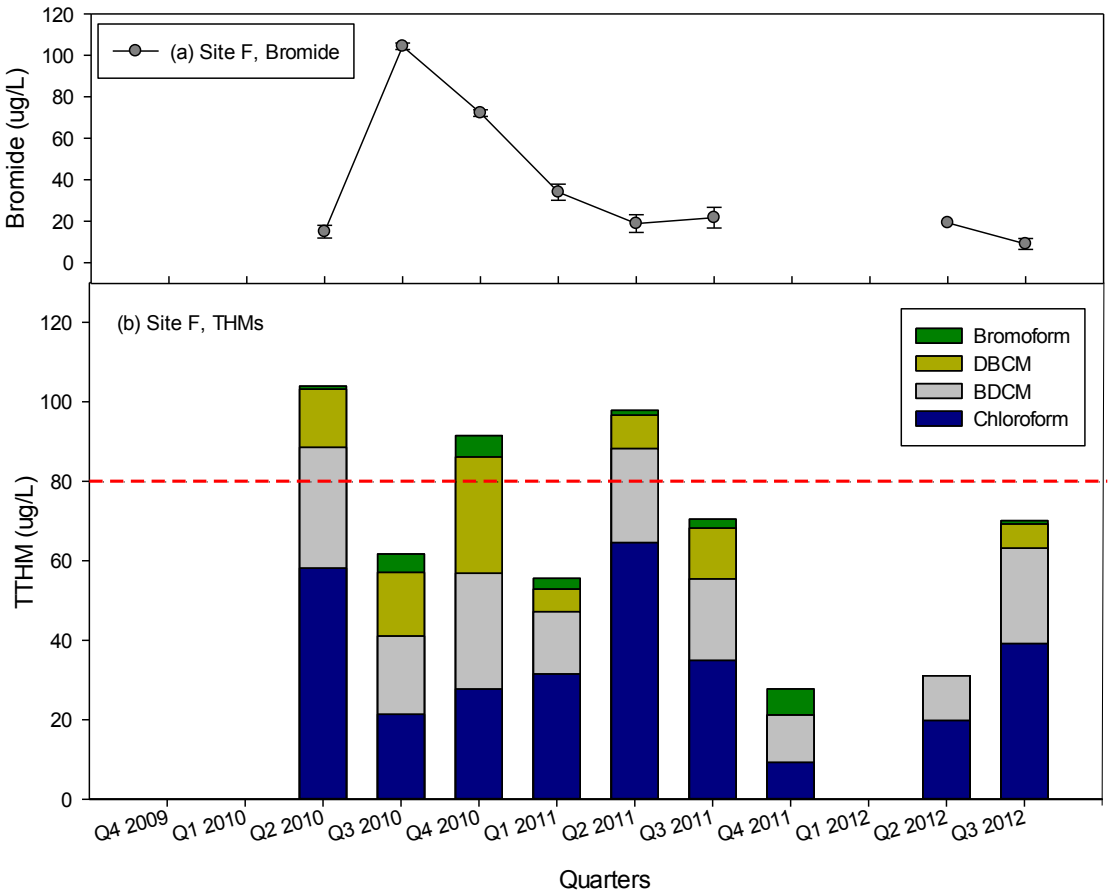

Figure 3.3 Quarterly bromide in source water and THMs levels in finished water at Site F. The red dash line indicates 80 µg/L TTHM standard.

Quarterly THM and bromide were further analyzed with Spearman rank correlation. Table 3.2 shows that bromide in source water is negatively correlated with quarterly chloroform level in finished water, and chloroform is not correlated with DBCM or bromoform; these results are similar to prior analyses based on ICR data (Francis et al., 2010). Source water bromide is strongly correlated with DBCM (Spearman coefficient = 0.748, p=0.005), again similar to results from the ICR analysis (Obolensky and Singer, 2008). Source water bromide is positively correlated with bromoform (Spearman coefficient = 0.671, p=0.017). The Spearman rank correlation results in Table 3.2 and scatterplots in Figure 3.4 demonstrate that TTHM level in finished water is strongly

correlated with chloroform (Spearman coefficient = 0.832, p=0.001) and BDCM (Spearman coefficient = 0.734, p=0.007). When bromide concentrations were low (see Figure 3.4(a)), chloroform levels in finished water were more predictive of TTHM levels (R^2=0.769) than when bromide concentrations were high (R^2=0.679) (see Figure 3.1(e)). Unlike chloroform, brominated THMs levels were observed to have better linear regression relationship with TTHM levels when bromide concentrations were high (see Figure 3.1(b,c,d and f,g,h)).

Table 3.2 shows that the correlations between brominated THMs and TTHM decrease as bromide substitution increases, again consistent with the findings based on ICR data (Francis et al., 2009). This is likely due to the fact that chloroform and BDCM levels dominate TTHM level in finished water. TTHM is strongly correlated with chloroform and BDCM, but has no correlation with DBCM and bromoform. The lack of correlations between TTHM and DBCM and bromoform indicates TTHM is not a good predictor of heavily brominated THMs (see Figure 3.4) (Keegan et al., 2001; Whitaker et al., 2003). TTHM is not correlated with bromide concentration (Spearman coefficient = 0.196, p=0.542) under any river conditions. Considering the strong seasonality of TTHM (see Figure 2(e)), and the known effect of temperature on chlorination rates, it is not surprising that source water temperature is significantly correlated with TTHM levels (Spearman coefficient = 0.891, p=0.001). The regression analysis between source water temperature and TTHM in Figure B.16 indicates that temperature alone is a reasonable prediction for TTHM formation in finished water for these drinking water plants (R^2=0.771).

Table 3.2 Spearman rank correlation cofeeicients shown for relationship between quarterly THMs and bromide concentrations at 6 drinking water treatment plants. P-values are shown in parenthesis. Gray and light gray indicate high and moderate correlation.

	Bromide	**Chloroform**	**BDCM**	**DBCM**	**Bromoform**	**TTHM**	**Percent Brominated THMs**	**BIF**
Bromide	1.00	-0.189 (0.557)	0.441 (0.152)	0.748 (0.005)	0.671 (0.017)	0.196 (0.542)	0.881 (0.00)	0.888 (0.00)
Chloroform		1.00	0.476 (0.118)	0.280 (0.379)	-0.196 (0.542)	0.832 (0.001)	-0.182 (0.572)	-0.217 (0.499)
BDCM			1.00	0.636 (0.026)	0.154 (0.633)	0.734 (0.007)	0.601 (0.039)	0.622 (0.031)
DBCM				1.00	0.671 (0.017)	0.573 (0.051)	0.748 (0.005)	0.734 (0.007)
Bromoform					1.00	0.112 (0.729)	0.510 (0.090)	0.524 (0.080)
TTHM						1.00	0.238 (0.457)	0.196 (0.542)
Percent Brominated -THMs							1.00	0.972 (0.000)
BIF								1.00

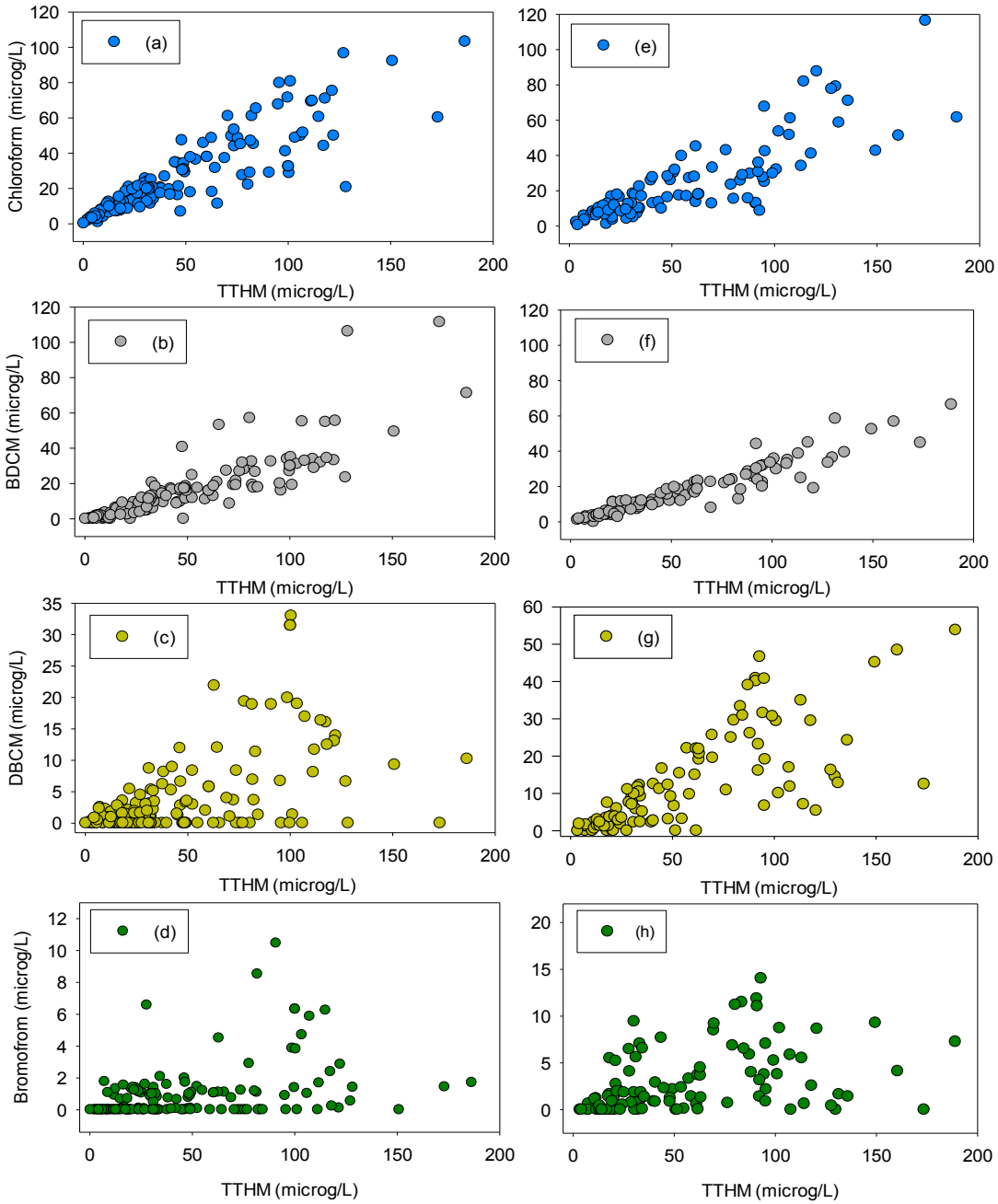

Figure 3.4 Scatterplots of each THM specie and THM concentrations of 6 drinking water plants during low and high bromide conditions. Panels (a-d) are THM levels during low bromide condition (≤50 µg/L); panels (e-h) are THMs during high bromide condition (>50 µg/L).

Effect of Rapid Changing Bromide Concentrations on THM Bromination

BIF, a representation of bromination on a molar basis (Equation 3), is significantly correlated with source water bromide concentration (Spearman coefficient=0.888, $p<0.05$). Figure 3.5 shows the linear regression of BIF and bromide concentrations ($R^2=0.810$), indicating that increasing or decreasing bromide in source water leads to proportional response in BIF in finished water. Table 2 shows that lightly brominated THM (BDCM) and source water bromide are not correlated, thus bromide concentration cannot be used to predict the changes of BDCM levels. The heavily brominated THM species DBCM and bromoform are strongly corrected with bromide concentrations in source water (see Table 2). Regression analysis between bromoform, DBCM and source water bromide are shown in Figure 3.6(a,b). Unlike the effect of changing bromide to DBCM, Figure 3.6 (b) suggests that the effect of changes of bromide in source water on bromoform level in finished water is not proportional (slope of the best fit line is 0.0441; $R^2=0.853$ in Figure 3.6(b)). Thus, changes of bromide affect bromoform formation more than DBCM formation in drinking water.

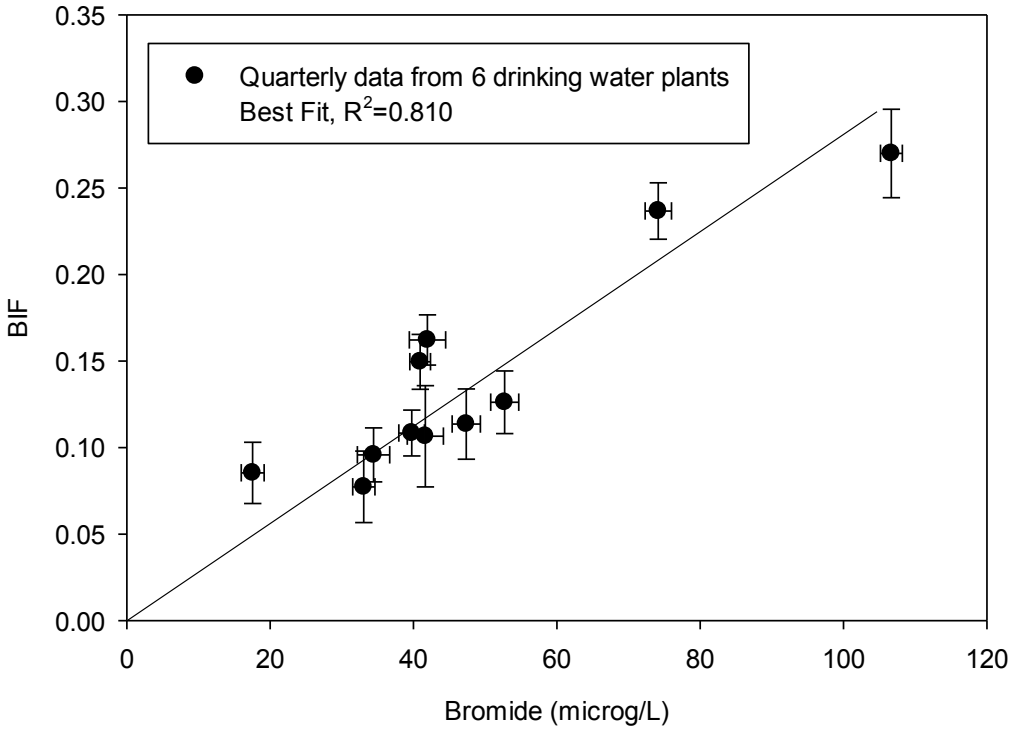

Figure 3.5 Linear regression between quarterly bromide concentrations and BIF values in source water. The vertical error bar shows the standard deviation of THM. The horizontal error bar shows the standard deviation for bromide.

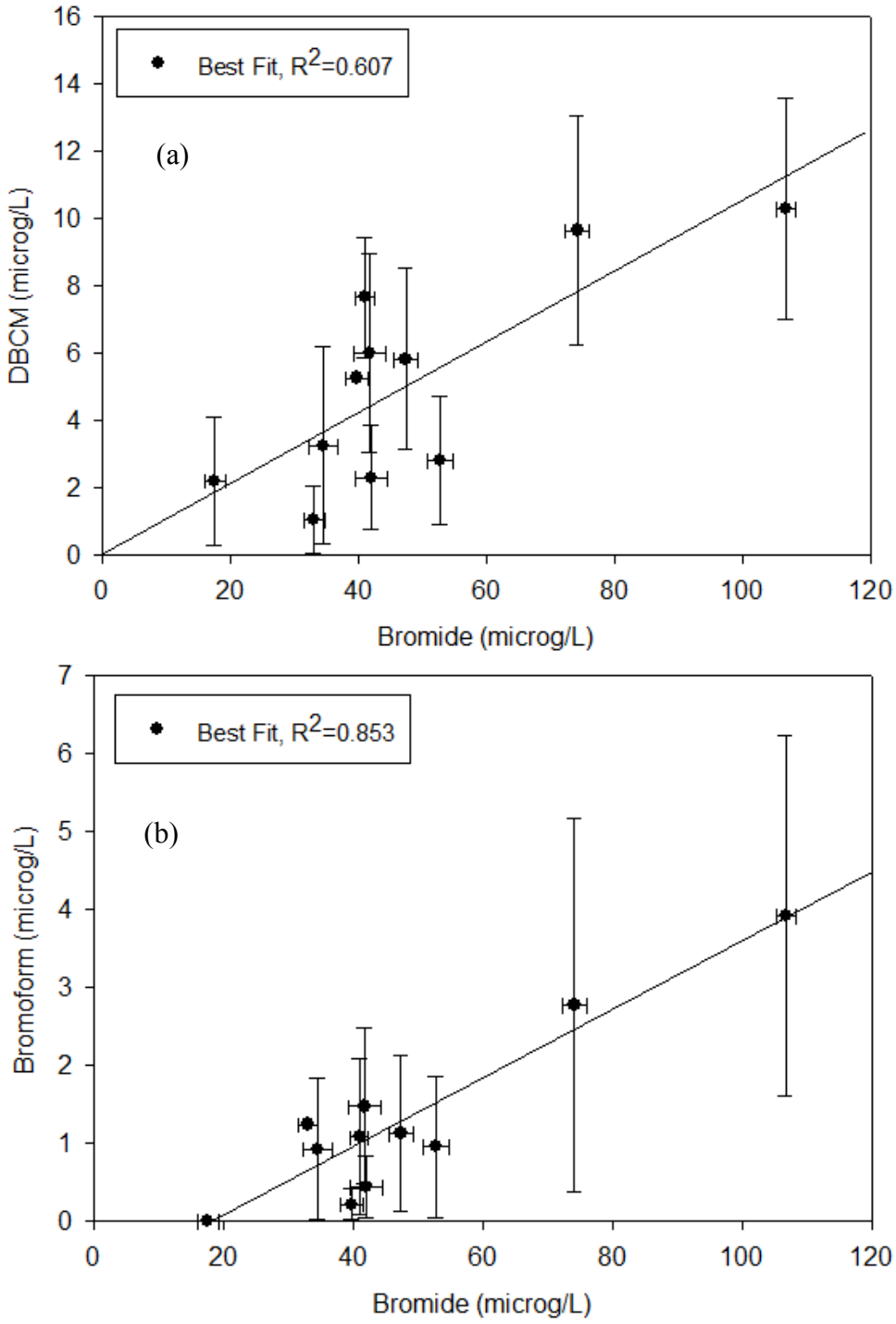

Figure 3.6 Linear regression between quarterly bromide concentrations and DBCM levels in panel (a) and bromoform levels in panel (b).

3.5 Conclusion

The bromide concentrations in source water in the Monongahela River basin changed significantly during 2009-2012 as a result of seasonal flow conditions and changes of disposal management methods of oil and gas wastewaters. The rapid changes of bromide concentrations led to significant changes in formation of brominated THMs, especially DBCM and bromoform. Source water bromide changes were correlated with increases in percent brominated-THMs but not correlated with TTHM, confirming TTHM is not a good surrogate for the effects of bromide on DBP formation. Further, TTHM changes are not a good indicator of changes in bromide, particularly due to seasonal variability in TTHM associated with temperature. Changes of source water bromide lead to the proportional changes of DBCM formation and BIF, but stronger changes of bromoform formation in finished water.

Chapter 4. Assessing the Risk Associated with Increasing Bromide in Drinking Water Sources

4.1 Abstract

Bromide ions present in drinking water sources can react with the applied chlorine disinfectant to form brominated disinfection by-products (DBPs). DBPs are carcinogenic, with brominated DBPs posing higher risk than chlorinated-DBPs. Recently, bromide concentrations increased significantly in source waters in southwestern Pennsylvania, leading to increases of trihalomethane (THM) levels in drinking water. THM regulations were developed based on chloroform-associated risk, reflecting the generally low source water bromide concentrations typically observed in the United States. An acceptable level of bromide in source waters has not been established, and bromide is not regulated in drinking water sources. This study presents a statistical simulation model to evaluate the effect of source water bromide on THM formation and speciation, and analyzes the changing cancer risks in water associated with changing bromide concentrations in the Monongahela River in Southwestern Pennsylvania from 2010 to 2012. Source water bromide concentration is significantly correlated with cancer risks from dibromochloromethane (DBCM) and bromoform in finished water. Elevated bromide concentrations increase the formation of DBCM and bromoform and their associated risks in finished water. Even very low bromide concentrations in the source water are associated with increased TTHM risk. Bromide concentrations should be monitored to identify and reduce bromide sources to surface waters.

4.2 Introduction

Bromide in source water has the potential to affect finished drinking water quality and has been a concern for drinking water plants for many years (USEPA, 2003c; Fiske et al., 2011; Wilson and VanBriesen, 2013b). Surface waters in the United States (US) usually have very low bromide concentrations from natural sources (Flury and Papritz, 1993), with elevated natural values reported near the coastlines (Pegram et al., 1997; CALFED, 2007).

Anthropogenic bromide can enter source water from human activities, including: agricultural applications (methyl bromide was widely used to fumigate crops and soil until it was phased out under the Montreal Protocol; road run-off (particularly when ethylene dibromide was used as a gasoline additive); and industrial discharges (Sollars et al., 1982; USEPA, 1991b). Recently, increasing concerns regarding bromide discharges to surface water from oil and gas produced water disposal and coal-fired power plant effluents have been raised (Fiske et al., 2011; States et al., 2013; Wilson and VanBriesen, 2013b).

The discharge of bromide to surface waters is currently unregulated in the US (DiCosmo, 2012) since bromide has high human and ecotoxicity thresholds (Flury and Papritz, 1993). While direct bromide toxicity is very unlikely (WHO, 2009), the formation of brominated disinfection by-products (DBPs) in drinking water plants is observed at very low source water bromide levels (Krasner et al., 1994).

DBPs form when applied disinfectants react with naturally-occurring organics, forming chlorinated organic compounds, many of which have negative human health impacts. Bromide

present in the source water reacts with the disinfectant to form bromine, which then also oxidizes organics, creating brominated and mixed bromo-chloro-DBPs. Higher concentrations of bromide increase the rate of DBP formation, leading to higher overall DBP concentrations (Obolensky and Singer, 2008; Francis et al., 2010), as well as increasing the incorporation of bromide into the formed DBPs (Symons et al., 1993; Clark et al., 2001; Xie, 2003; Hong et al., 2007). Brominated DBPs exhibit negative effects on human health at lower concentrations than chlorinated DBPs (Richardson et al., 2003; Richardson et al., 2007), thus, higher source water bromide is expected to lead to higher risk associated with the finished water DBPs (Richardson et al., 2003). Source water bromide concentrations are not significantly removed by conventional drinking water treatment process, and thus, bromide continues to be a driver for DBP formation and compliance problems despite treatment plant changes to address other DBP precursors, e.g., enhanced coagulation to remove natural organic matter (Francis et al., 2010; Bond et al., 2014).

The Stage 1 Disinfectants/Disinfection By-Products (D/DBP) Rule was established in 1998 to regulate total trihalomethanes (TTHM) at a maximum contaminant level (MCL) of 80 μg/L and a group of five haloacetic acids (HAA_5) at an MCL of 60 μg/L (USEPA, 1998b). TTHM is the sum of *mass concentrations* of chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform. The MCL of 80 μg/L for TTHM was based on the presumption that the majority of THM in a chlorinated drinking water system will be chloroform. The use of a mass sum was designed to account in part for the greater risk assumed to be associated with brominated THM, in the absence of adequate toxicity testing for the brominated compounds (Cotruvo, 1986). Each individual THM species was assigned a

maximum contamination level goal (MCLG); MCLGs are non-enforceable contaminant levels at which no adverse health effects are likely to occur, allowing for a margin of safety (USEPA, 2006). The MCLGs for chloroform, BDCM, DBCM and bromoform are 70 µg/L, 0 µg/L, 60 µg/L and 0 µg/L, respectively (USEPA, 2006).

Recently, increasing bromide concentrations in surface waters have been reported in a number of locations where drinking water plants are observing higher levels of THMs in finished water (Fiske et al., 2011; States et al., 2013). Coagulation process in drinking water treatment generally removes more HAAs precursors than THMs precursors (Liang and Singer, 2003; USGS, 2013b). High bromide source waters are likely to be more problematic for water utilities with respect to THMs formation than for HAAs (Bond et al., 2014). The role of source water bromide in the observed increase in THM bromination is clear; however, the significant differences observed in finished water quality associated with different source water bromide levels makes it difficult to determine a source water concentration that would be protective for drinking water consumers. While EPA is considering setting an in-stream water quality criteria for bromide (DiCosmo, 2012), adequate methods for determining such a standard for particular water bodies do not exist. The changing risk profile for THMs associated with changing bromide concentrations in source waters has not been evaluated for source waters in the US, including the Monongahela River Basin. An improved understanding of species-specific THM risk and its relationship to source water bromide is needed to inform in-stream bromide criteria decision-making.

The present study is based on the results of a three-year field study in the Monongahela River in Pennsylvania, which included collection of source water bromide concentration and finished

water disinfection by-product speciation at six drinking water plants. The study evaluates the cancer risk associated with each THM species on a quarterly basis, aligned with the regulatory timetable. Methods to assess acceptable bromide concentrations for source water protection based on the MCL, MCLGs, and risk are evaluated and compared.

4.3 Materials and Methods

Sampling Sites, Sample Collection and Measurement

Source water sampling, including site locations and detailed information about the procedure of sample collection and laboratory analytical method of bromide were fully described previously (Wilson and VanBriesen, 2013b). Analytical methods for finished water analyses were also described previously in Chapter 3. Raw data for source and finished water are included in the Appendix C for the present work as well as provided in previous publications (Wilson and VanBriesen, 2013b).

Censored Data Handling

Censored data are concentrations not observed due to analytical detection limitations. Censored bromide and THM concentrations were observed at all drinking water plants. Censored bromide data were handled using the same procedures employed in a previous study (Wilson and VanBriesen, 2013b) summarized, the censored data were extrapolated using a log-normal distribution fit to the observed data. For censored THM data, EPA requires results below the detection limit be reported as zero for the calculation of annual average (USEPA, 2012a). Thus, censored THM concentrations in this study are replaced with zero for statistical analysis.

EPA Risk Data

EPA conducted a quantitative estimation of carcinogenic risk for THM species in drinking water (USEPA, 2005). Unit risk is used to estimate the cancer risk associated with exposure to a chemical of concern. The unit risks for chloroform, BDCM, DBCM and bromoform in drinking water are 1.2×10^{-7}, 1×10^{-6}, 1.2×10^{-6} and 1.3×10^{-7} per μg/L, respectively (USEPA, 1998a). Thus,

DBCM represents the most serious cancer risk, followed in order by BDCM, bromoform and chloroform (Jurenka, 2009).

Risk Analysis

EPA recommends three approaches to quantitative health risk assessment of chemical mixtures. The first approach directly uses the available toxicity data of the mixture to evaluate the risk (USEPA, 2000c). In the second approach, when toxicity data are not available for the mixture, EPA recommends using health effects data on a similar mixture (Rice et al., 2009). The third approach is to evaluate the mixture risk through its components by using dose addition or response addition, based on the assumption that interaction effects are insignificant and negligible to the risk estimate (USEPA, 2000c, b). The additivity approach is appropriate "when the effect of the mixture can be estimated directly from the sum of the scaled exposure levels (dose addition) or the response (response addition) of individuals components" (USEPA, 2000c). Dose addition is only applied when individual components exhibit similar toxicity (USEPA, 2000c). The response addition procedure requires first to determine the individual risk of each component, then add the individual together to evaluate the mixture risk (USEPA, 2000c).

In the present work, unit risk is multiplied by the concentration of each THM species to obtain the risk for one cancer case in a population of 1 million. The species-specific risk of total THM is then calculated by EPA's response additivity approach by summing the calculated individual risks and is referred to as TTHM species-specific risk in the present work. While risk additivity is an acceptable method for mixture assessment, the maximum contaminant level for TTHM was set based on the potential carcinogenicity of chloroform alone as EPA concluded at the time that

it would be inappropriate to consider differences among THM species as the carcinogenic potential of brominated-THMs was not then known (Cotruvo, 1986). Thus, the risks of brominated THMs are not directly included in the TTHM regulation. The TTHM-derived risk that represents current regulation is calculated by multiplying the total THM concentration (the sum of the mass concentrations of the four THM species) by the unit risk for chloroform. Quarterly risks of each THM species at the 6 drinking water treatment plants in this study (Site A to Site F) were calculated in this manner.

Statistical Data Analysis

Geometric means of quarterly bromide concentrations and quarterly species-specific THM concentrations are used for analysis to avoid sensitivity to outliers and to best represent the central tendency of the data (Helsel and Hirsch, 2002). The Mann-Whitney (MW) rank sum test was employed to evaluate the statistical significance of TTHM species-specific risk and TTHM derived risk. The MW test allows evaluation of datasets with both non-normally distributed and censored data (Wilson and VanBriesen, 2013b), was implemented in Sigmaplot (Systat Software, San Jose, CA) and was applied due to the non-normally distributed data and the presence of censored data (Wilson and VanBriesen, 2013b). Correlations among bromide concentration and individual THM species concentrations were computed with Spearman rank correlation analysis in Minitab (Statistical software, State College, PA) due to the non-normally distributed data (Obolensky and Singer, 2005; Francis et al., 2009). Linear regression was applied to evaluate the relationships between finished water THM concentrations and source water bromide concentrations.

Monte Carlo simulation has been used previously by EPA to support regulatory impact analysis of DBPs (Gelderloos et al., 1992) and was used in the present work to generate an extension of TTHM concentrations that consider correlation and interaction among all THM species (USEPA, 1997a). Monte Carlo simulation enables quantitative characterization of the uncertainty and variability in estimated concentrations and provides more information to forecast full range of possible values in the future (USEPA, 1997a; Poulter, 1998; Baron, 2007). By considering correlations among species, the simulated THM concentrations better represent the true variability and uncertainty in finished water quality, and reflect the best available knowledge about drinking water quality from the data set (Grayman et al., 2006). A number of alternative multivariate probability distribution functions have been used to fit and simulate the joint distribution of THM species and other chemical concentrations in surface and drinking waters (Francis et al., 2009). A joint lognormal distribution was assumed and fitted to the field sampled concentrations of chloroform, BDCM, DBCM, and bromoform in each of seven bromide concentration ranges: 0-20 μg; 20-40 μg/L; 40-60 μg/L; 60-80 μg/L; 80-100 μg/L; 100-120 μg/L; and >120 μg/L. THMs levels (μg/L) were converted into nanogram/L then used for the joint lognormal distribution due to some THMs levels were below 1 μg/L and could not be performed in joint lognormal distribution. The data were aggregated across sites and sampling dates to estimate a separate multivariate lognormal model representative of each bromide interval. Each joint lognormal distribution was characterized by:

- a_i (i = 1,4) = the means of the ln(concentrations) for each of the four THM species (4 parameters);
- b_i (i = 1,4) = the standard deviations of the ln(concentrations) for each of the four THM species (4 parameters); and

- $\rho_{i,j}$ (i,j = 1,4) = the correlation coefficients between the ln(concentrations) of each of the four THM species (6 parameters).

As such, there were a total of 14 parameters fitted for each bromide interval, with separate models fitted for each of the seven intervals. Monte Carlo samplings for each interval were simulated 10,000 iterations to generate correlated normally distributed values through Excel @risk (Palisade Corporation, Newfield, NY). Table C.1 shows the correlation parameters for field sampling THMs data and Monte Carlo simulated data. Table C.2 shows the other parameter estimates for each interval and the estimated mean concentration for each species i in each interval k, computed as:

$$\mu_{i,k} = exp(a_{i,k} + 0.5\mu_{i,k}^2) \qquad \text{(Equation 1)}$$

The $\mu_{i,k}$ (k = 1,7) value in nanogram/L then converted back to µg/L.

A cumulative distribution function (CDF) plot represents possible values of a variable and the proportion of observations of that variable that are less than the value specified on the horizontal axis (USEPA, 2010). The advantage of viewing a distribution with a CDF is that it clearly indicates the likelihood of having an observation that is equal to or less than a specified value of the variable (USEPA, 2010). CDF plots were employed with the generated Monte Carlo simulation THM data to view the distribution and determine the probability of obtaining finished water that meets the TTHM standard.

4.4 Results and discussion

Source Water Bromide and THMs

Bromide concentrations in the source water changed significantly over the three-year period from 2009-2012 in the Monongahela River basin (Wilson and VanBriesen, 2013b), affecting the formation and speciation of THMs in finished drinking water.

As an example, Figure 4.1 shows Site D mean quarterly bromide concentrations in the source water and the quarterly concentration of each THM species in the finished water (results for all sites are provided in Figures 9.1-9.5 in Appendix C; data are provided in Table C.3). Figure 4.1(a) shows that the source water bromide concentration continuously increased in 2010 and then decreased in 2011 and 2012, with the exception of fourth quarter 2011. Flow is seasonally low in the summer (quarter 3) in this basin, and the bromide concentration would be expected to show seasonality with flow-impacted concentration; however, changes in management of discharging oil and gas wastewaters in the region likely account for the decreasing trend after 2010 (Wilson and VanBriesen, 2013b). When source water bromide concentrations are stable, THM concentrations are expected to follow a seasonal pattern, with higher values in the summer months when warmer water temperature increases formation rates and higher chlorine doses are applied to ensure adequate residual chlorine in the distribution system. In 2010, chloroform did not show this expected seasonal increase; however, it did in 2011 and 2012 (see Figure 4.1(b)). The increased BDCM, DBCM and bromoform in the summer of 2010, caused by the increase in bromide in the source water (above 100 μg/L), likely accounts for the lower chloroform than would be expected. More rapid formation

of brominated THM reduces the available organic carbon for chloroform formation. Similar trends to Site D are observed at other sites (see Appendix C).

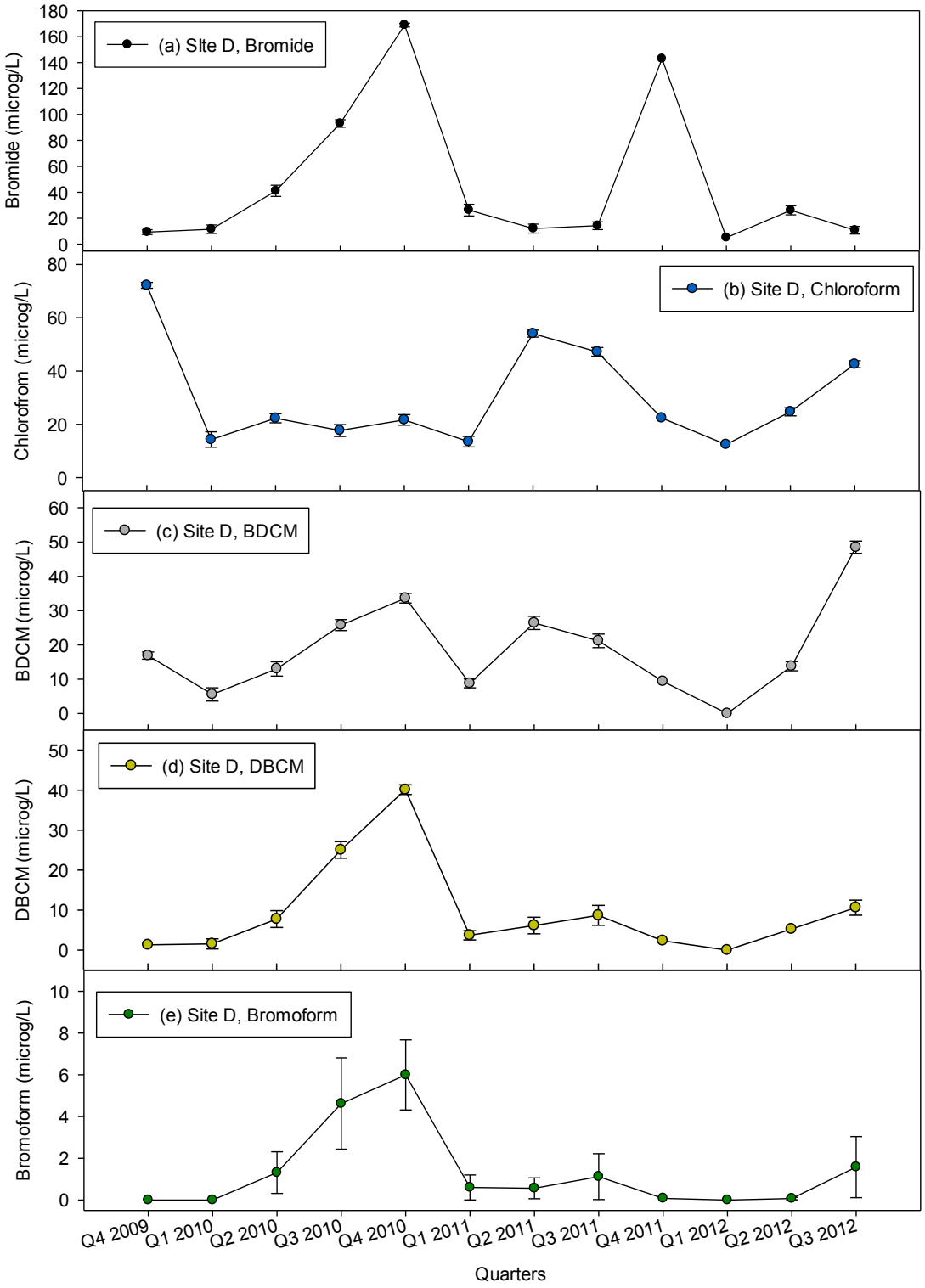

Figure 4.1 Quarterly geometric means of bromide concentrations and individual THM species levels in finished water of Site D. Ranges show are one standard deviation.

THM Risk Analysis

The species-specific THM concentrations are affected by source water bromide concentrations; however, it is the risk associated with these compounds, not their concentration, that is of interest in determining acceptable bromide concentrations for source water. The risk of each THM species is directly proportional to its concentration through its unit risk value. Figure 4.2 shows the quarterly risk computed for each of the four THM species for site D (other sites are shown in the Figure C.6-C.10 in Appendix C). The additive nature of the risk values computed allows the results to show the total TTHM species-specific risk when stacked as shown in Figure 4.2. Although chloroform was the highest concentration THM in finished water (see Figure 4.1), Figure 4.2 shows that the risk related to chloroform only accounted for a small portion (8.02% to 18.6%) of TTHM risk. Figure 4.2 shows that the BDCM and DBCM together generally dominated the risk of TTHM, ranging from 0% (when both were undetectable in quarter 1, 2012) up to 95.4% in quarter 4, 2010. Similar results to Site D are observed at other sites (see Appendix C). Although DBCM concentrations were significantly lower than chloroform concentrations ($p=0.001$), the risk of DBCM is not significantly different from the risk of chloroform ($p=0.583$), highlighting the importance of DBCM as a risk-driver. Bromoform accounted for the smallest portion of the risk of TTHM due to its very low concentration in finished water throughout the study period and across the different drinking water plants. The red dots shown in Figure 4.2 represent the TTHM-derived risk based on the assumption that all THM are equivalent to chloroform in risk. This TTHM-derived risk is significantly lower than the THM species-specific risk ($p<0.001$).

As expected, the cancer risk associated with mixtures of TTHM that include significant concentrations of brominated compounds could significantly exceed the TTHM derived risk based on the assumption that chloroform would dominate the speciation.

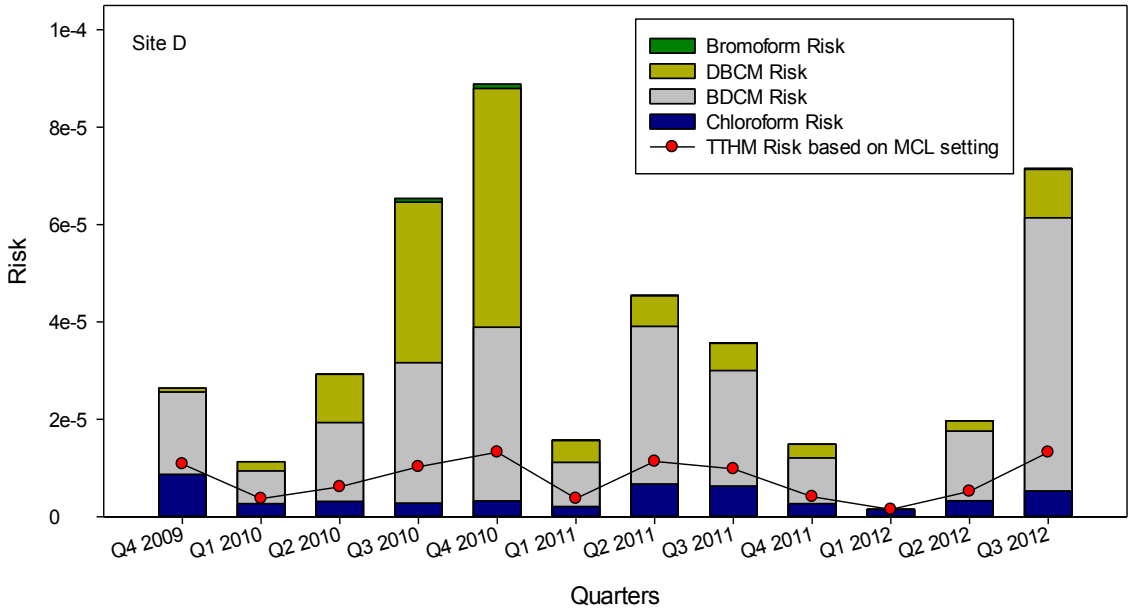

Figure 4.2 Risks of THM species on a quarterly basis at Site D.

Monte Carlo Simulation Results

To assess the effect of increasing bromide concentrations to the risk of THMs, the THM risk from 6 drinking water plants at different bromide concentration ranges (e.g., 0-20, 20-40, ..., 100-120, >120 µg bromide/L) were evaluated using a Monte Carlo simulation. As an example, Figure 4.3 shows the empirical CDF of the TTHM *concentration* in panel (a) and the empirical CDF of the species-specific TTHM *risk* in panel (b) for finished water when source water bromide concentrations ranged from 20-40 µg/L. Figure 4.3(a)

shows that 77.3% of finished water samples met the 80 µg/L TTHM standard, while Figure 4.3(b) shows that 50.5% of finished water samples met the target risk that based on the MCL setting of TTHM. Thus, the regulatory requirement is likely to be met when bromide concentrations are below 40 µg/L, but the target risk is not. The empirical CDFs of TTHM concentrations and TTHM species-specific risk are plotted for other bromide concentration ranges in Figure C.11-C.16 in Appendix C.

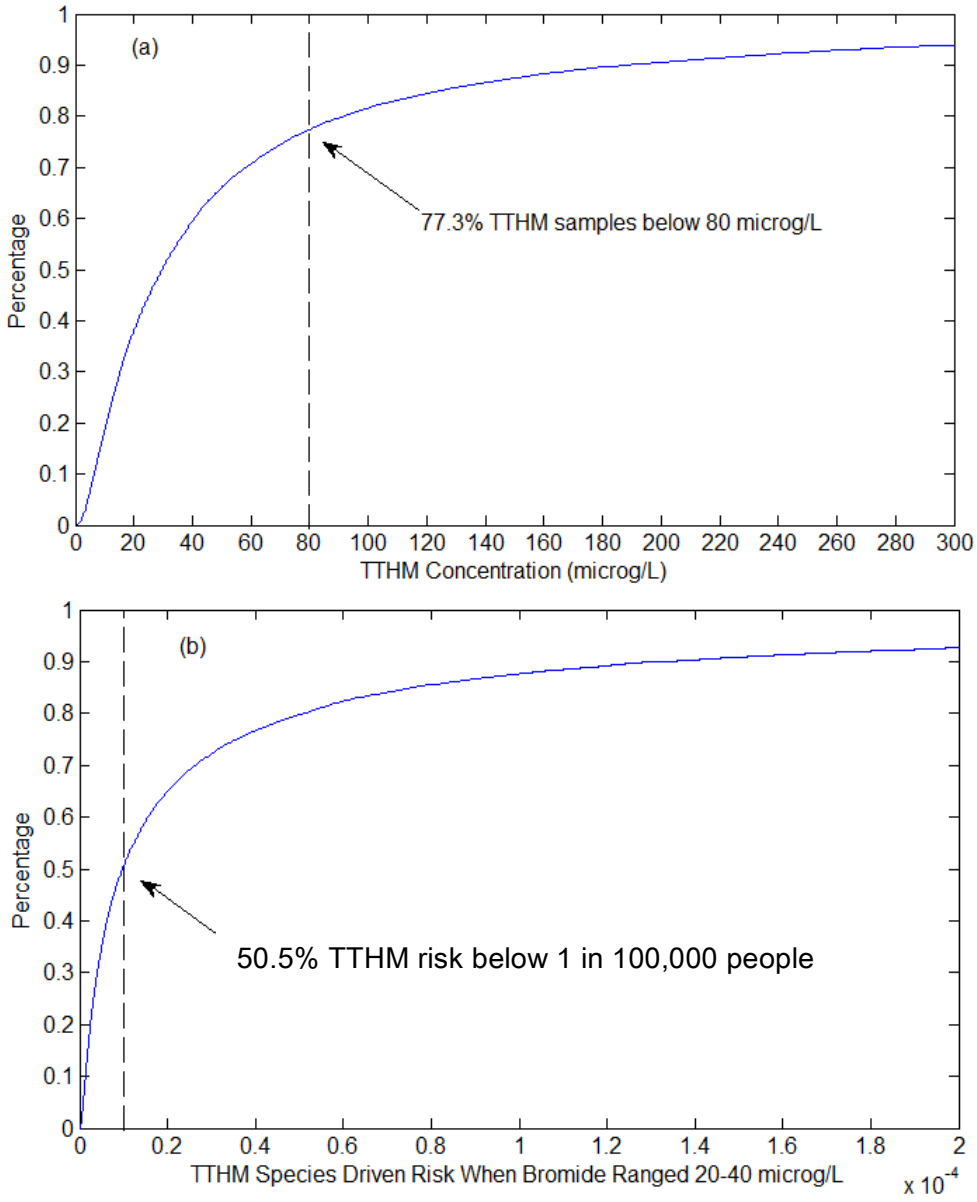

Figure 4.3 Empirical CDF of TTHM concentration (a) and empirical CDF of TTHM species-specific TTHM risk (b) when bromide ranges 20-40 µg/L.

Considering all the concentration ranges and all sites, the likelihood of meeting target risk and meeting TTHM standard are summarized in Table C.3 and plotted in Figure 4.4. Figure 4.4 shows that the probability of meeting the 80 μg/L TTHM standard at all bromide levels was significantly higher than the probability of meeting the target risk ($p<0.001$). Both the probabilities decreased when bromide concentrations in source water increased. The probability of meeting the 80 μg/L TTHM standard remained high (64.4%-81.3%) when bromide concentrations were below 120 μg/L, and decreased to 61.3% when bromide concentrations were above 120 μg/L. The probability of meeting the target risk was always quite low and continuously decreasing when bromide increased, due to the increase in brominated THM with their higher unit risk values. The probability of meeting the target risk decreased from 50.5% when bromide ranged 20 to 40 μg/L to 13.5% when the bromide exceeded 120 μg/L. Figure 4.4 shows that although the probability of meeting the target risk was always below 50%, the finished water had a high likelihood of meeting the TTHM 80 μg/L mass standard when source water bromide concentrations were below 120 μg/L. Thus, although the finished water may be in compliance most of the time, the risk associated with consumption of this water is higher than it would be if the source water contained no bromide.

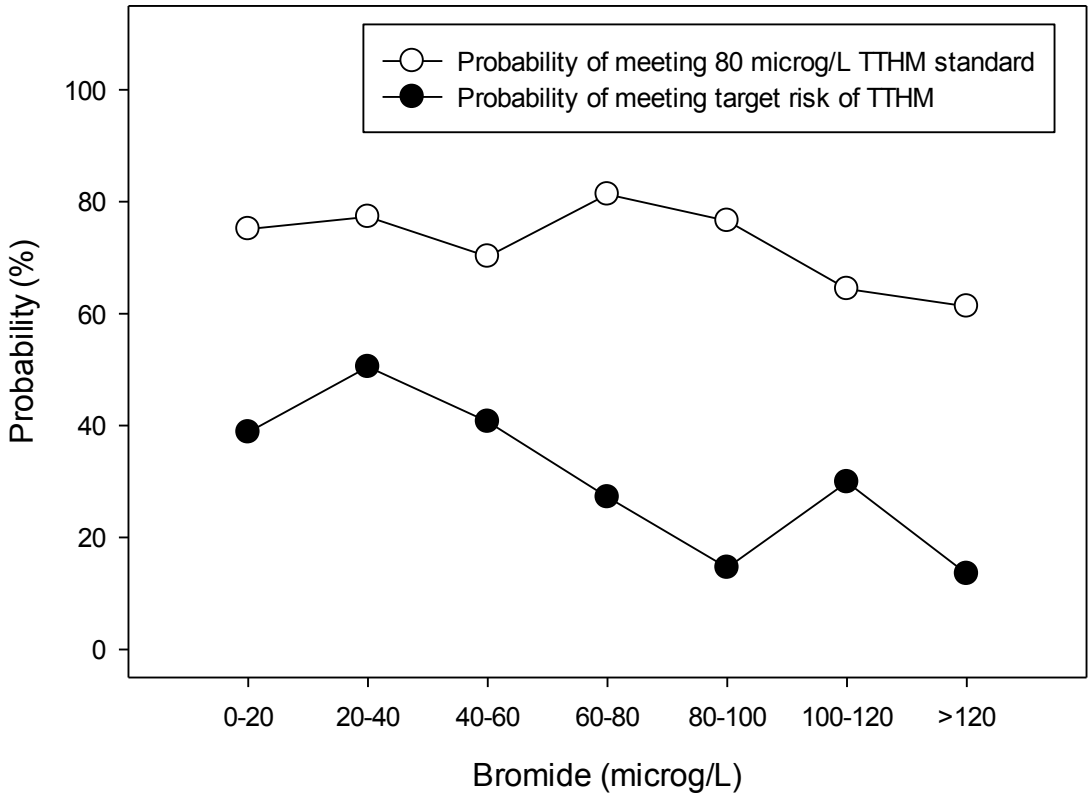

Figure 4.4 Probabilities of meeting the 80 μg/L TTHM standard and meeting the target risk (1 cancer case in 100,000 people) of TTHM.

Since the probability of meeting the target risk of TTHM is low and decreases when bromide concentrations are elevated (Figure 4.4), it is informative to quantify the excess TTHM risk associated with the water under increasing bromide conditions. Figure 4.5 shows the TTHM species-specific risk compared to the TTHM-derived risk, using data from the 6 plants. As expected, the TTHM derived risk did not change significantly with increasing bromide when a single unit risk (based on chloroform) was used. However, the TTHM species-specific risk was significantly higher and was dependent on source water bromide concentration. Figure 4.5 also shows that when bromide concentrations

were below detection limit (10 µg/L), the TTHM species-specific risk was still higher than the TTHM derived risk, which indicates that even very low bromide concentrations could lead to excess risk of the TTHM target risk. When bromide concentration was above 120 µg/L, the TTHM species-specific risk was computed as 1 in 25,252 people (3.96×10^{-5}), while using the regulatory framework, the TTHM-derived risk was computed as 1 in 133,155 people (7.51×10^{-6}). Thus, increasing bromide in source water leads to higher cancer risk in the finished water that may not be adequately assessed using TTHM measurements alone.

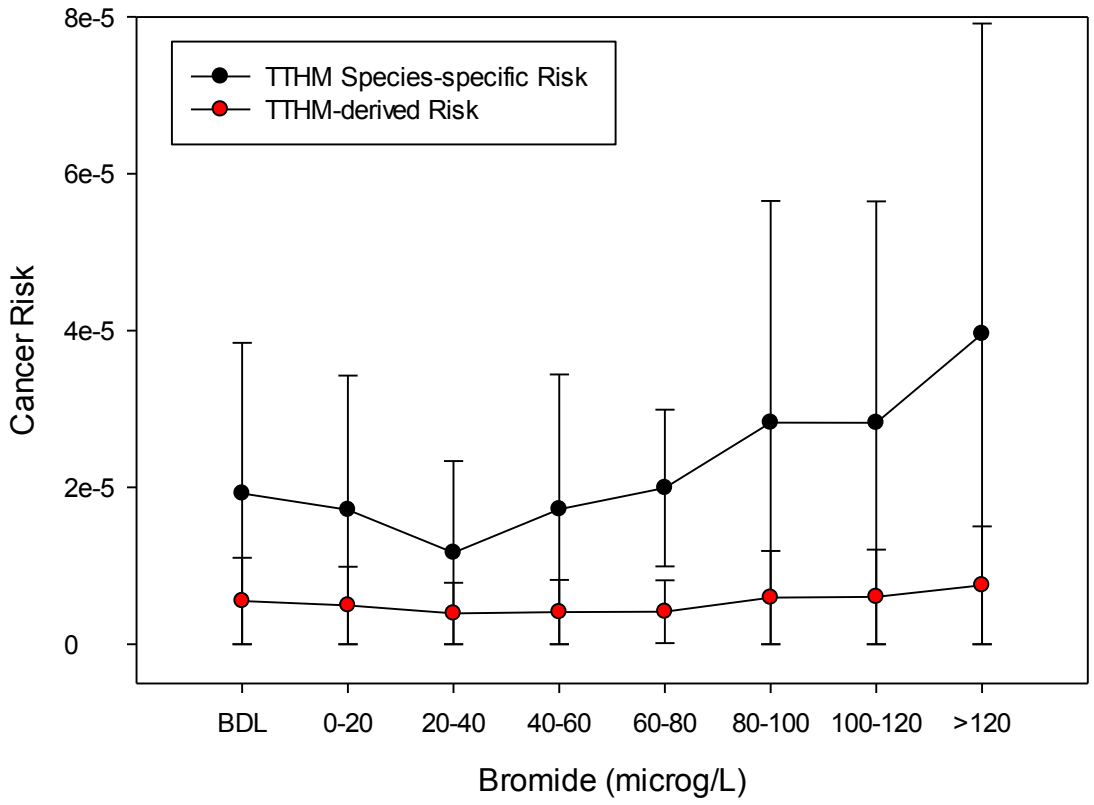

Figure 4.5 Excess risk of TTHM simulated by Monte Carlo simulation. The solid dots show the mean and the error bar shows the standard deviation. BDL stands for below detection limit.

In-stream acceptable bromide concentration assessment

The risk analysis above suggests that source water bromide concentrations must be quite low to reduce risk from brominated DBPs to desired target levels, while higher bromide levels may be acceptable if meeting TTHM standards is the only expectation. The present analysis provides insight into methods to select acceptable in-stream bromide concentrations by using data from the 6 drinking water treatment plants that all use the Monongahela River as a source.

Considering quarterly data, the relationship between source water bromide concentration and finished water TTHM is shown in Figure C.17 along with a linear regression of the data. As expected, the correlation is quite poor (R^2=0.0006), and thus a target in-stream bromide concentration to protect drinking water users cannot be determined based on the existing TTHM standard.

Unlike TTHM, DBCM and bromoform were strongly correlated with source water bromide concentrations (Spearman coefficient = 0.784, p=0.005 and Spearman coefficient = 0.671, p=0.017, respectively) as shown in Table C.4 in Appendix C. Figure C.18 in SI includes the quarterly data and the linear regression for bromoform (panel a) and DBCM (panel b). By substituting the MCLGs for bromoform (0 μg/L) and DBCM (60 μg/L) into the linear regression equations, acceptable source water bromide concentrations to ensure finished water below the MCLGs can be assessed. To ensure bromoform is undetectable (required to meet its MCLG of zero), source water bromide must be below 19.1 μg/L, while ensuring DBCM meets its MCLG (of 60 μg/L) requires only that bromide be below 569 μg/L. Chloroform and BDCM levels in finished water

are not correlated with source water bromide concentrations, and thus, no target bromide concentrations can be suggested from this type of analysis for those products.

4.5 Conclusion

Table 4.1 summarizes the bromide concentrations that ensure *finished water* below the MCL, MCLGs, and target risk of THMs. It is important to note that these values are based on analysis of TTHM in finished water leaving the plant; however, THMs continue to form in the distribution system during water distribution, and the regulatory compliance point for TTHM concentration is at the consumers' point of consumption.

Table 4.1 Bromide concentrations to ensure finished water below MCL, MCLGs, and target risk of THMs.

Regression Relationship	MCL, MCLG, or Target Risk of THMs	Best Fit	Recommended Bromide Concentration
Bromide vs Bromofrom	0 µg/L	Bromofrom=0.0441×Bromide-0.842 (R^2=0.853)	19.1 µg/L
Bromide vs DBCM	60 µg/L	DBCM=0.1054×Bromide (R^2=0.607)	569 µg/L
Bromide vs TTHM	80 µg/L	None	None
Bromide vs Target Risk	1 in 100,000 people	See Figure 4.5	Lower than 10 µg/L (As low as possible)

While the Monongahela River drinking water plants show variable responses to source water bromide, overall the results indicate that to prevent the adverse health effect associated with brominated THMs, the bromide concentrations in source water must be very low. Even at low bromide concentrations, when the finished water meets the TTHM standard, the risk analysis indicates that the cancer risk may still exceed the target risk. To protect the consumers of chlorinated drinking water, in-stream bromide concentration

should be monitored and discharges of bromide-containing wastewaters to surface water should be reduced where they are affecting downstream drinking water sources. Identification of bromide discharges, proximity to drinking water intakes, and seasonal flow conditions in the river should all be considered in evaluating methods to control source water bromide to reduce risks associated with brominated THM in finished water.

Chapter 5. Conclusion and Implications

The overall research objective of this work was to evaluate acceptable bromide concentrations in source water for the protection of drinking water quality in Southwestern Pennsylvania. The dissertation demonstrates the relationship between source water bromide and formation and speciation of THM species and their related health risks, and proposes a statistical simulation model to determine the acceptable bromide concentration in source water for drinking water protection.

5.1 Conclusions

It was determined in Chapter 2 that water sample types (river water samples vs drinking water intake samples) can lead to different conclusions about water quality in a large river. Water samples collected during low flow conditions are likely to show the most variability due to sample types and sampling locations, and these samples are the most relevant for regulatory decision-making. Sampling for compliance should be taken at drinking water intake points to represent source water quality.

In Chapter 3, quarterly bromide concentrations are shown to lead to changes of heavily brominated THMs (DBCM and bromofrom) and the BIF value in finished water. While prior work across multiple drinking water systems has demonstrated this general relationship between source water bromide and brominated THM, the unique experience of the Monongahela River basin undergoing rapid *changes* of bromide concentrations at drinking water plants provides important information about how THM formation will change over time as bromide concentrations in source waters increase in response to changes in water quantity as well as

changes in bromide loading. Changes of bromide cause proportional changes of DBCM levels and BIF in finished water while causing a two-fold increase in bromoform. These changes happen quickly in response to source water bromide changes.

In Chapter 4, assessment of the risk associated with the changes in THM speciation indicates that to prevent the adverse health effect associated with brominated THMs, the bromide concentrations in source water must be very low. Even at low bromide levels (less than 20 μg/L), although the drinking water meets the TTHM standard, the health risk associated with the water exceeds the target. A novel statistical simulation method to assess the safe bromide concentration for the protection of drinking water quality was presented. Drinking water treatment plants should monitor the bromide concentration in source water to protect consumers of chlorinated drinking water. The proposed method could be used by water utilities to determine for their own system what source water bromide concentration should trigger changes in operations or consideration of alternative disinfectants.

5.2 Research Implications

This research describes a method to determine the in-stream bromide concentration that is protective of human health for those consuming chlorinated drinking water. This research has important implications for wastewater discharge management, drinking water treatment plants monitoring, and regulatory decision making.

The results in this dissertation suggest it is important to identify possible bromide discharges and their proximity to drinking water intakes in watersheds. Elevated bromide concentrations can be attributed by many factors, including oil and gas extraction wastewaters and power plants

wastewaters. Bromide discharges to surface water should be monitored and reduced to reduce the risk from exposure to brominated DBPs in consumers of chlorinated drinking water.

This work suggests that drinking water providers should monitor bromide concentrations in their source water, and use these data along with TTHM compliance data to assess risk. Most drinking water plants send their finished water samples to external testing laboratories to measure the TTHM level in finished water; they do not measure the concentration of each THM species. Thus, risk from brominated THM in finished waters in not typically assessed. Bromide monitoring by drinking water treatment facilities can serve as a predictor for increases in brominated THMs in finished water, and thus, represents an early warning of changes in risks associated with exposure to chlorinated water.

This work also has important implications for regulation of bromide. EPA is considering setting an in-stream bromide criteria, but adequate methods for determining such a criteria for particular water bodies do not exist. This research proposed a novel method and analysis structure to assess the safe in-stream bromide concentrations for drinking water protection based on the current MCL, MCLGs settings, and health risk. The results of this work could serve as reference for EPA's future regulation of bromide and other trace elements in source water.

Chapter 6. Future Work

6. 1 Future Work: Assessing the applicability of existing THMs models using 3 years field sampling data

DBPs formation has been modeled using regression models that incorporate source water quality parameters and treatment plant operations (Chen and Weisel 1998; Gang et al. 2003; Singer et al. 1995). However, there are significant limitations to existing models. For example, most of the models were developed under controlled laboratory conditions or using data from one single drinking water plant and not predictive in other systems.

Minear and Morrow (1983) first proposed an empirical model including bromine as an explanatory variable but without considering contact time. Malcolm et al. (1992, 1993) proposed empirical models for THM species and TTHM. Based on the ICR database, Francis et al. (2010) conducted statistical methods and generated a nationwide empirical model predicting bromine incorporation in THMs. Mechanistic models of TTHM were first developed by Adin et al. (1991) using TOC concentration, chlorine dose and contact time, considering first-order reaction with chlorine, and second-order reaction independent of chlorine. Then Clark et al. (1998) developed a second order kinetic model including consideration about pH and temperature. In Clark's work, prediction of TTHM concentration is linearly related to chlorine decay model they proposed. The parameters of the THM model and the chlorine decay model were estimated with laboratory bench-scale chlorination experiments, requiring inputs of initial chlorine, TOC, pH, temperature, contact time. Later Clark et al. (2001) revised their model incorporating the influence of bromine and generated sets of coefficients for several DBP species. Boccelli

et al. (2003) applied Clark's model (1998) as the basis, adjusting it under rechlorination conditions to predict TTHM. It is unclear whether these models can use field sampling data to predict THM formation or whether they can be modified to predict individual THM speciation and thus, risk. Future work involves applying the 3 years field sampling data to test the applicability and sufficiency of the existing mechanistic models and empirical models. Preliminary results based on existing models have been unsuccessful, and new approaches to modeling THM speciation are needed to develop a predictive framework.

6.2 Future Work: Effect of bromide in source water to the formation and speciation of Haloacetic acid (HAAs) in the Monongahela River

In conjunction with the 3 years field sampling, HAA concentrations in finished water were also measured at the 6 drinking water treatment plants. HAA_s are the other major formed DBPs in the chlorinated drinking water. There are a total of nine HAA species containing chlorine and/or bromine (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromoacetic acid (BCAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), dichlorobromoracetic acid (DCBAA), and dibromochloroacetic acid (DBCAA). Figure 1 shows the names and structures of the 9 HAA species. Figure 1 shows that 6 out of 9 HAA_s are brominated species. The future work will analyzes the effect of changing bromide concentrations in source water on the formation and speciation of HAA_9 using 3 years field sampling data form 6 drinking water plants on the Monongahela River.

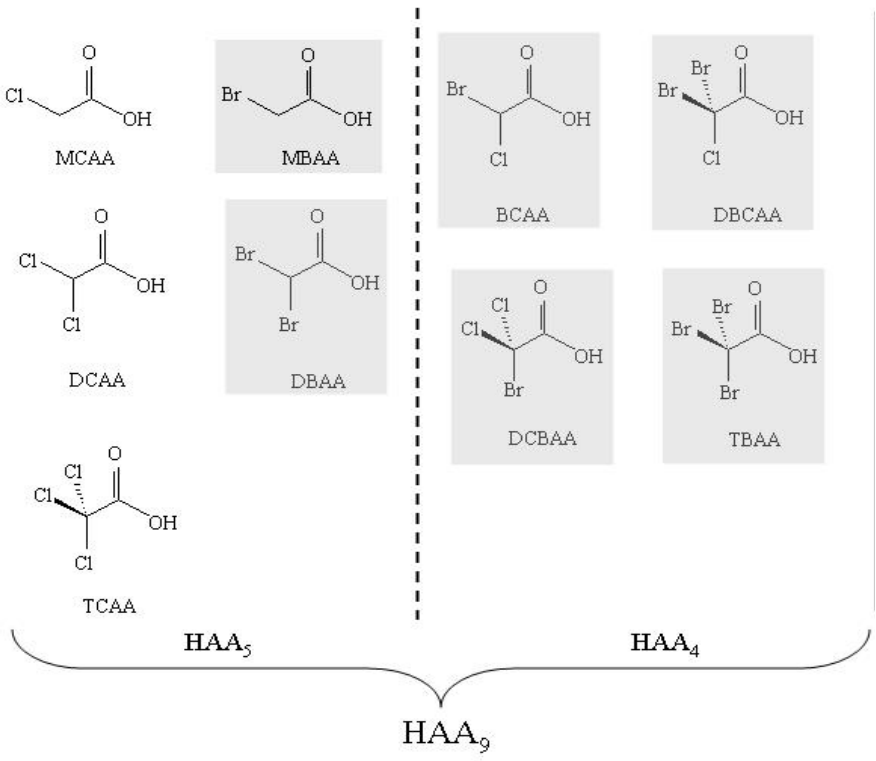

Figure 6.1. Names and structures of HAA_9. The gray HAA species are brominated HAA_s.

6.3 Future Work: Acceptable bromide concentrations in source water relating to HAAs

Currently, only 5 HAA species out of 9 HAA species are regulated by EPA. EPA sets a MCL of 60 μg/L for HAA_5, which are shown on the left side in Figure 1. The MCL setting is determined based on the MCLGs of MCAA and TCAA, which are 70 μg/L and 20 μg/L, respectively (USEPA, 2003c). Future study will apply the unique statistical analytical method proposed in this dissertation to assess the associated safe bromide concentrations in source water based on the MCL and MCLG settings of HAA_s.

Appendix A. The Effect of Sampling Strategies on Assessment of Water Quality Criteria Attainment

Introduction

The Supplementary Data includes text information, tables and figures and serves as supplement the main body of the paper, which could not be included in the manuscript due to space limits. The Supplementary Data includes 10 Tables, 3 figures and text information described statistical analysis and results of the data in further detail in the paper. Each part of the text information has a title that links the information back to the main body of the paper.

Additional Information about Statistical Assessments for Section 303(d) Listing Decision and Their Results (This part of supporting material details the "*Statistical Assessment for Section 303(d) Listing Decision"* section in the main body of the paper.)

(1) U.S. EPA statistical assessment

EPA listing methodology requires determination of whether the annual mean value exceeds the human health criteria for drinking water (USEPA, 2002b). To identify and include a specific impaired water body on the 303(d) list, regulatory guidance is followed (USEPA, 1993, 1997b, 2003b). The EPA regulations 40 CFR 130.7(b) provide general guidance for states to identify impaired waters that require TMDLs (USEPA, 2011a). States are expected to assemble and evaluate all existing and readily available water

quality data and information to develop the list (USEPA, 2011a, 2012b). The available water quality data include but are not limited to data from federal agencies, members of the public, and academic institutions that are actively conducting or reporting water quality problems (USEPA, 2011a). By following the general regulations 40 CFR 130.7(b), EPA develops a methodology for states to document how they use water quality data and information for water decision making. The methodology provides a process to determine and identify impaired waters to be listed on the 303(d) list, or to identify waters that can be removed from the list (USEPA, 2002a).

The EPA methodology does not recommend making water quality decisions based on a single river sample or small data sets for impairment or attainment (USEPA, 2002b). However, decisions are often based on limited environmental data, and thus they are subject to error (PaDEP, 2009a). To minimize decision errors, the EPA methodology takes into consideration practical realities affecting the availability of information and the strength of the available data by employing statistical approaches (USEPA, 2002b). Two options are available to determine if the criteria is exceeded for a dataset that is approximately normal: one is to compute the upper one-sided 95% confidence interval on the mean, and the other is to evaluate by one-sided t-test (USEPA, 2003a). Generally, EPA will assume a data set is normally distributed when the sample size exceeds 20 (USEPA, 2003b). Alternatively, EPA employs Chen's modified t-test for data that are not normally distributed, instead of the one-sided t-test (USEPA, 2003a, b). Chen's modified t-test has good power to analyze skewed data (USEPA, 2003b). The results for the data normality test (Anderson-Darling normality test) are provided in Table A1. The

Anderson-Darling normality test has a hypothesis H_0 that data are normally distributed with the 0.05 significant level. For the Chen's modified t-test, if the t-statistic is larger than the t-critical at 0.05 significant level, then we reject the hypothesis that the annual mean concentration of TDS is less than or equals the criteria. Thus, there is 95% probability that the annual mean concentration exceeds the criteria. The results of the EPA listing methodology are provided in Table 3 in the main body of the paper.

Table A7 shows the results of the listing decision calculations based on EPA using two methods: assuming normality of the data (as there are more than 20 data points and normality is generally assumed in this case) and using the upper 1-sided 95% confidence interval for the mean, and alternatively, assuming non-normality and using Chen's modified t-test for the mean. Further, the DEP sampling data are analyzed in two groups: river water samples and drinking water intakes. Each sampling year is considered separately in the analysis.

The third column in Table A7 contains the upper 1-sided 95% confidence interval for TDS mean in each sampling year, used because EPA assumes normality for data sets larger than 20 (USEPA, 2003b). The upper 1-sided 95% confidence intervals for the mean of DEP river water and drinking water intake samples in the first sampling year (09/2008-08/2009) exceed the 500 mg/L TDS criteria. The results of the Chen's modified t-test (used for non-normally distributed data) (USEPA, 2003b) generally support the finding from the upper 1-sided 95% confidence interval result, with exception for DEP drinking water intake samples collected in 09/2008-08/2009, likely because this

particular data set is not normally distributed. The different findings between the two methods suggest that EPA's assumption of normality for data sets with larger than 20 samples may introduce error when making listing decisions. The results for 2009-2012 indicate that the river was meeting the TDS criteria based on analysis of DEP, WV and CMU data. When comparing river water samples collected by DEP and WV, the upper 1-sided 95% confidence intervals for the mean of DEP samples are 30 to 50% higher than WV samples. When comparing the drinking water samples collected by DEP and CMU, the upper 1-sided 95% confidence interval for year 2009-2010 is 493 mg/L, which is approaching the 500 mg/L criteria and is 50% higher than that (327 mg/L) based on CMU samples. However, the drinking water samples collected from 2010-2012 by DEP and CMU are comparable by this measure, and are higher than the river water samples taken by WV.

(2) Pennsylvania statistical assessment

The state of Pennsylvania measures various chemical water quality data to evaluate its water quality status and determine attainment or impairment of a water body by following EPA's regulations. However, there are some differences between PaDEP and EPA's methodology. The approach of PaDEP categorizes water chemical datasets based on sampling size since decision error is related to the sample size (PaDEP, 2009a). With fewer than eight observations, PaDEP considers the limited observations to lead to high potential decision errors for impairment decisions, and thus additional samples must be collected for further evaluation (PaDEP, 2009a); no data sets in the current work are this small. For data sets with 8 to 23 observations, a binomial test is applied to the data first.

If this test suggests impairment (with binomial test p-value<0.05), the water body is listed as impaired. If the test suggests attainment, then the data are further tested using the 10% rule following EPA guidance (USEPA, 2003b; PaDEP, 2009a). If the 10% rule also indicates attainment, then the water body will not be listed on the 303(d) list. If the 10% rule indicates impairment, while the binomial test did not, then PaDEP considers that the water body needs further evaluation. For samples with more than 23 observations, the Anderson-Darling and Ryan-Joiner tests are first employed to test the normality of the data. If both of the normality tests obtain p-values larger than 0.05 the data are considered normally distributed (PaDEP, 2009b). Data that are not normally distributed are tested using the same two tests used for 8-23 samples. Data that are normally distributed are evaluated with the one-sided t-test to evaluate impairment (following the EPA method). If the results suggest the water body is impaired, then the water body will be listed. Otherwise, the dataset is again subject to the subsequent 10% rule test (USEPA, 2002b; PaDEP, 2009b) to further evaluate the water status (USEPA, 2003b; PaDEP, 2009a). If the 10% rule test suggests the water is meeting criteria, the water body will not be listed. If the 10% rule test suggests that the water is not meeting the criteria, then the water body needs further evalution. To ensure the water samples are representative of the overall conditions of the ware body, PaDEP requires the data to be collected quarterly at minimum and must cover at least one year, to be used in supporting listing decision (PaDEP, 2009b).

Table A8 shows the results of detailed results of the components analyzed to make a listing decision via the PaDEP methodology. River water and drinking water intake

samples collected by DEP at 09/2009-08/2010 indicate the TDS concentration exceeded the criteria. However, in 2009-2010, the drinking water samples indicate the TDS level is impaired, while the river water samples suggest additional samples or information must be collected for further evaluation. In the last sampling years (2010-2012), both the drinking water and river water samples collected by PaDEP suggest the TDS level is meeting the criteria.

The samples of WV 09/2008-09/2009 indicates that additional samples should be taken for further analysis, which is likely due to the start date of WV sampling (summer 2009). Although CMU samples suggest the TDS levels are meeting the criteria in each sampling year, the upper 90% percentile of TDS levels are higher compared to those of WV river water samples, which confirm the result from earlier significance testing indicating that TDS levels in CMU and WV samples are different, likely due to the difference between drinking water source water sampling and river water sampling.

In addition, PaDEP conducts analyses of surface water quality trends in the Commonwealth (PaDEP, 2009a). PaDEP uses Seasonal Kendall test (Hirsch et al., 1982) to detect increase or decrease trends in a waterbody (PaDEP, 2009a). The seasonal Kendall test is a nonparametric test, which is valid for use with seasonal data, evenly or unevenly spaced observations, missing observations, censored data and ties (the same concentration observed more than once) (Hirsch et al., 1982; Hipel and McLeod, 1994). The Seasonal Kendall test was performed using the DOS program Kendall.exe released by U.S. Geological Survey (Helsel, 2006).

Full Data Set Analyses

Considering the full three years of data from all sources, TDS levels reported in drinking water intake samples collected by DEP are statistically significantly *higher* than levels in samples collected by CMU ($p<0.001$), as evaluated by the right-tailed Mann-Whitney rank sum test. Similarly, TDS levels reported in DEP river water samples are also significantly *higher* than levels in river water samples collected by WV ($p<0.001$), using the same statistical analysis. This is likely due to the selective time period sampling used by DEP, with a focus on low-flow conditions that concentrate river water contaminants. This will be evaluated in subsequent paired time period analyses below.

Statistical differences for individual sampling years (September. 1st to next year August. 31th) were also evaluated, with results presented in Table A3. During each sampling year, DEP river water samples are significantly higher ($p\leq0.0027$) than river water samples from WV, again likely due to the temporal selectivity of DEP sampling. During the first sampling year (2009-2010), DEP drinking water intake samples are significantly higher ($p=0.001$) than those collected by CMU. No significant differences ($p>0.05$) between TDS in drinking water samples of DEP and CMU are observed in the later sampling years (2010-2012). Differences are likely due to temporal differences in DEP sampling; however, this will be more fully evaluated below.

Seasonal trend analysis (This part of supporting material details the "*Effect of sample type on assessment of water quality*" section in the main body of the paper.)

Seasonal trend analysis was applied to CMU and WV data sets that have sufficient data in each season in each sampling year. To evaluate the effect of sample type on assessment of water quality, the seasonal Kendall test was employed to data sets collected at very near locations (e.g., KM40 and KM37) the same week in the same year (defined as paired samples) to evaluate the seasonal effects at these targeted paired sampling locations. There are 3 paired locations, CMU sampled at KM40 vs WV sampled at KM37, CMU sampled at KM114 vs WV sampled at KM132, CMU sampled at KM142 vs WV sampled at KM143. When investigating a given water quality variable at a specified sampling location, the seasonal Kendall test can be used to detect trends in each month during the sampling year (Hipel and McLeod, 1994; Helsel et al., 2006). The seasonal Kendall test is a nonparametric test, which is valid for the use with seasonal data, evenly or unevenly spaced observations, missing observations, censored data and ties (the same concentration observed more than once) (Hirsch et al., 1982; Hipel and McLeod, 1994). Table A4-A5 summarize the monthly TDS median values of paired WV and CMU data sets that are used for this trend analysis. By utilizing the USGS Kendall.exe program for monthly median data across all the years, the Seasonal Kendall test results were calculated (see Table A6). The Seasonal Kendall test results for trend of TDS at paired sampling locations by WV and CMU indicate a significant decreasing temporal trend over the sampling period from WV data but no temporal trend with CMU data at the paired location KM40. No significant decreasing trends have been found for the other 2 paired locations. Thus, we again observe the water quality data from the WV and CMU groups could lead to different conclusions concerning the temporal trend of TDS concentrations in the Monongahela River.

A further complexity is that PaDEP has additional requirements to evaluate source waters.

PaDEP considers a minimum of 24 water samples collected over 12-24 months within the last five years to be a complete dataset for regulated chemical parameters in a drinking water source (such as chloride, sulfate, TDS) (PaDEP, 2009a).

The PaDEP methodology discussed above has been applied to the water quality data from the individual three sampling groups in Minitab 16 (Minitab Inc., State College, PA). Results are presented in Table A8, with detailed intermediate calculations provided in this Supplemental Information.

Paired location and time analysis (This part of supporting material also details the "*Effect of sample type on assessment of water quality*" section in the main body of the paper.)

None of the groups sampled at the same location at the same time; however, as noted before, CMU and WV groups were often sampling at very near locations (e.g., KM40 and KM37) the same week in the same year. These paired samples, while not representing field or analytical duplicates, do provide insight into differences in results based on the sampling locations targets. WV sampled at KM37, which is downstream of the Elizabeth L/D structure (at KM38.6). This sample was intended to be representative of well-mixed river conditions, which are often observed directly downstream of navigational structures that provide significant mixing. Alternatively, CMU sampled at KM40 from a drinking

water plant extracting water from the river upstream of the L/D, where stagnant water conditions would not be expected to lead to well-mixed samples. Notched Box-and-Whisker plots (McGill et al., 1978) (Figure A2) applied using Matlab enable evaluation of the significance differences in paired TDS among different data sets (Hipel and McLeod, 1994; Potter, 2006). In a Notched Box-and-Whisker plot, the notches on both sides of the box display confidence intervals around the median, which allows evaluation of the significance of the differences between medians (McGill et al., 1978; Hipel and McLeod, 1994). Specifically, if the median line in one box overlaps within the notches in the other, then there are no significantly differences in the median between the two observations at 5% significant level (Hipel and McLeod, 1994). Additionally, the Mann-Whitney rank sum test at the same significant level is employed to confirm the significant differences displayed in the plot. Figure A2(a) clear shown that neither the median line overlap with the other's notches, indicating that the two medians of water quality samples in WV and CMU data at the paired location and sampling dates are statistically significantly different, which is confirmed by significance test ($p=0.0119$). The median of WV data is reaching the 25% percentile of CMU data. This significant difference observed is likely due to the L/D effect on the water quality, with the Elisabeth L/D located between WV and CMU sampling locations. Figure A2(b) represents sampling for WV at KM132 and for CMU at KM114. These two locations are in the same pool; however, significant difference ($p=0.0473$) is still observed, which may be because the locations are 18 kilometers away. This suggests that the water quality in the same pool could be different based on different sampling locations. The final paired data set (KM142 by WV and KM141 by CMU; Figure A2(c)) that are from different sources

(river vs drinking water plant) but in the same pool and with close sampling locations do not show significant differences (p=0.209).

These results indicate that drinking water intake sampling and river water sampling could provide different assessments; source water evaluation should take place at drinking water intakes.

Table A.1 P-values of data normality test (Anderson-Darling normality test).

	Sampling year 09/01/2008-08/31/2009	Sampling year 09/01/2009-08/31/2010	Sampling year 09/01/2010-08/31/2011	Sampling year 09/01/2011-08/31/2012
DEP RW[1]	p<0.005	p=0.014	p<0.005	p=0.023
DEP DW[1]	p<0.005	**p=0.816**[2]	**p=0.446**	p=0.021
DEP RW and DW	p<0.005	p=0.044	p=0.020	p<0.005
WV RW	**p=0.229**	p=0.012	p<0.005	p<0.005
CMU DW	NA	p<0.005	p=0.019	p<0.005

[1] RW denotes River Water Samples, DW denotes Drinking Water Intake Samples.
[2] Bold values indicate normally distributed data.

Table A.2 Statistical description of TDS data (mg/L) during overlapping sampling periods.

	Number of Samples	Mean	Median	Standard deviation	Range (min-max)
DEP RW[1]	135	369	380	94.1	(152, 730)
DEP DW[1]	88	292	276	96.4	(98, 580)
WV RW	86	296	310	88.2	(135, 491)
CMU DW	172	296	316	119	(46, 596)

[1] RW denotes River Water Samples, DW denotes Drinking Water Intake Samples.

Table A.3 Significant test of TDS level for all samples and individual sampling year.

		2008-2012		2008-2009		2009-2010		2010-2011		2011-2012		2008-2012	2009-2010	2010-2011	2011-2012	2009-2012	2009-2010	2010-2011	2011-2012
		DEP RW[1]	DEP DW[1]	DEP RW	DEP DW	DEP RW	DEP DW	DEP RW	DEP DW	DEP RW	DEP DW	WV RW	WV RW	WV RW	WV RW	CMU DW	CMU DW	CMU DW	CMU DW
2008-2012	DEP RW		**p= 0.00012**									**p< 0.0001**				**p< 0.0001**			
	DEP DW											**p< 0.0001**				**p< 0.0001**			
2008-2009	DEP RW				p= 0.138														
	DEP DW																		
2009-2010	DEP RW						p= 0.529						**p< 0.0001**				**p< 0.0001**		
	DEP DW												**p< 0.0001**				**p< 0.0001**		
2010-2011	DEP RW								**p< 0.0001**					**p< 0.0001**				**p< 0.0001**	
	DEP DW													**p= 0.0002**				p= 0.251	
2011-2012	DEP RW										p= 0.109				**p= 0.0027**				**p= 0.0041**
	DEP DW														p= 0.0607				p= 0.412
2008-2012	WV RW															**p< 0.0001**			
2009-2010	WV RW																**p= 0.0024**		
2010-2011	WV RW																	**p= 0.0027**	
2011-2012	WV RW																		p= 0.128

[1] RW denotes River Water Samples, DW denotes Drinking Water Intake Samples.

[2] Bold values are significant p-values which indicate statistically significant difference.

Table A.4 Monthly TDS median values (mg/L) for trend analysis by Seasonal Kendall test at WV sampling sites.

	Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
KM37 (paired to KM40)	2009							411	259	337	415	182	176
	2010	200	187	167	187	194	281	354	483	400	372	347	156
	2011	208	222	128	156	174	279	312	369	230	173	176	121
	2012	197	156	220	276	134	243	373	271	295			
KM132 (paired to KM114)	2009							499	214	453	378	218	266
	2010	159	179	122	156	179	290	317	345	310	236	187	149
	2011	185	133	116	142	168	253	243	337	227	170	174	106
	2012	157	152	209	341	180	359	282	321	250			
KM143 (paired to KM142)	2009							549	164	373	363	154	212
	2010	181	153	143	212	160	281	339	373	258	280	190	223
	2011	187	183	175	196	156	316	366	341	236	176	202	129
	2012	147	266	271	315	146	444	376	229	269			

Blank spaces in the Table means no data available.

Table A.5 Monthly TDS median values (mg/L) for trend analysis by Seasonal Kendall test at CMU sampling sites.

	Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
KM 40 (paired to KM37)	2010					350	308	468	450	432	346	205	130
	2011	223	241	452	354	258	291	313	366	249	176	226	
	2012	140			262	289	307	444					
KM114 (paired to KM132)	2009									462	214	198	206
	2010	160	148	256	466	226	284	382	363	319	228	334	142
	2011	158	167	198	121	184	311	199	223	164	143	174	
	2012	220	222	238	332	431							
KM142 (paired to KM143)	2009									345	246	106	147
	2010	94	207	201	467	292	228	303	278	291	249	116	100
	2011	120	204	228	180	140	241	216	183	201	163	170	
	2012	102	172	308	318	392							

Blank spaces in the Table means no data available.

Table A.6 Season Kendall test results for trend TDS (mg/L) at various sampling locations. Bold value indicates significant changes in trend.

		Paired KM40	Paired KM114	Paired KM142
CMU	tau	-0.467	-0.071	0
	p-value	0.1456	0.8625	1
WV	tau	**-0.378**	-0.333	0.067
	p-value	**0.0372**	0.0684	0.7946

Table A.7 Lisitng decisions for TDS based on EPA's methodology.

	Year (Sample Type)	Upper 1-sided 95% Confidence Interval on mean (mg/L)	Chen's Modified t-statistic	t-critical	Listing Decision
DEP	09/2008-08/2009 (RW[1])	614	2.05	1.67	**Impair**
	09/2008-08/2009 (DW[1])	539	-5.04	1.66	Attain
	09/2009-08/2010 (RW)	436	-9.79	1.68	Attain
	09/2009-08/2010 (DW)	493	-2.64	1.77	Attain
	09/2010-08/2011 (RW)	383	-39.8	1.67	Attain
	09/2010-08/2011 (DW)	303	-54	1.68	Attain
	09/2011-08/2012 (RW)	343	-9.14	1.71	Attain
	09/2011-08/2012 (DW)	277	-41.9	1.69	Attain
WV	09/2008-08/2009 (RW)	418	-3.47	1.86	Attain
	09/2009-08/2010 (RW)	282	-16.7	1.67	Attain
	09/2010-08/2011 (RW)	255	-28.6	1.67	Attain
	09/2011-08/2012 (RW)	258	-30.0	1.66	Attain
CMU	09/2009-08/2010 (DW)	327	-20.2	1.65	Attain
	09/2010-08/2011 (DW)	286	-27.6	1.65	Attain
	09/2011-08/2012 (DW)	284	-36.7	1.66	Attain

[1] RW denotes River Water Samples; DW denotes Drinking Water Intake Samples.

Table A.8 Detailed listing decisions for TDS based on PaDEP methodology.

	Year (Sample Type)	Number of Samples	Normality Test (p-value) Anderson-Darling Test	Ryan-Joiner Test	Binomial Test /One-sided t-test (p-value)	10% Rule with 90% Upper Limit (mg/L)	Listing Decision
DEP	09/2008-08/2009 (RW[1])	74	<0.005	<0.01	<0.05	---[3]	**Impair**
	09/2008-08/2009 (DW[1])	112	<0.005	<0.01	<0.05	---	**Impair**
	09/2009-08/2010 (RW)	51	0.014	0.025	0.0643	508	**Further Evaluation**
	09/2009-08/2010 (DW)	14	-[4]	-	0.0441	-	Impair
	09/2010-08/2011 (RW)	69	<0.005	<0.01	0.999	428	Attain
	09/2010-08/2011 (DW)	52	0.446	>0.1	1.00[2]	374	Attain
	09/2011-08/2012 (RW)	27	0.023	0.061	1.00	442	Attain
	09/2011-08/2012 (DW)	39	0.021	0.03	1.00	376	Attain
WV	09/2008-08/2009 (RW)	9	-	-	0.613	549	**Further Evaluation**
	09/2009-08/2010 (RW)	75	0.012	0.041	1.00	407	Attain
	09/2010-08/2011 (RW)	75	<0.005	<0.01	0.997	360	Attain
	09/2011-08/2012 (RW)	84	<0.005	<0.01	0.999	377	Attain
CMU	09/2009-08/2010 (DW)	200	<0.005	0.01	1.00	477	Attain
	09/2010-08/2011 (DW)	157	0.019	0.045	1.00	388	Attain
	09/2011-08/2012 (DW)	76	<0.005	<0.01	1.00	418	Attain

[1] RW denotes River Water Samples, DW denotes Drinking Water Intake Samples.
[2] This value based on the data set that is normally distributed, thus this p-value results from One-sided t-test rather than binomial test.
[3]The 10% test is not performed (---) when the binomial test already indicates impairment.
[4] Normality test is not performed (-) when the sample size ranges from 8 to 23 based on DEP listing methodology.

Table A.9 Listin decisions for summer TDS based on EPA's methodology.

	Year (Sample Type)	Upper 1-sided 95% Confidence Interval on mean (mg/L)	Chen's Modified t-statistic	t-critical	Listing Decision
DEP	Summer 2010 (RW[1])	438	-14.7	1.69	Attain
	Summer 2010 (DW)	442	-6.00	1.86	Attain
	Summer 2011 (RW)	359	-37.2	1.86	Attain
	Summer 2011 (DW)	296	-32.1	1.70	Attain
	Summer 2012 (RW)	411	-11.6	1.75	Attain
	Summer 2012 (DW)	308	-13.5	1.72	Attain
WV	Summer 2009 (RW)	418	-3.47	1.86	Attain
	Summer 2010 (RW)	375	-11.6	1.74	Attain
	Summer 2011 (RW)	411	-14.5	1.74	Attain
	Summer 2012 (RW)	356	-14.5	1.71	Attain
CMU	Summer 2010 (DW)	398	-11.4	1.67	Attain
	Summer 2011 (DW)	311	-20.4	1.67	Attain
	Summer 2012 (DW)	401	-8.22	1.65	Attain

[1] RW denotes River Water Samples; DW denotes Drinking Water Intake Samples.

Table A.10 Detailed listing decisions for summer TDS based on PaDEP's methodology.

	Year (Sample Type)	Number of Samples	Normality Test (p-value) Anderson -Darling Test	Normality Test (p-value) Ryan-Joiner Test	Binomial Test (p-value)	10% Rule 90% Upper Limit (mg/L)	Listing Decision
DEP	Summer 2010 (RW[1])	39	0.090	<0.01	0.556	504	**Further Evaluation**
	Summer 2010 (DW)	9	-[2]	-	1.00	474	Attain
	Summer 2011 (RW)	9	-	-	1.00	416	Attain
	Summer 2011 (DW)	28	0.111	>0.1	1.00	374	Attain
	Summer 2012 (RW)	16	-	-	1.00	454	Attain
	Summer 2012 (DW)	22	-	-	1.00	400	Attain
WV	Summer 2009 (RW)	9	-	-	0.613	549	**Further Evaluation**
	Summer 2010 (RW)	18	-	-	1.00	474	Attain
	Summer 2011 (RW)	18	-	-	1.00	398	Attain
	Summer 2012 (RW)	24	0.484	>0.1	1.00	422	Attain
CMU	Summer 2010 (DW)	71	0.058	>0.1	1.00	480	Attain
	Summer 2011 (DW)	57	0.583	>0.1	1.00	388	Attain
	Summer 2012 (DW)	23	0.460	>0.1	1.00	274	Attain

[1] RW denotes River Water Samples; DW denotes Drinking Water Intake Samples.
[2] Normality test is not performed (-) when the sample size ranges from 8 to 23 based on PaDEP listing methodology.

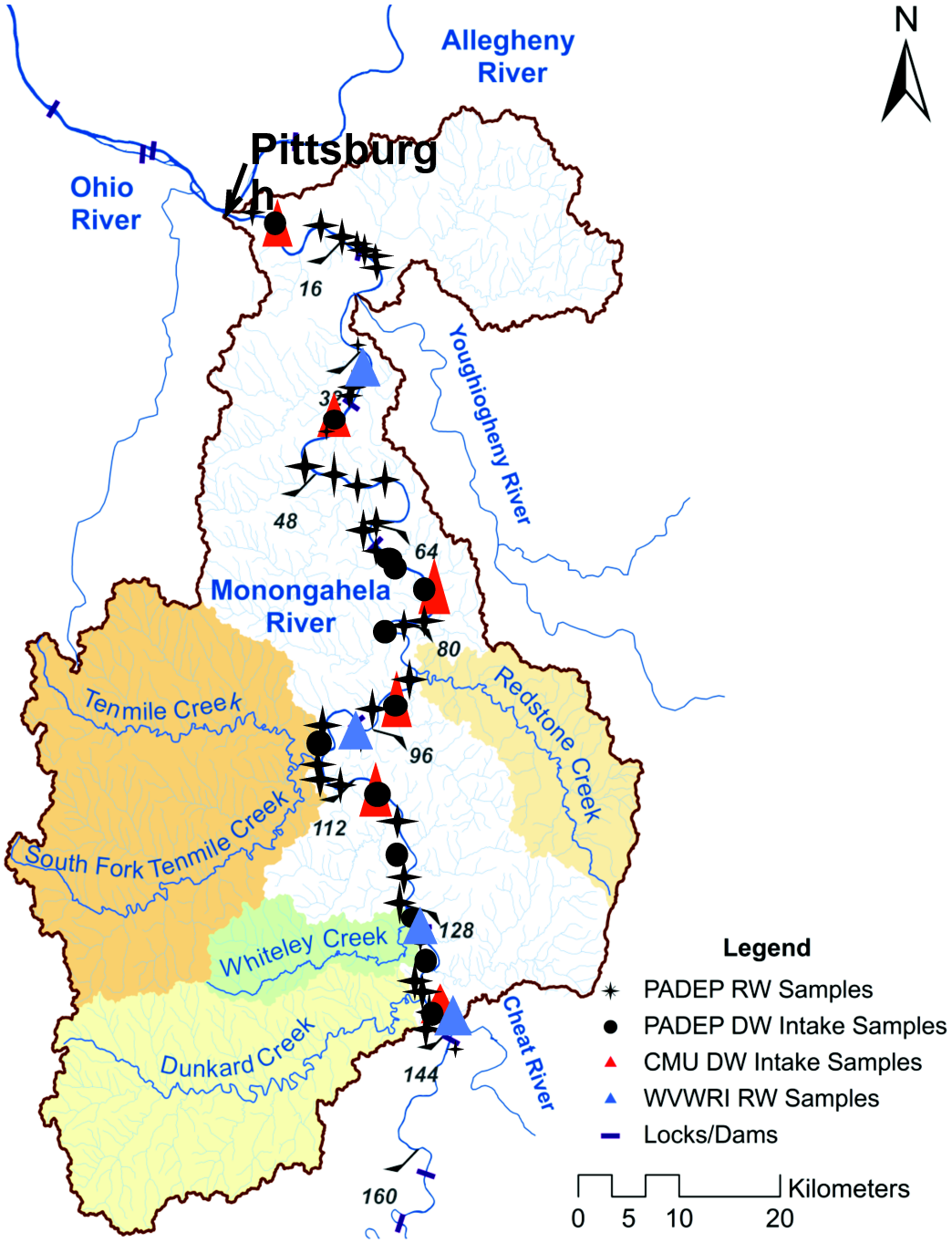

Figure A.1 Sampling locations on the Monongahela River.

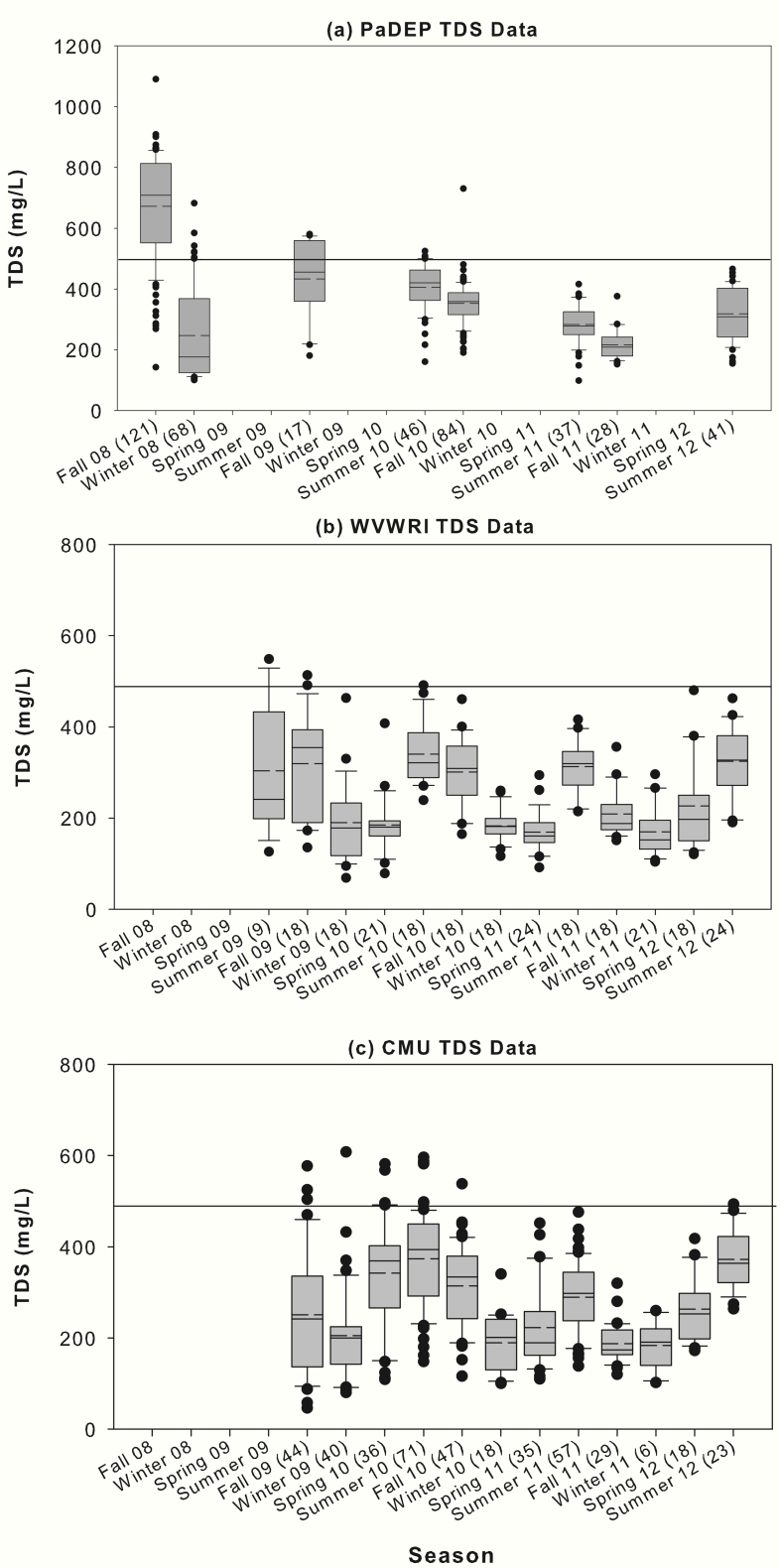

Figure A.2 Box-and-Wisker plots of seasonal TDS concentrations (mg/L) of water samples collected by (a) DEP, (b) by WV, and (c) by CMU.

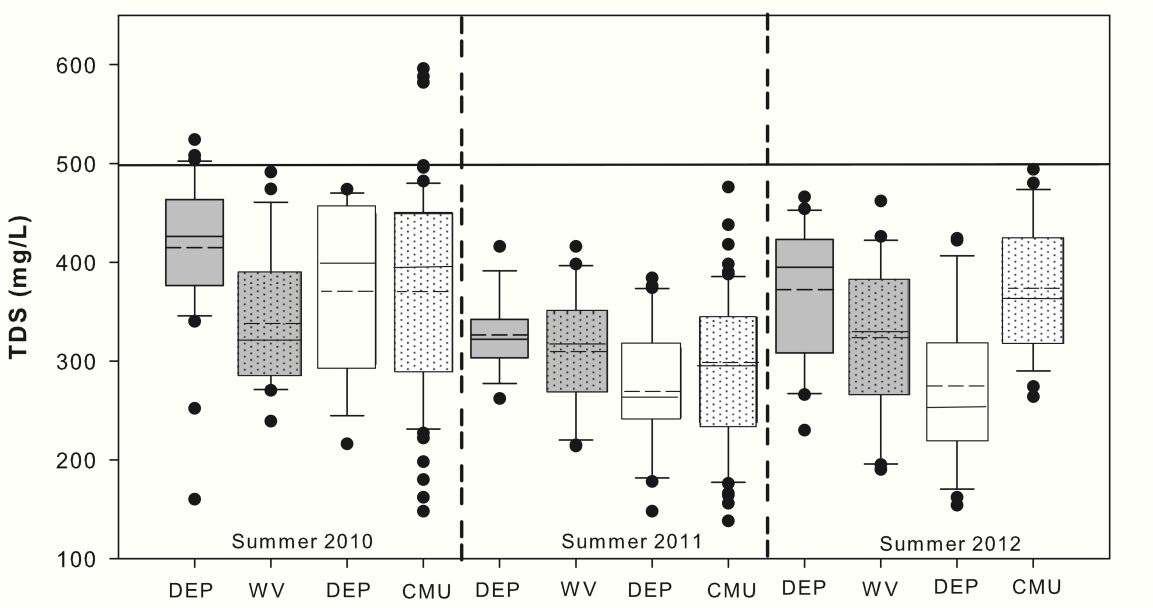

Figure A.3 TDS concentrations (mg/L) in summer seasons. The gray box and open box indicate river water samples and drinking water samples from DEP. The dotted gray box indicates river water samples from WV. Dotted open box are drinking water samples from CMU.

Appendix B. Disinfection By-Product Speciation in Finished Drinking Water from the Monongahela Basin during changing source water bromide conditions

Table B.1 Sitatistical summary of quarterly bromide and THMs concentrations at 6 drinking water plants. In the value cell, the top values are the range of concentrations (min, max); the bottom values in each cell are geometric mean and standard deviation.

	Quarters	Bromide (µg/L)	Chloroform (µg/L)	BDCM (µg/L)	DBCM (µg/L)	Bromoform (µg/L)
Site A	Q4, 2010	(12.0, 99.0) 39.3±2.41	(0.943, 10.5) 4.49±3.02	(1.91, 11.3) 4.46±2.07	(2.54, 12.2) 5.69±1.90	(1.19, 2.05) 1.623±1.26
	Q1, 2011	ND[1] ND	(3.46, 7.77) 5.19±1.50	(2.28, 2.66) 2.46±1.08	(0.948, 2.25) 1.46±1.54	(ND, 0.921) 0.921±0
	Q2, 2011	ND ND	(4.03, 15.4) 10.5±1.74	(3.56, 8.92) 5.90±1.39	(ND, 2.23) 2.10±1.05	(ND, 1.24) 0.518±3.22
	Q3, 2011	(ND, 66.0) 15.4±2.81	(6.27, 18.5) 13.4±1.50	(3.19, 11.3) 7.62±1.60	(ND, 3.09) 2.30±1.26	(ND, 1.40) 1.178±1.25
	Q4, 2011	(ND,104) 18.4±4.56	(7.82, 11.4) 9.43±1.21	(ND, 20.6) 20.6±0	(ND, 2.25) 2.25±0	(0.810, 1.22) 0.994±1.23
	Q1, 2012	ND ND	(7.71, 9.82) 8.70±1.13	(ND, 6.91) 6.91±0	ND ND	(0.170, 1.08) 0.428±2.52
	Q2, 2012	(ND, 36.5) 13.5±2.70	(12.7, 15.4) 14.0±1.10	(6.11, 8.65) 7.31±1.19	ND ND	(1.05, 1.35) 1.19±1.13
	Q3, 2012	ND ND	(11.3,20.9) 15.7±1.27	(ND, 53.1) 19.7±1.86	(ND, 8.35) 5.14±1.62	(1.10, 2.09) 1.44±1.23
Site B	Q4, 2009	(ND, 31.7) 9.40±2.13	(10.2, 25.6) 18.6±1.43	(4.64, 8.31) 5.72±1.25	(ND, 2.50) 1.62±1.53	ND ND
	Q1, 2010	(ND, 51.1) 22.6±2.13	(1.76, 7.87) 3.99±1.67	(0.308, 1.57) 0.695±1.97	(ND, 0.22) 0.123±1.83	ND ND
	Q2, 2010	(12.5, 92.5) 33.0±2.06	(7.00, 30.2) 13.7±1.62	(0.380, 14.6) 4.00±2.98	(ND, 11.6) 2.28±3.35	(ND, 7.06) ND
	Q3, 2010	(62.1, 171) 88.8±1.35	(1.22, 25.7) 8.74±2.31	(2.90, 12.8) 7.71±1.64	(1.00, 33.3) 8.62±2.27	(ND, 11.5) 3.19±2.38
	Q4, 2010	(ND, 80.4) 34.6±2.73	(3.10, 42.9) 15.4±2.45	(1.89, 21.9) 8.16±2.25	(ND, 10.9) 5.71±2.43	(ND, 2.18) 0.973±1..59
	Q1, 2011	(ND, 54.2) 21.0±2.80	(2.25, 11.4) 4.99±1.94	(1.14, 2.60) 1.77±1.40	(ND, 1.22) 1.22±0	ND ND
	Q2, 2011	(ND, 90.0) 19.9±2.58	(12.1, 28.2) 17.9±1.38	(3.61, 15.4) 5.54±1.70	(1.09, 3.11) 1.91±1.40	(ND, 1.40) 1.20±1.16
	Q3, 2011	(ND, 79.0) 20.7±3.28	(6.07, 36.3) 19.1±1.87	(3.48, 20.2) 9.46±1.94	(ND, 9.73) 3.47±2.08	(0.05, 1.41) 0.614±3.54
	Q4, 2011	(ND, 28.0) 15.4±2.21	(8.03, 13.3) 10.2±1.23	(5.83, 6.24) 6.03±1.23	ND ND	(0.06, 1.15) 0.361±3.62
Site C	Q4, 2009	ND ND	(45.5, 80.6) 60.4±1.34	(19.2, 26.5) 22.5±1.18	(1.35, 11.3) 3.91±2.90	ND ND
	Q1, 2010	(12.6, 47.2) 29.3±1.59	(7.52, 34.7) 14.2±1.77	(4.68, 9.34) 6.56±1.25	(0.79, 5.43) 1.94±2.03	(ND, 1.24) 1.24±0

	Q2, 2010	(ND, 274) 36.1±3.29	(20.6, 116) 46.1±1.70	(5.97, 44.8) 21.8±1.88	(2.20, 26.1) 8.07±2.23	(ND, 8.53) 5.09±1.46
	Q3, 2010	(82.4, 234) 120±3.04	(4.17, 42.6) 13.7±1.99	(7.91, 52.4) 17.0±1.82	(9.88, 45.1) 19.8±2.25	(2.30, 11.2) 5.13±1.72
	Q4, 2010	(ND, 100) 41.2±2.99	(7.00, 53.5) 23.7±2.04	(5.38, 44.9) 21.4±2.07	(2.53, 29.5) 12.3±2.37	(1.55, 8.71) 3.26±1.76
	Q1, 2011	(20.0, 67.8) 41.6±1.69	(7.13, 39.6) 12.9±2.21	(5.57, 11.8) 7.92±1.35	(2.80, 3.96) 3.28±1.15	(ND, 1.36) 0.40±3.39
	Q2, 2011	(ND, 94.0) 16.7±3.10	(16.9, 61.0) 34.9±1.52	(8.67, 31.8) 13.3±1.66	(1.48, 19.1) 3.87±2.35	(ND, 2.17) 1.35±1.61
Site D	Q4, 2009	(ND, 17.1) 9.25±1.85	(65.2, 79.7) 72.1±1.11	(16.0, 17.8) 16.9±1.06	(ND, 1.31) 1.31±0	ND ND
	Q1, 2010	(ND, 61.6) 11.5±3.27	(3.50, 45.7) 14.3±2.90	(2.29, 11.0) 5.55±1.93	(1.14, 1.99) 1.54±1.26	ND ND
	Q2, 2010	(ND, 599) 41.2±4.31	(12.3, 61.0) 22.3±1.71	(3.76, 34.9) 13.0±2.08	(ND, 15.0) 7.76±2.09	(ND, 2.00) 1.31±1.65
	Q3, 2010	(ND, 234) 93.1±2.91	(3.58, 51.2) 17.7±2.23	(11.0, 66.4) 25.8±1.62	(ND, 53.8) 25.1±2.09	(1.10, 11.9) 4.62±2.19
	Q4, 2010	(94.0, 254) 169±1.44	(8.60, 34.3) 21.7±1.97	(23.7, 56.7) 33.6±1.40	(29.4, 48.4) 40.1±1.22	(3.79, 14.0) 5.99±1.68
	Q1, 2011	(ND, 191) 26.3±4.51	(6.47, 71.5) 13.5±2.00	(6.11, 11.4) 8.78±1.30	(3.34, 4.50) 3.71±1.15	(0.095, 1.60) 0.60±3.69
	Q2, 2011	(ND, 70.0) 12.1±3.47	(37.7, 103) 54.0±1.31	(11.7, 58.4) 26.4±1.93	(ND, 12.8) 6.15±2.08	(0.076, 1.65) 0.56±4.11
	Q3, 2011	(ND, 62.0) 14.3±2.98	(20.3, 71.2) 47.2±1.60	(ND, 71.2) 21.2±1.98	(ND, 24.2) 8.70±2.48	(ND, 1.71) 1.12±1.29
	Q4, 2011	(143, 143) 143±0	(22.4, 22.4) 22.4±0	(2.34, 9.38) 9.38±0	(0.08, 2.34) 2.34±0	(0.08, 0.080) 0.08±0
	Q1, 2012	ND ND	(ND, 12.4) 12.4±0	ND ND	ND ND	ND ND
	Q2, 2012	(ND, 97.3) 26.1±3.44	(9.19, 45.1) 24.7±1.53	(ND, 17.1) 9.17±1.33	(0.06, 5.26) 5.26±0	(0.06, 0.080) 0.07±1.12
	Q3, 2012	(ND, 63.8) 10.8±2.99	(15.8, 60.2) 42.5±1.30	(ND, 111) 15.8±1.78	(1.02, 16.1) 10.6±1.89	(0.102, 2.86) 1.58±1.47
Site E	Q2, 2010	(ND, 61.0) 19.8±2.55	(2.16, 12.7) 5.84±2.01	(ND, 9.34) 0.91±8.98	(ND, 8.69) 2.96±2.23	(ND, 0.498) 0.498±0
	Q3, 2010	(63.0, 153) 111±1.34	(0.509, 11.6) 6.17±2.46	(1.82, 5.68) 3.43±1.36	(0.618, 3.69) 1.74±1.67	(ND, 0.913) 0.62±1.47
	Q4, 2010	(46.6, 99.2) 75.3±1.32	(4.20, 17.8) 9.96±1.73	(1.28, 6.88) 3.58±1.81	(0.493, 7.04) 2.31±2.43	(ND, 9.42) 2.13±3.25
	Q1, 2011	(ND, 43.8) 10.3±2.78	(0.269, 18.2) 2.49±5.64	(ND, 2.46) 1.06±2.32	(ND, 0.845) 0.85±0	ND 0.00±0
	Q2, 2011	(ND, 23.0) 6.45±1.77	(9.78, 61.0) 20.69±1.73	(1.97, 8.54) 3.79±1.69	(ND, 1.93) 1.38±1.31	(ND, 1.00) 1.00±0
	Q3, 2012	(ND, 49.3) 8.69±2.44	(8.49, 26.8) 17.82±1.40	(9.15, 106) 21.53±2.23	(ND, 8.93) 7.43±1.20	(ND, 1.41) 0.539±3.12
Site F	Q2, 2010	(ND, 67.0) 14.9±3.05	(31.6, 77.7) 58.1±1.37	(20.8, 34.5) 30.4±1.19	(12.0, 19.0) 14.6±1.18	(ND, 6.25) 0.80±5.09
	Q3, 2010	(33.1, 127) 87.1±1.56	(8.21, 51.6) 21.4±1.97	(11.6, 32.9) 19.7±1.51	(ND, 30.9) 16.0±2.19	(1/84, 6.86) 4.63±1.63
	Q4, 2010	(36.0, 136) 72.2±1.60	(18.0, 34.1) 27.7±1.29	(18.5, 38.6) 29.1±1.31	(21.9, 34.9) 29.3±1.19	(4.50, 6.31) 5.36±1.13

	Q1, 2011	(ND, 89.0) 34.0±3.88	(16.9, 87.6) 31.5±2.07	(11.9, 19.0) 15.7±1.22	(5.09, 6.60) 5.66±1.11	(1.37, 8.64) 2.73±2.27
	Q2, 2011	(ND, 148) 18.9±4.28	(37.8, 96.6) 64.6±1.36	(15.8, 32.9) 23.6±1.27	(5.77, 16.9) 8.42±1.47	(0.55, 5.87) 1.22±2.21
	Q3, 2011	(ND, 240) 21.7±5.00	(18.0, 67.6) 34.9±1.60	(15.8, 29.9) 20.5±1.26	(5.77, 31.4) 12.8±2.08	(0.89, 6.32) 2.28±2.37
	Q2, 2012	(19.2, 19.2) 19.2±0	(19.8, 19.8) 19.8±0	(11.3, 11.3) 11.3±0	ND ND	ND ND
	Q3, 2012	(ND, 58.5) 9.04±2.61	(30.3, 92.2) 39.2±1.45	(17.1, 49.4) 24.0±1.44	(ND, 9.30) 6.09±1.53	(ND, 1.00) 0.88±1.12

[1] ND indicates non-detected.

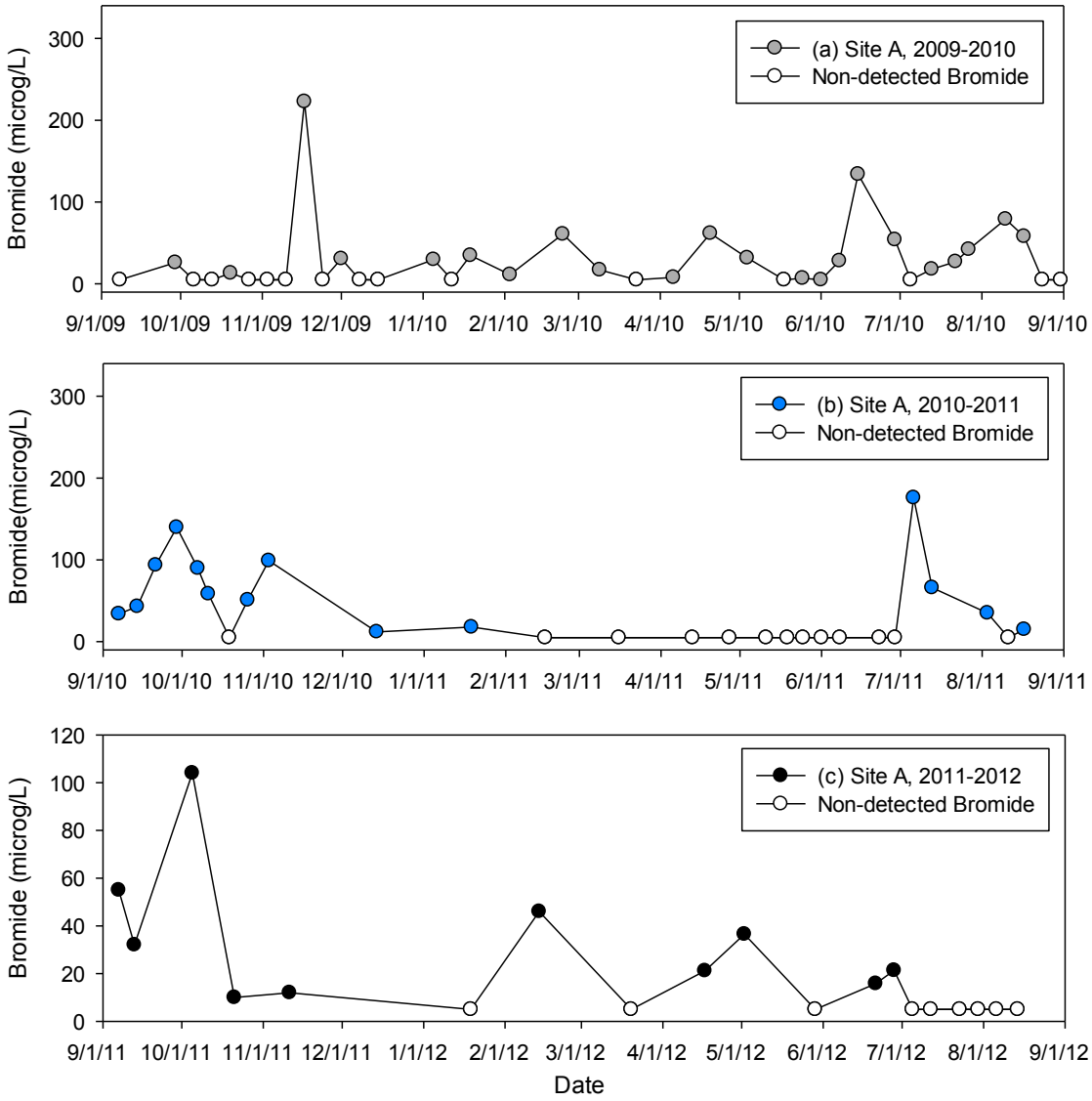

Figure B.1 Bromide concentrations at Site A on the Monongahela River.

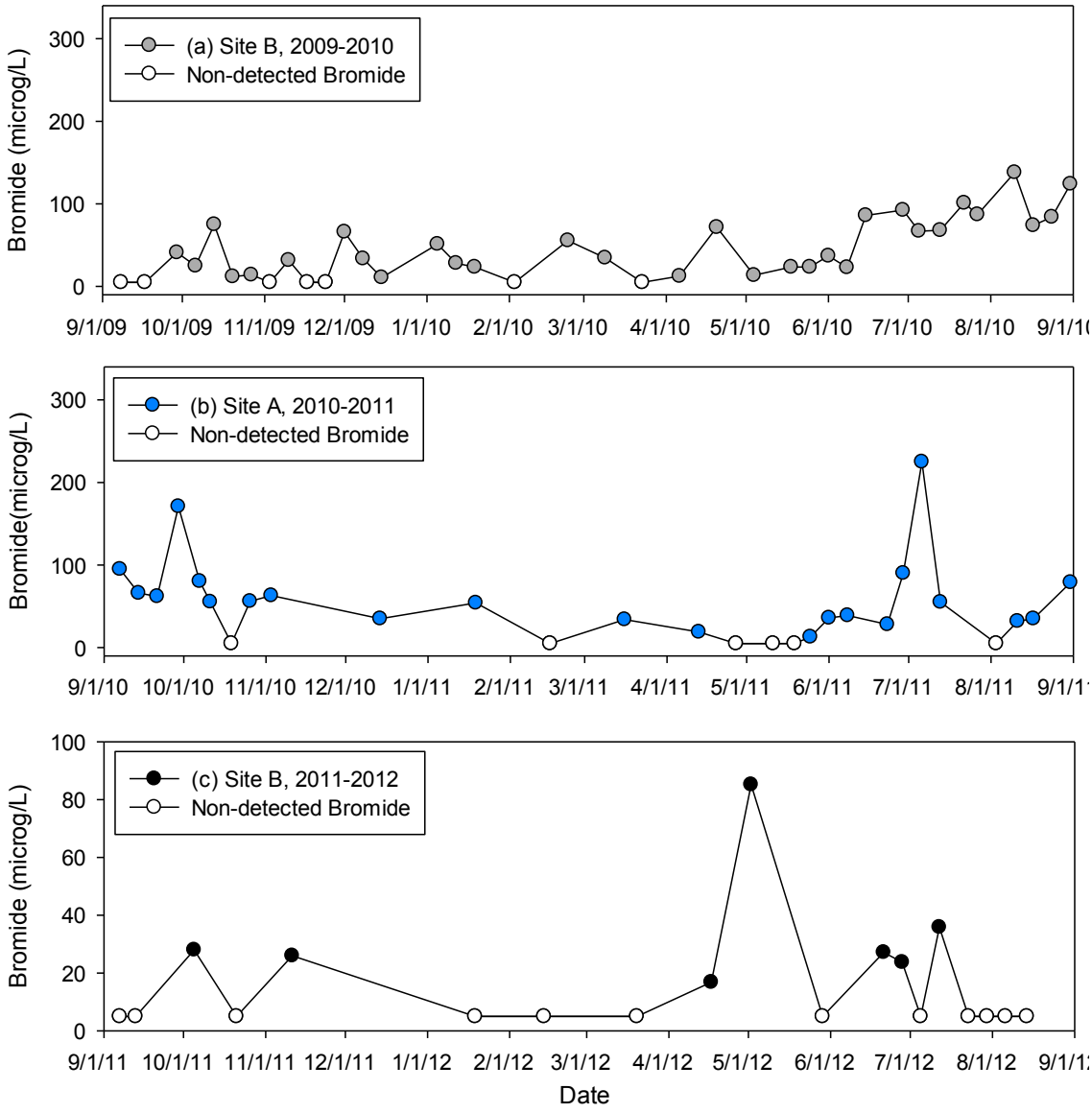

Figure B.2 Bromide concentrations at Site B on the Monongahela River.

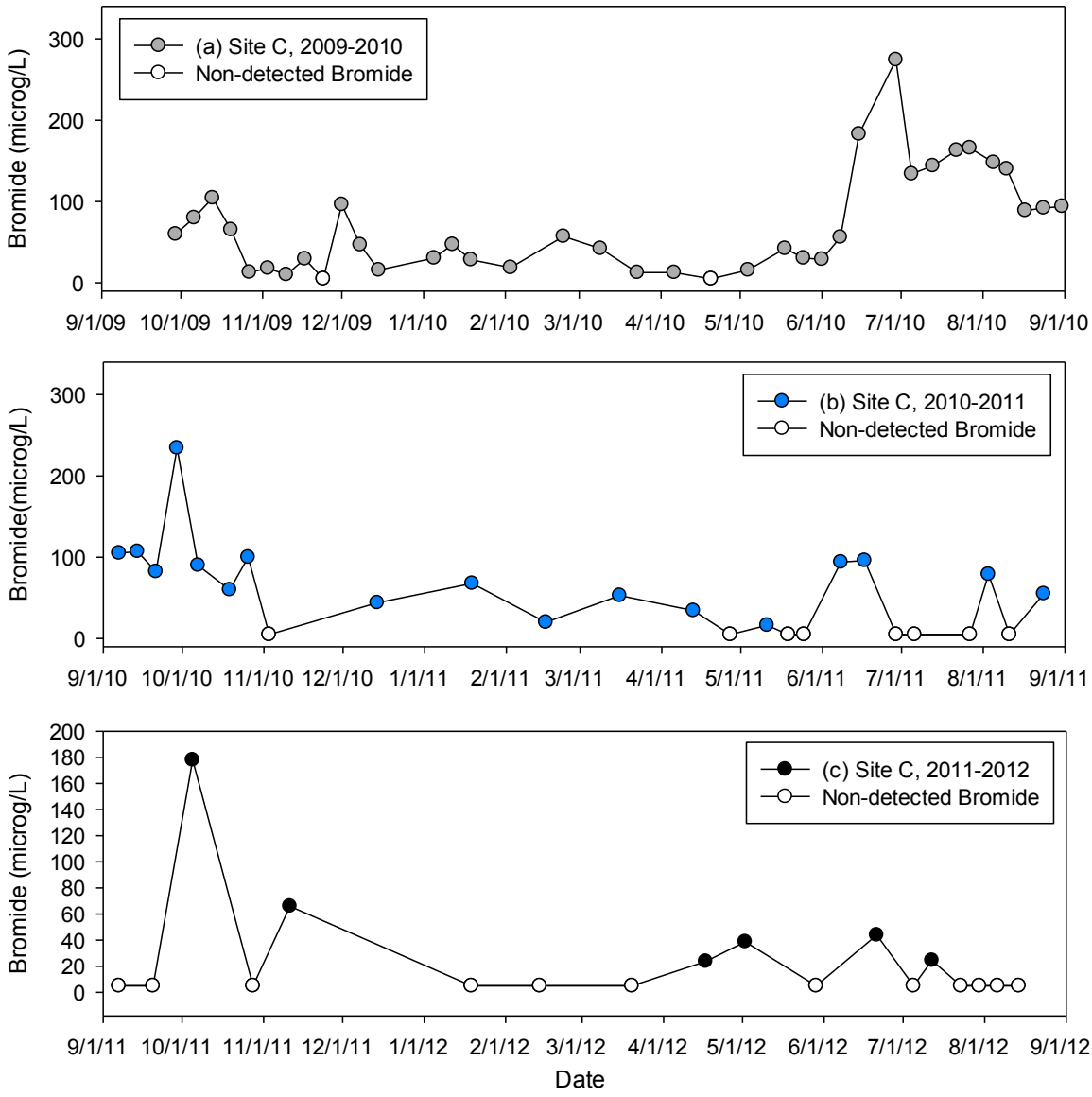

Figure B.3 Bromide concentrations at Site C on the Monongahela River.

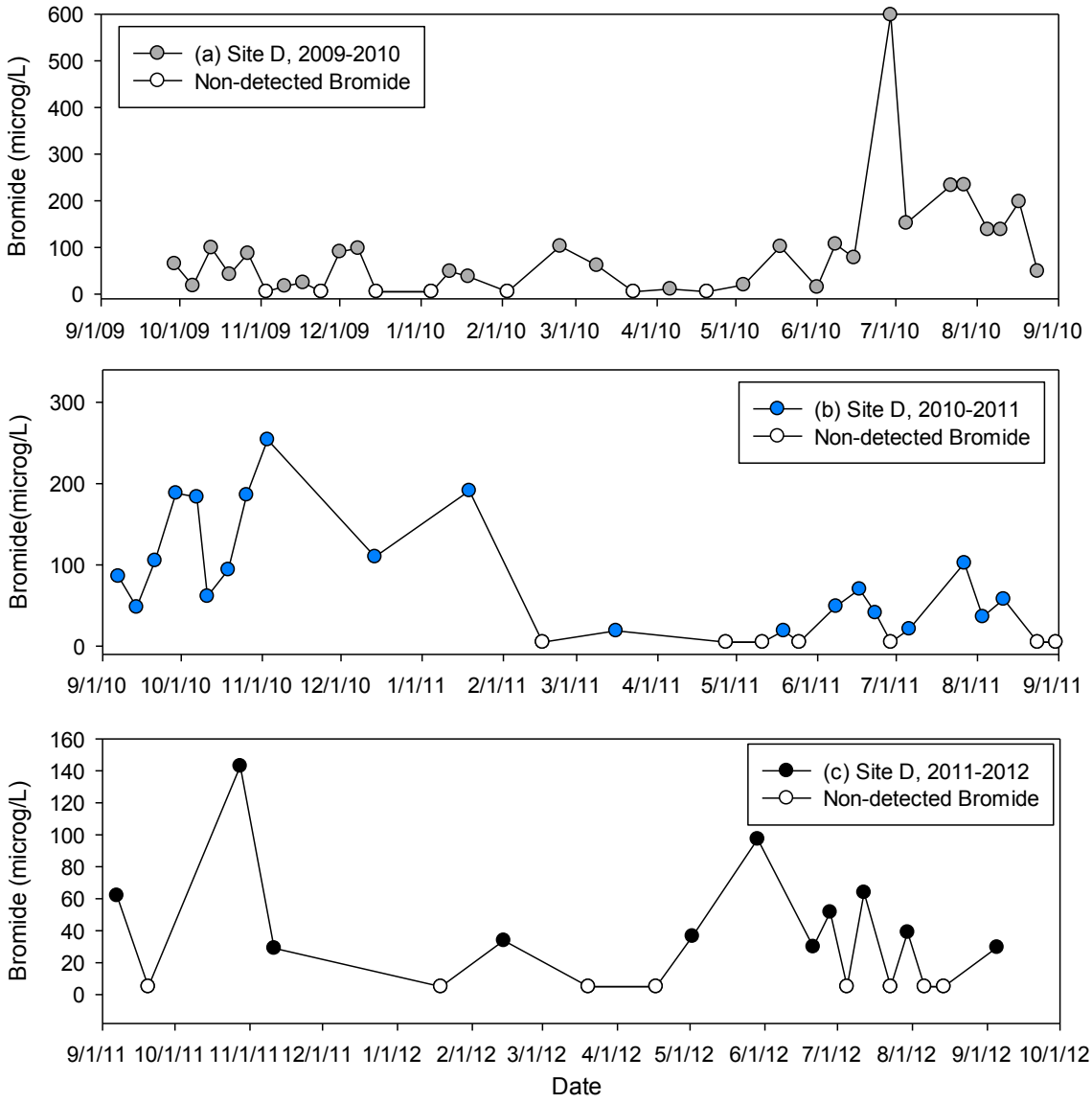

Figure B.4 Bromide concentrations at Site D on the Monongahela River.

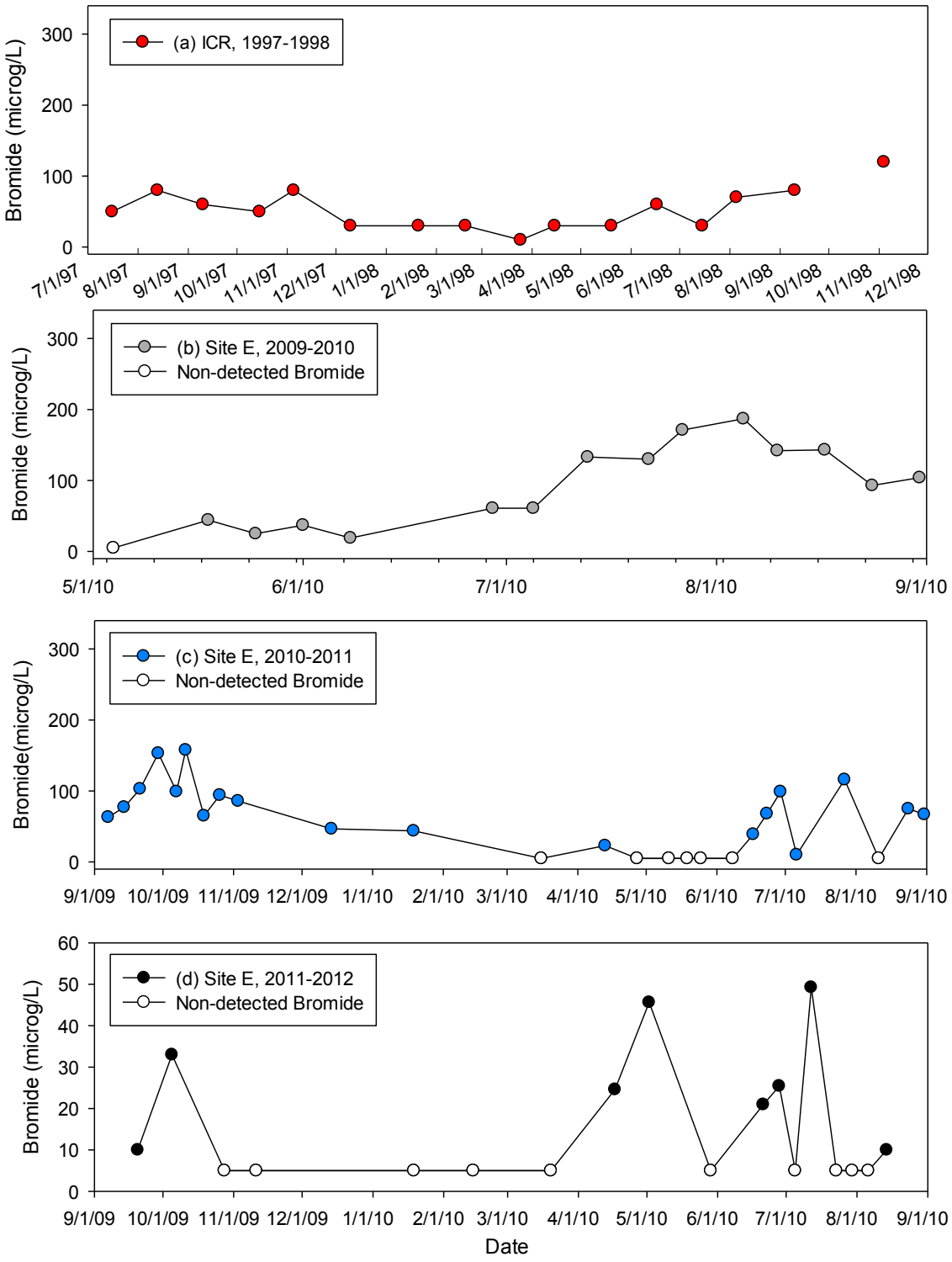

Figure B.5 Bromide concentrations at Site E on the Monongahela River.

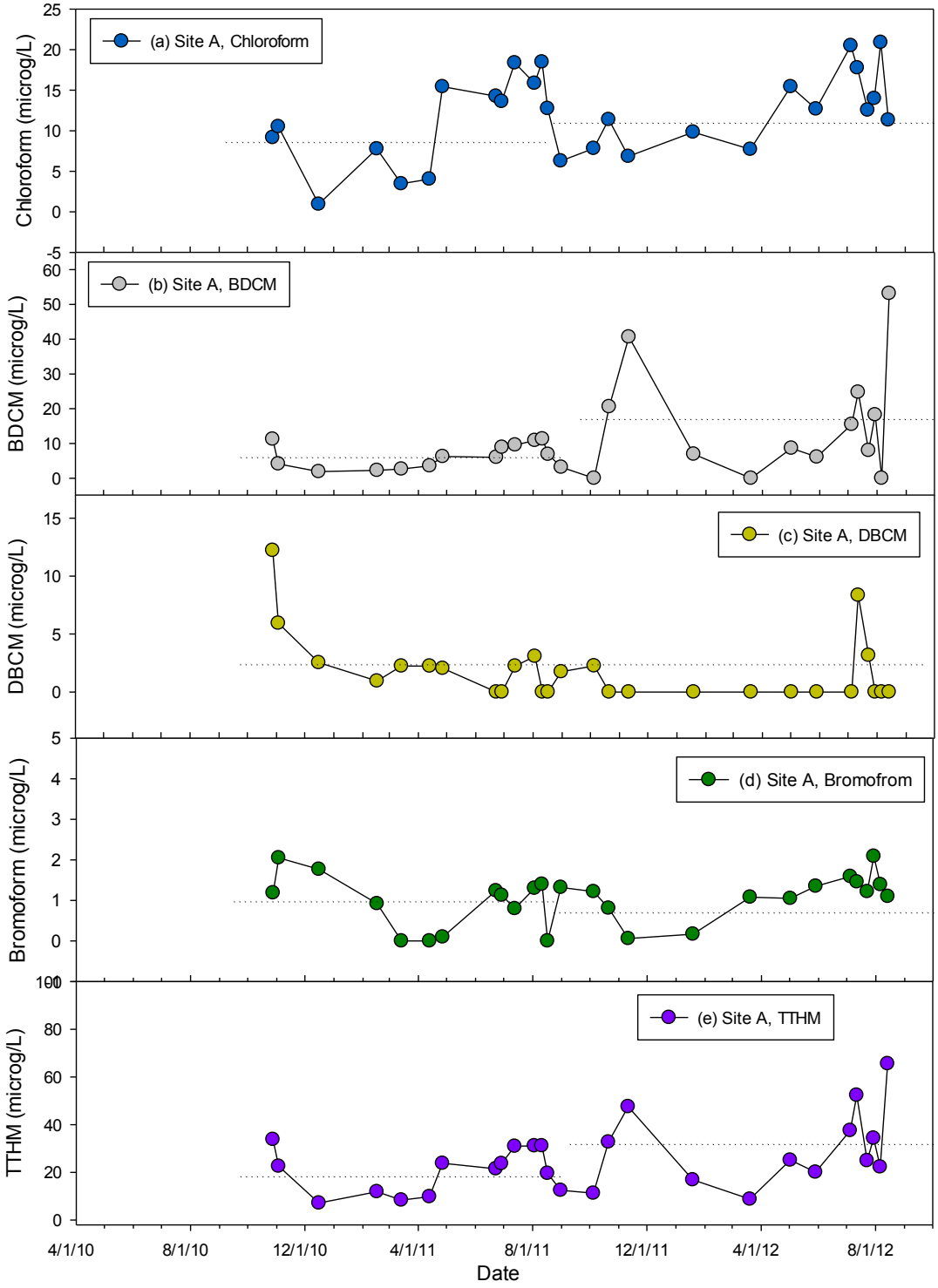

Figure B.6 Concentrations of THMs at Site A.

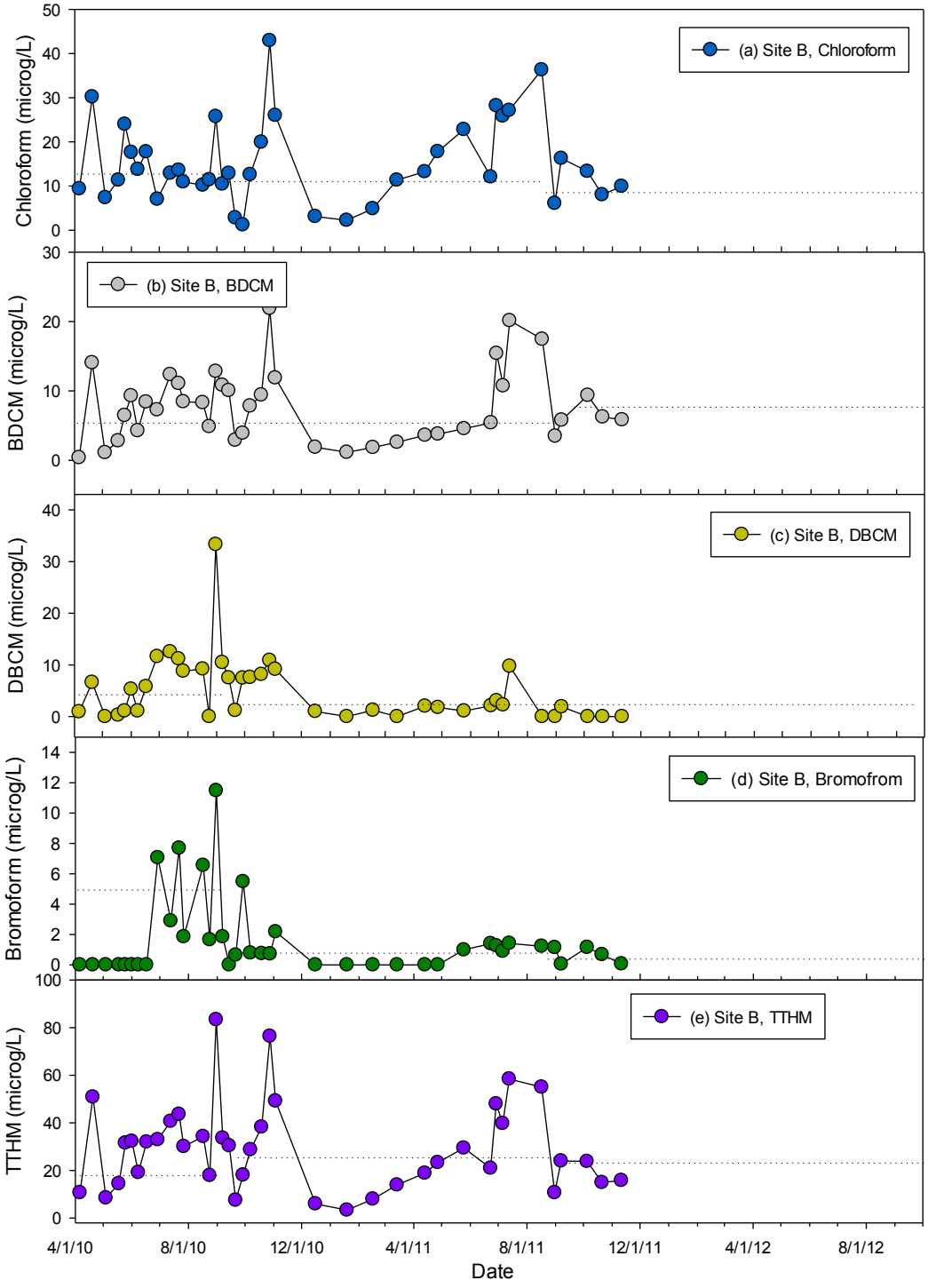

Figure B.7 Concentrations of THMs at Site B.

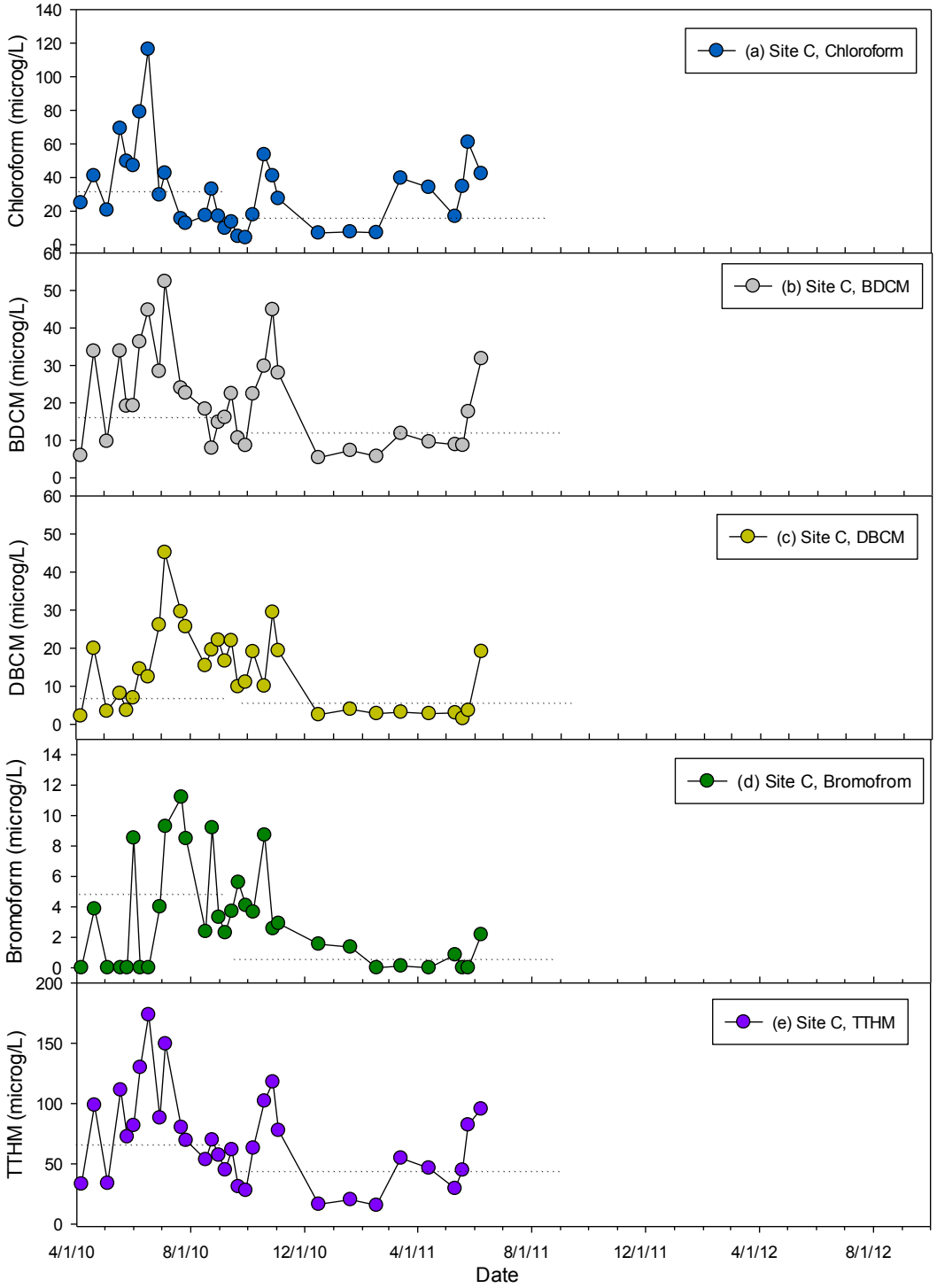

Figure B.8 Concentrations of THMs at Site C.

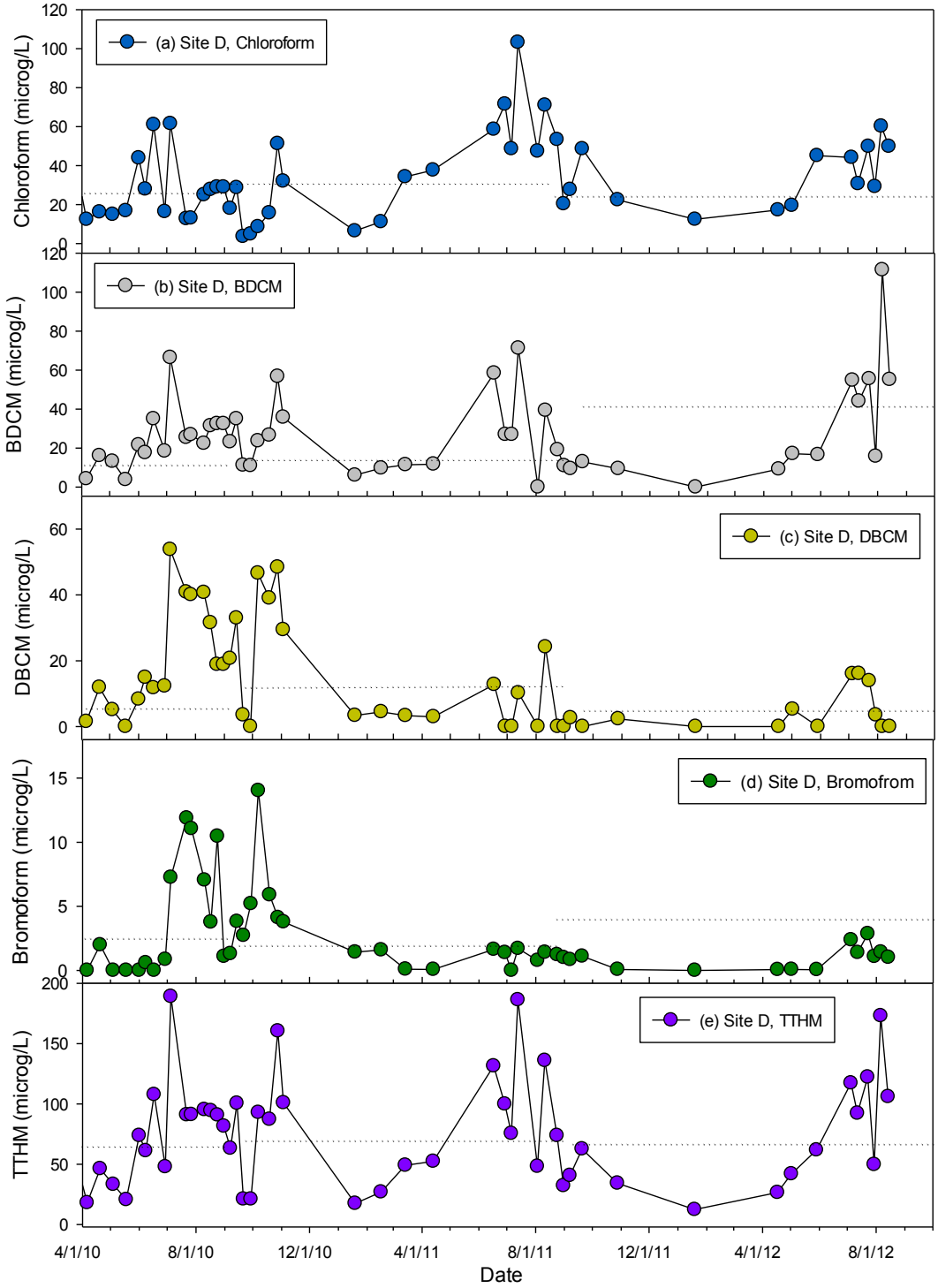

Figure B.9 Concentrations of THMs at Site D.

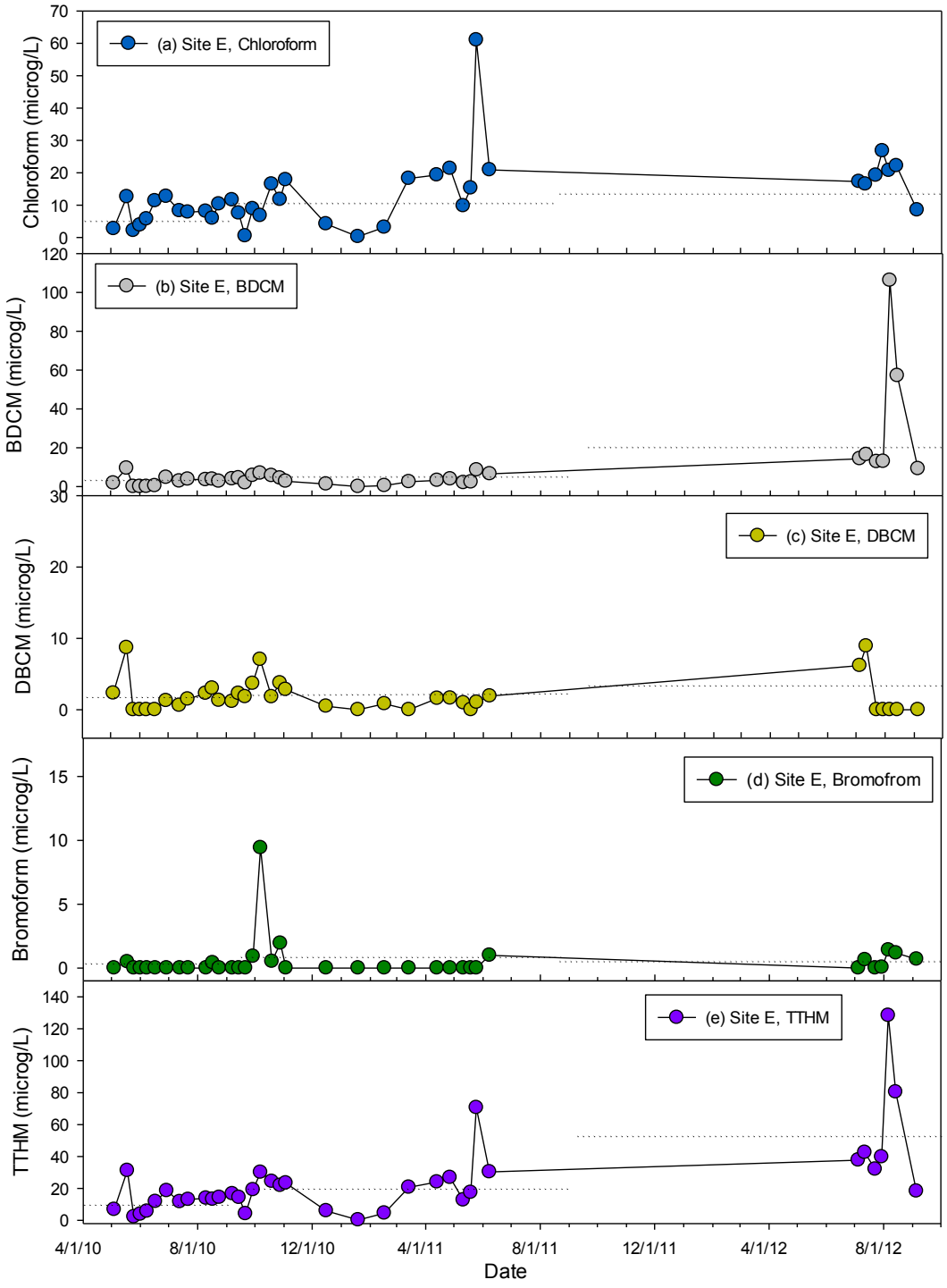

Figure B.10 Concentrations of THMs at Site E.

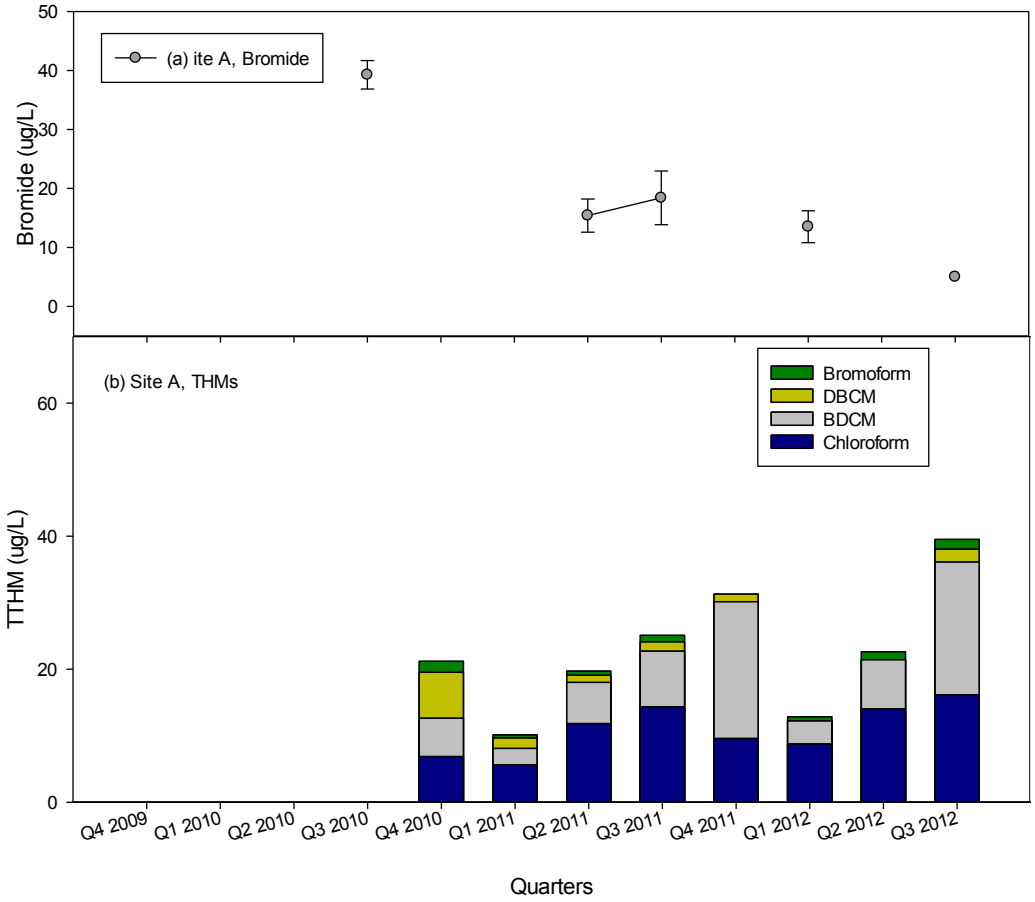

Figure B.11 Quarterly bromide in source water and THM levels in finished water at Site A.

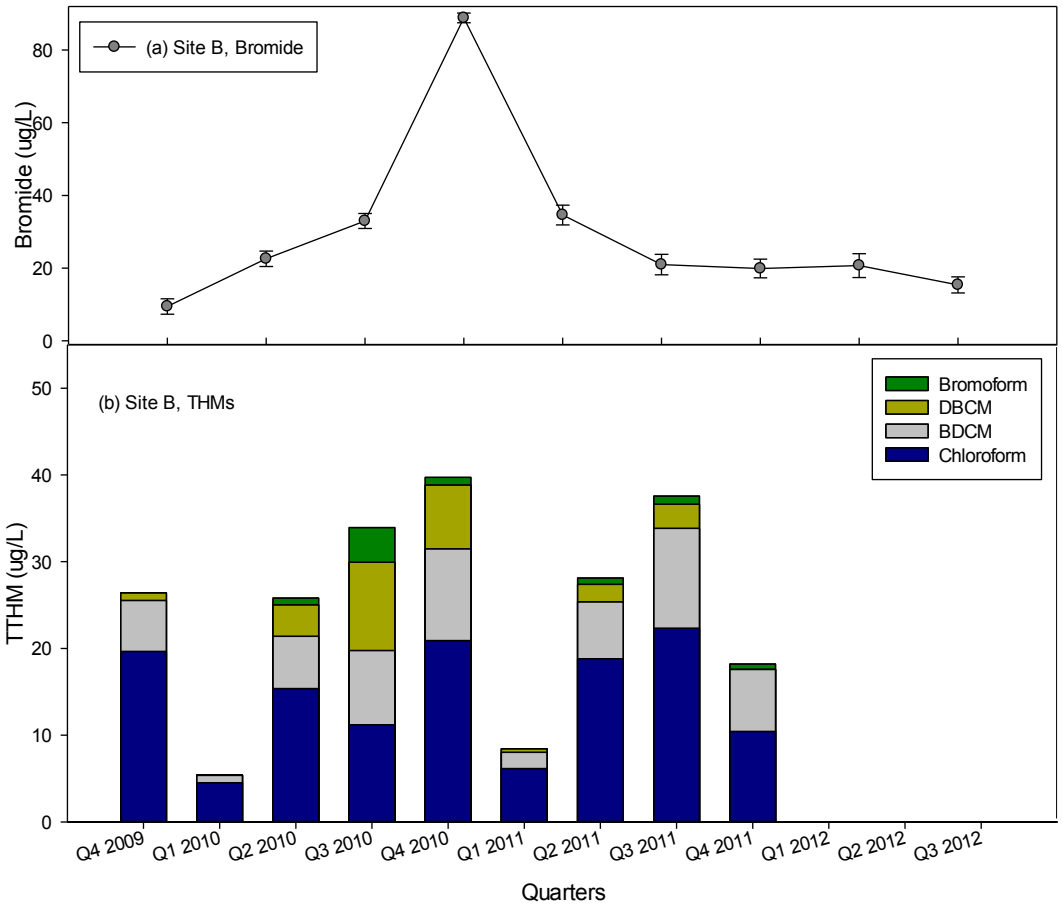

Figure B.12 Quarterly bromide in source water and THM levels in finished water at Site B.

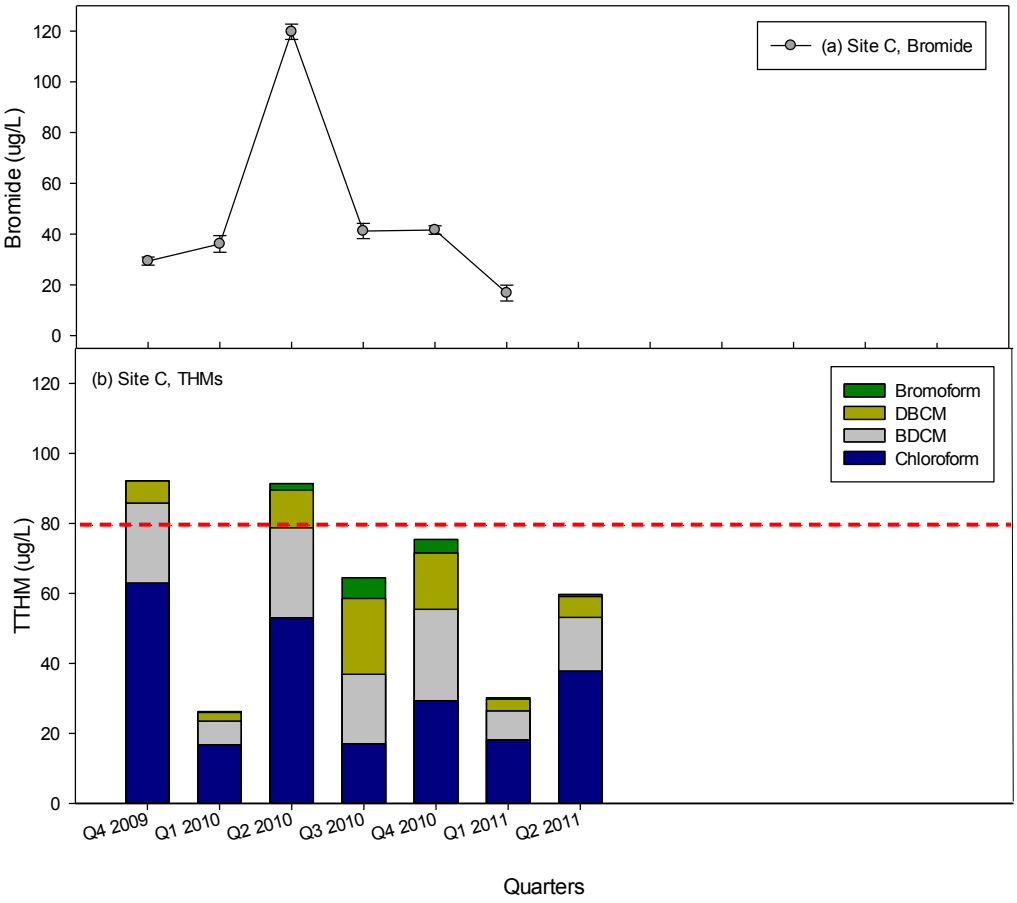

Figure B.13 Quarterly bromide concentrations in source water and THM levels in finished water at Site C.

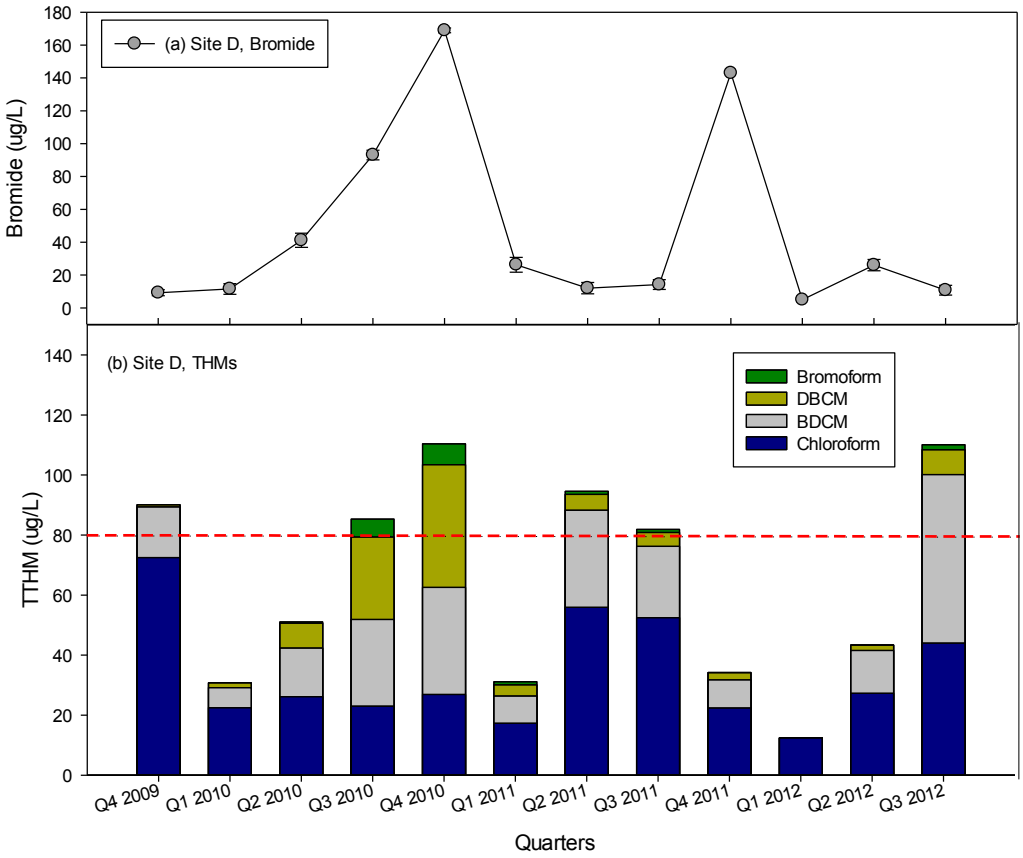

Figure B.14 Quarterly bromide in source water and THM levels in finished water at Site D.

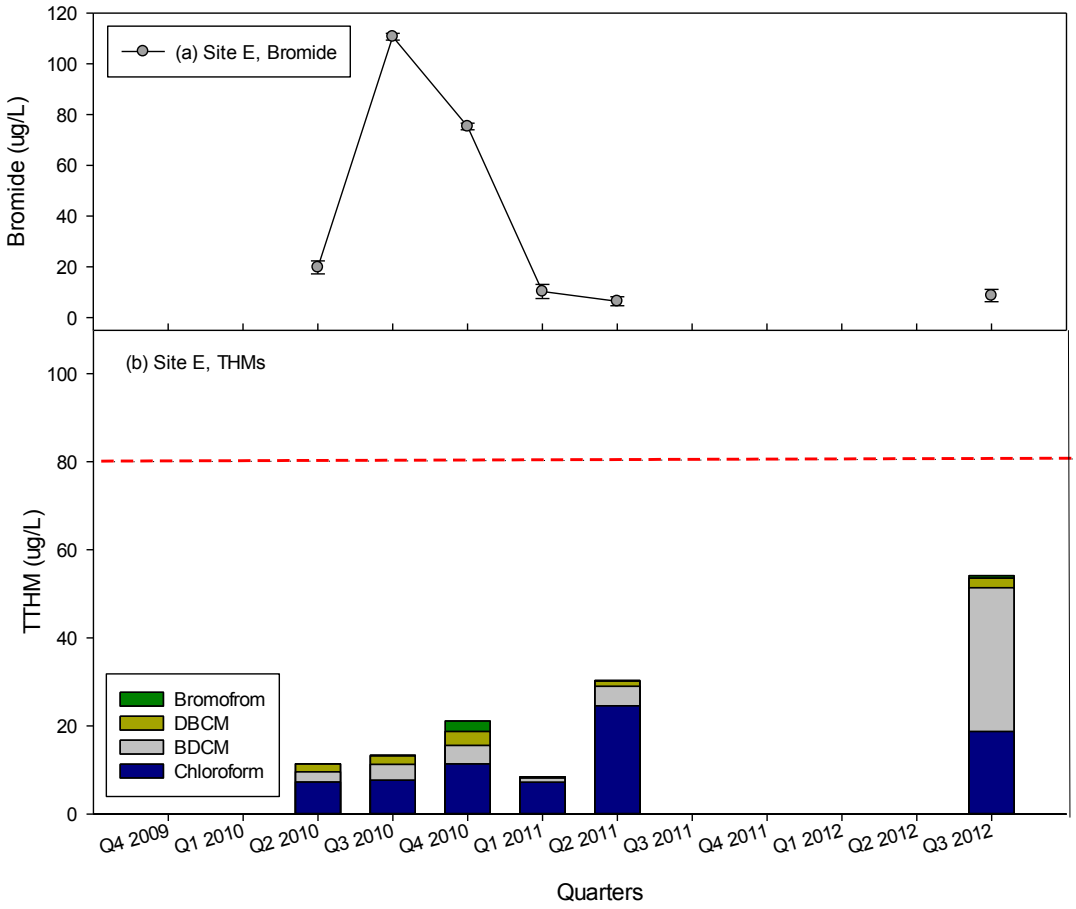

Figure B.15 Quarterly bromide in source water and THM levels in finished water at Site E.

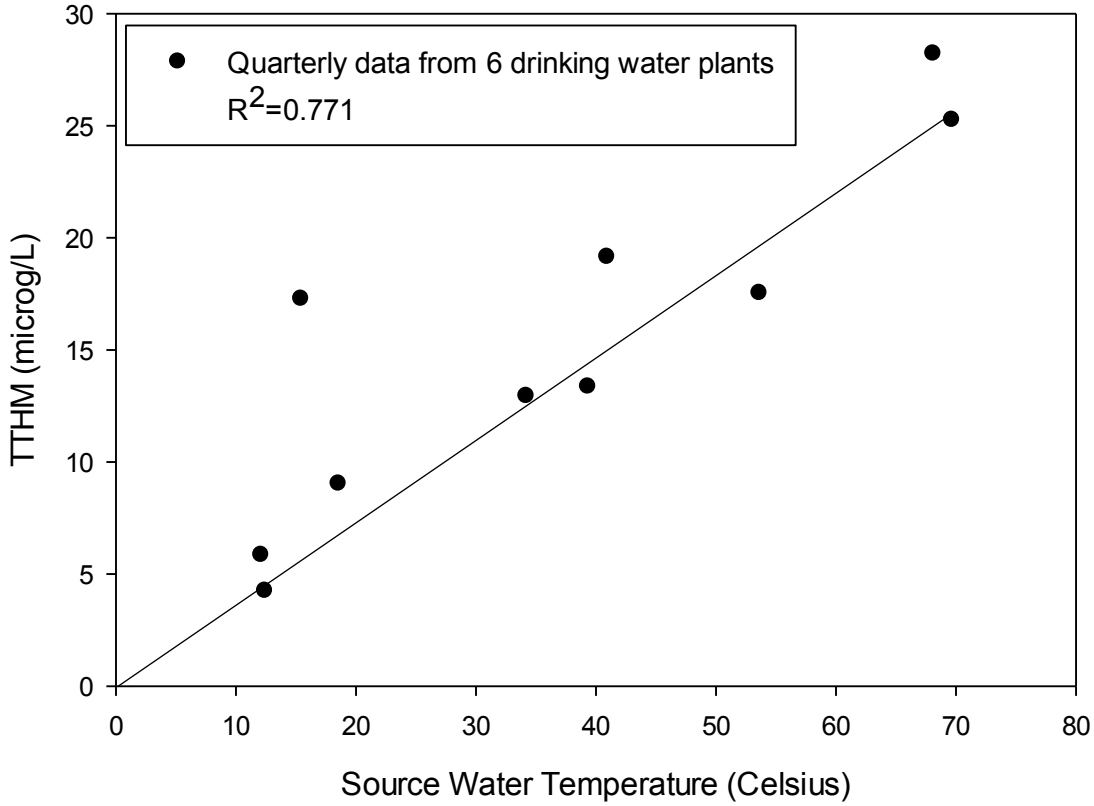

Figure B.16 Linear regression between source water temperature and quarterly TTHM levels in finished water. Data are from 6 drinking water plants.

Appendix C. Assessing the Risk Associated with Increasing Bromide in Drinking Water Sources

Table C.1 Correlation results of natural logarithm of field sampling THMs and correlation results of Monte Carlo simulated THMs. Field sampling data are from 6 drinking water plants.

When Bromide Ranges 0-20 µg/L									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform	BDCM	DBCM	Bromofrom		Chloroform	BDCM	DBCM	Bromofrom
Chloroform	1				Chloroform	1			
BDCM	0.532	1			BDCM	0.524	1		
DBCM	0.161	0.238	1		DBCM	0.162	0.240	1	
Bromofrom	0.145	0.289	0.0535	1	Bromofrom	0.145	0.282	0.0607	1
When Bromide Ranges 20-40 µg/L									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform	BDCM	DBCM	Bromofrom		Chloroform	BDCM	DBCM	Bromofrom
Chloroform	1				Chloroform	1			
BDCM	0.613	1			BDCM	0.606	1		
DBCM	0.475	0.501	1		DBCM	0.468	0.500	1	

Bromofrom	0.443	0.335	0.231	1	Bromofrom	0.435	0.331	0.238	1
When Bromide Ranges 40-60 µg/L									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform	BDCM	DBCM	Bromofrom		Chloroform	BDCM	DBCM	Bromofrom
Chloroform	1				Chloroform	1			
BDCM	0.934	1			BDCM	0.934	1		
DBCM	0.655	0.711	1		DBCM	0.659	0.715	1	
Bromofrom	0.356	0.466	0.664	1	Bromofrom	0.360	0.470	0.665	1
When Bromide Ranges 60-80 µg/L									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform	BDCM	DBCM	Bromofrom		Chloroform	BDCM	DBCM	Bromofrom
Chloroform	1				Chloroform	1			
BDCM	0.881	1			BDCM	0.883	1		
DBCM	0.578	0.717	1		DBCM	0.590	0.724	1	
Bromofrom	0.121	0.342	0.215	1	Bromofrom	0.129	0.346	0.221	1
When Bromide Ranges 80-100 µg/L									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform	BDCM	DBCM	Bromofrom		Chloroform	BDCM	DBCM	Bromofrom
Chloroform	1				Chloroform	1			

BDCM	0.532	1			BDCM	0.546	1		
DBCM	-0.0338	0.369	1		DBCM	-0.0389	0.365	1	
Bromofrom	-0.0469	0.420	0.453	1	Bromofrom	-0.0505	0.415	0.453	1
When Bromide Ranges 100-120 µg/L									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform	BDCM	DBCM	Bromofrom		Chloroform	BDCM	DBCM	Bromofrom
Chloroform	1				Chloroform	1			
BDCM	0.366	1			BDCM	0.364	1		
DBCM	0.222	0.341	1		DBCM	0.217	0.340	1	
Bromofrom	0.406	0.238	0.773	1	Bromofrom	0.399	0.228	0.774	1
When Bromide > 120 µg/L									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform	BDCM	DBCM	Bromofrom		Chloroform	BDCM	DBCM	Bromofrom
Chloroform	1				Chloroform	1			
BDCM	0.773	1			BDCM	0.774	1		
DBCM	0.443	0.557	1		DBCM	0.445	0.561	1	
Bromofrom	0.0231	0.543	0.330	1	Bromofrom	0.0295	0.545	0.338	1

Table C.2 Parameter estimates and estimated mean concentration for each THM species in each bromide ranges. The correlation parameters p(1,i=1,4) are shown in the above Table. Parameters are compared with field sampling THMs and Monte Carlo simulation THMs.

When Bromide Ranges 0-20 µg/L (k=1)									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4		Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4
a_i	9.90	8.94	5.93	5.27	a_i (i = 1,4)	9.90	8.94	5.93	5.27
b_i	0.853	1.83	2.99	2.03	b_i (i = 1,4)	0.853	1.83	2.98	2.03
$\mu_{i,k}$ in µg/L	28.5	40.8	32.3	1.54	Simulated Mean by Monte Carlo	28.5	43.4	32.0	1.51
When Bromide Ranges 20-40 µg/L (k=2)									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4		Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4
a_i	9.77	8.36	5.79	4.98	a_i (i = 1,4)	9.77	8.36	5.79	4.98
b_i	1.01	2.35	2.98	2.03	b_i (i = 1,4)	1.01	2.35	2.98	2.03
$\mu_{i,k}$ in µg/L	29.3	67.7	29.3	1.15	Simulated Mean by Monte Carlo	29.3	67.7	27.8	1.15
When Bromide Ranges 40-60 µg/L (k=3)									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4		Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4
a_i	9.61	8.96	7.61	5.62	a_i (i = 1,4)	9.61	8.96	7.61	5.62
b_i	1.39	2.07	2.87	2.21	b_i (i = 1,4)	1.39	2.07	2.87	2.22

$\mu_{i,k}$ in µg/L	39.5	66.4	125	3.24	Simulated Mean by Monte Carlo	39.6	65.1	111	3.15
When Bromide Ranges 60-80 µg/L (k=4)									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4		Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4
a_i	9.69	9.25	8.29	5.96	a_i	9.69	9.24	8.29	5.96
b_i	0.884	0.943	1.72	2.10	b_i	0.884	0.943	1.72	2.10
$\mu_{i,k}$ in µg/L	24.0	16.2	17.5	3.52	Simulated Mean by Monte Carlo	24.0	16.2	17.5	3.52
When Bromide Ranges 80-100 µg/L (k=5)									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4		Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4
a_i	9.71	9.31	8.60	7.27	a_i	9.71	9.31	8.60	7.27
b_i	0.664	0.737	2.03	1.81	b_i	0.664	0.737	2.03	1.81
$\mu_{i,k}$ in µg/L	20.6	14.5	42.4	7.36	Simulated Mean by Monte Carlo	20.6	14.5	42.4	7.36
When Bromide Ranges 100-120 µg/L (k=6)									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4		Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4
a_i	9.42	8.70	8.51	6.91	a_i	9.42	8.70	8.51	6.91
b_i	1.35	2.50	2.27	2.00	b_i	1.35	2.50	2.27	2.00
$\mu_{i,k}$ in µg/L	30.7	136	65.7	7.48	Simulated Mean by Monte Carlo	30.6	128	66.0	7.52

When Bromide > 120 µg/L (k=7)									
Field Sampling THMs					**Monte Carlo simulated THMs**				
	Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4		Chloroform i=1	BDCM i=2	DBCM i=3	Bromofrom i=4
a_i	9.70	9.67	9.00	7.53	a_i	9.70	9.67	9.00	7.53
b_i	1.00	0.935	2.22	2.10	b_i	1.00	0.935	2.22	2.10
$\mu_{i,k}$ in µg/L	26.8	24.5	95.6	16.8	Simulated Mean by Monte Carlo	26.8	24.5	92.8	16.8

Table C.3 Probability of meeting target risk, and meeting TTHM standard under each bromide range.

Bromide range (µg/L)	Probability of meeting Target TTHM risk	Probability of meeting TTHM standard by mass
0-20	38.8%	75.1%
20-40	50.5%	77.3%
40-60	40.7%	70.2%
60-80	27.2%	81.3%
80-100	14.6%	76.6%
100-120	29.9%	64.4%
>120	13.5%	61.3%

Table C.4 Spearman rank correaltion coefficients shown for relationship between quarterly bromide and THMs concentrations of all drinking water plants.

	Bromide	**Chloroform**	**BDCM**	**DBCM**	**Bromoform**	**TTHM**	**Percent Brominated THMs**	**BIF**
Bromide	1.00	-0.189 (0.557)	0.441 (0.152)	0.748 (0.005)	0.671 (0.017)	0.196 (0.542)	0.881 (0.00)	0.888 (0.00)
Chloroform Risk		1.00	0.476 (0.118)	0.280 (0.379)	-0.196 (0.542)	0.832 (0.001)	-0.182 (0.572)	-0.217 (0.499)
BDCM Risk			1.00	0.636 (0.026)	0.154 (0.633)	0.734 (0.007)	0.601 (0.039)	0.622 (0.031)
DBCM Risk				1.00	0.671 (0.017)	0.573 (0.051)	0.748 (0.005)	0.734 (0.007)
Bromoform Risk					1.00	0.112 (0.729)	0.510 (0.090)	0.524 (0.080)
TTHM						1.00	0.238 (0.457)	0.196 (0.542)
Percent Brominated -THMs							1.00	0.972 (0.000)
BIF								1.00

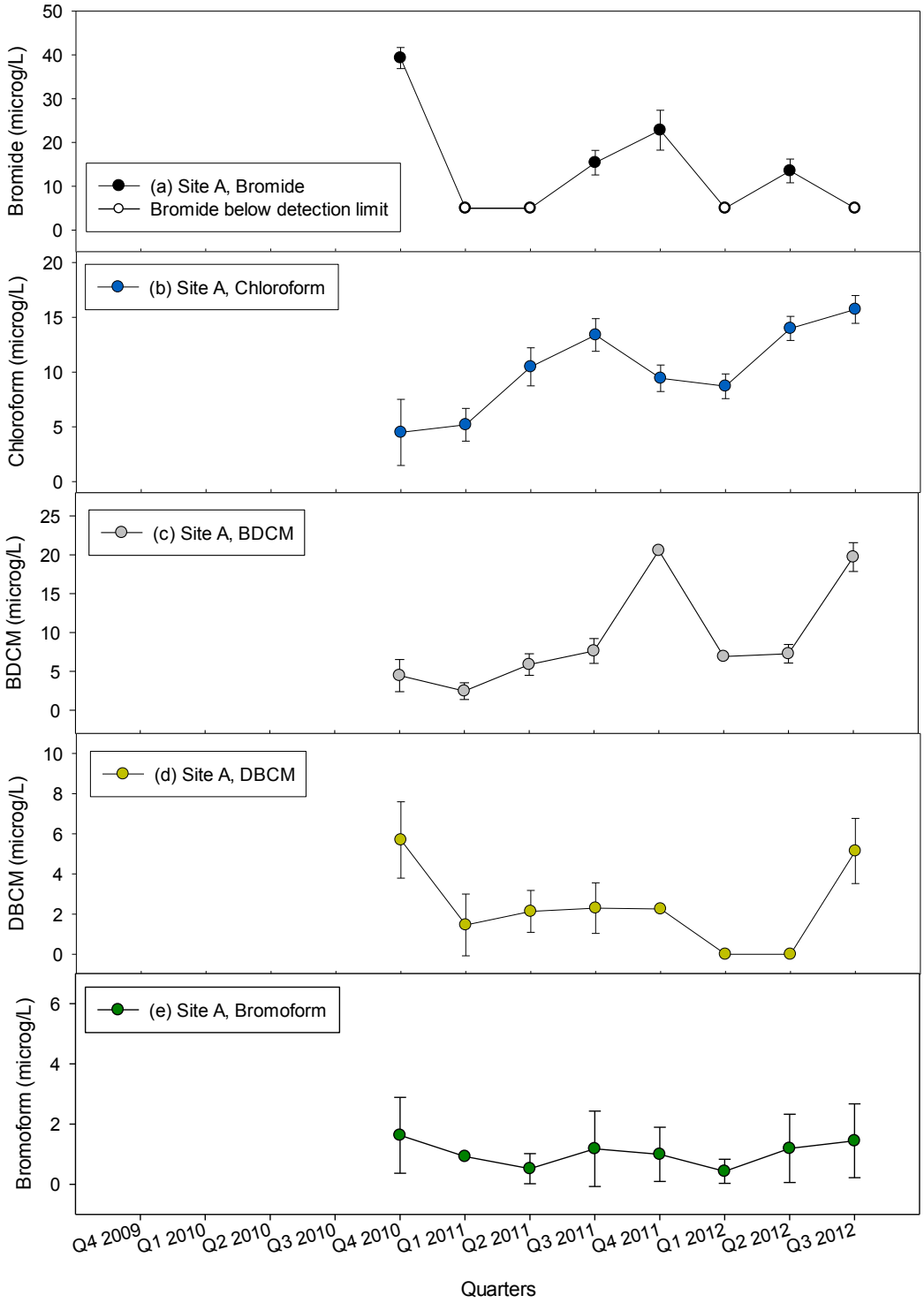

Figure C.1 Quarterly bromide concentrations and each THM levels in finished water at Site A.

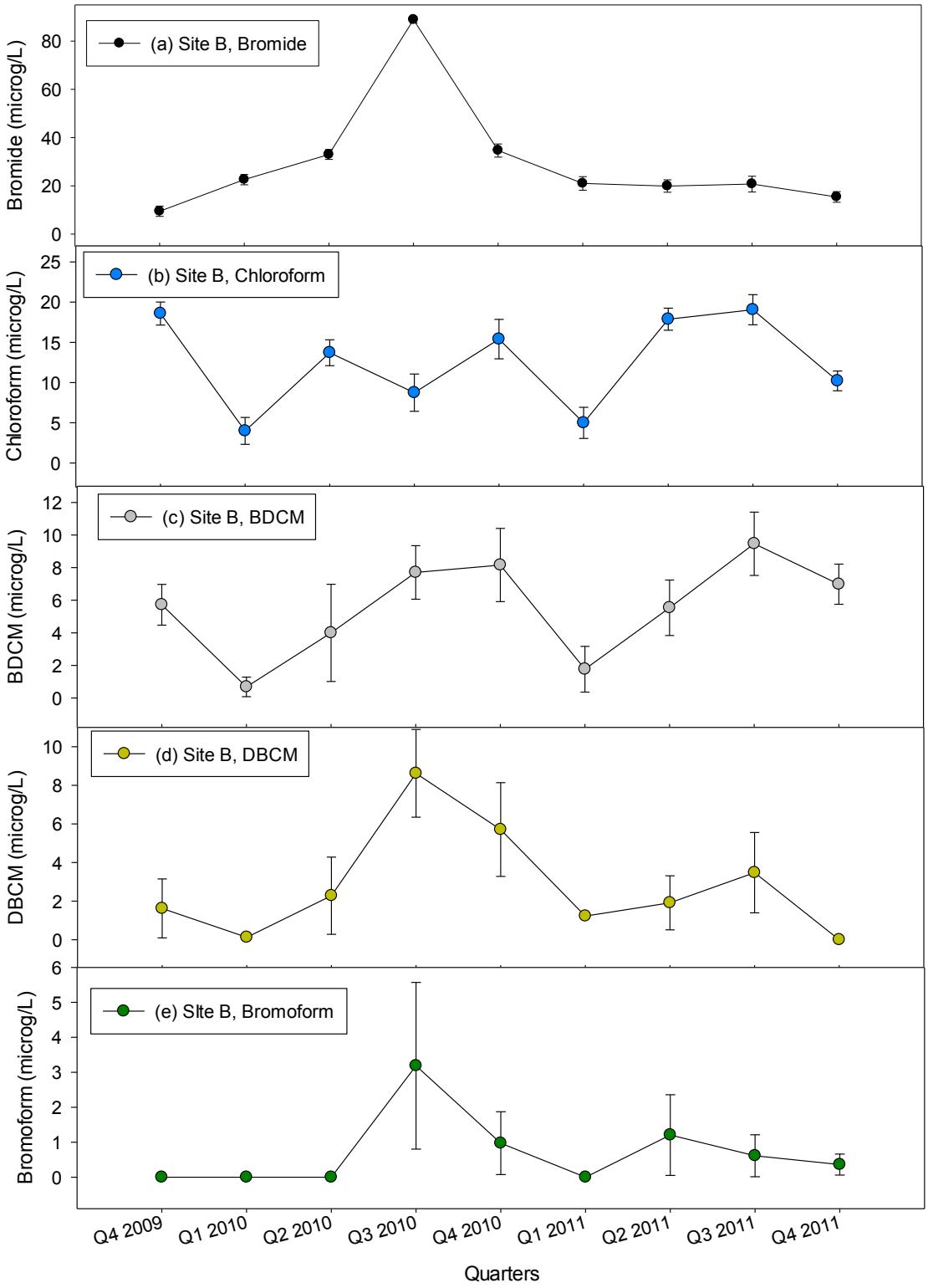

Figure C.2 Quarterly bromide concentrations and each THM levels in finished water at Site B.

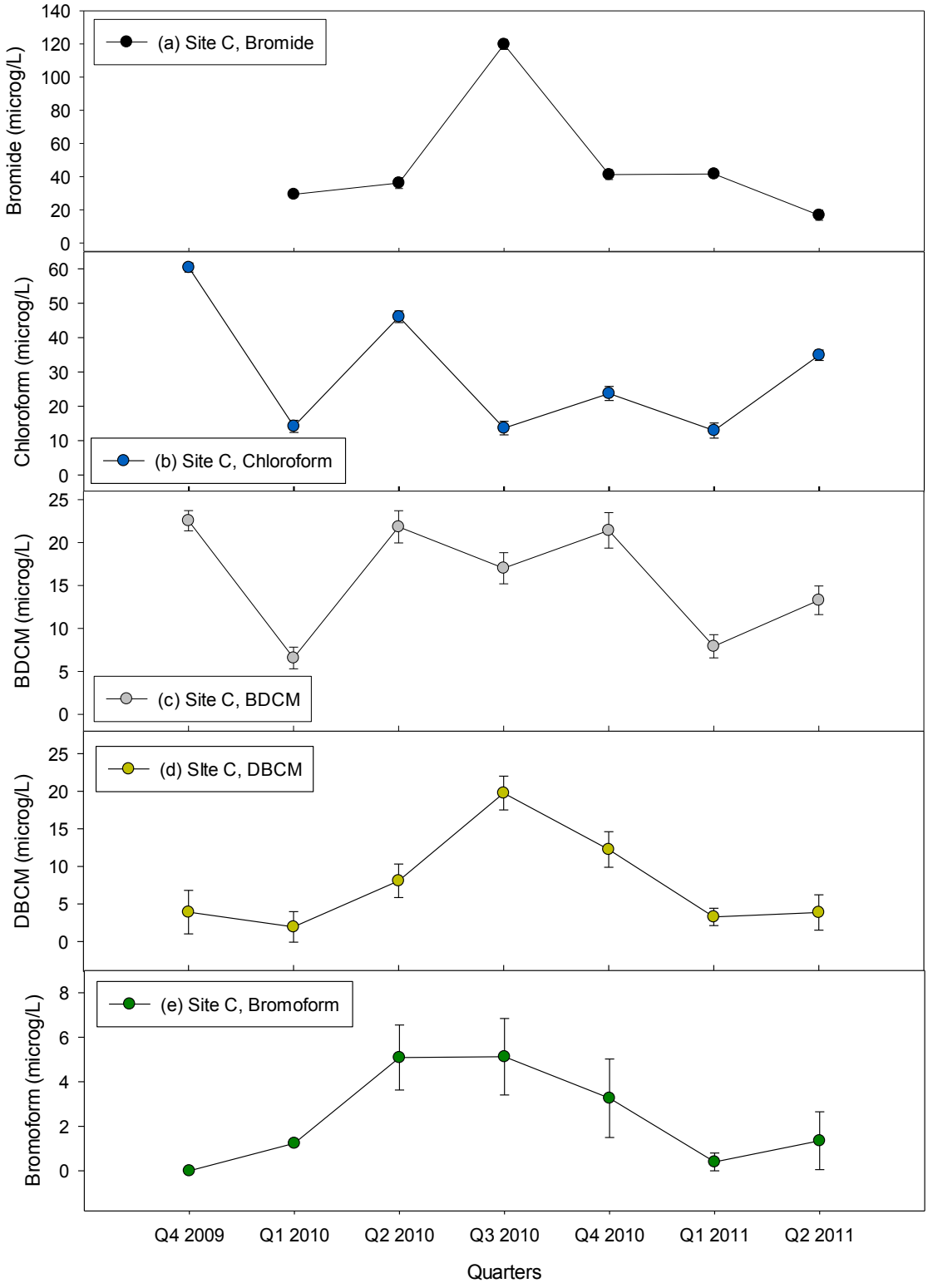

Figure C.3 Quarterly bromide concentrations and each THM levels in finished water at Site C.

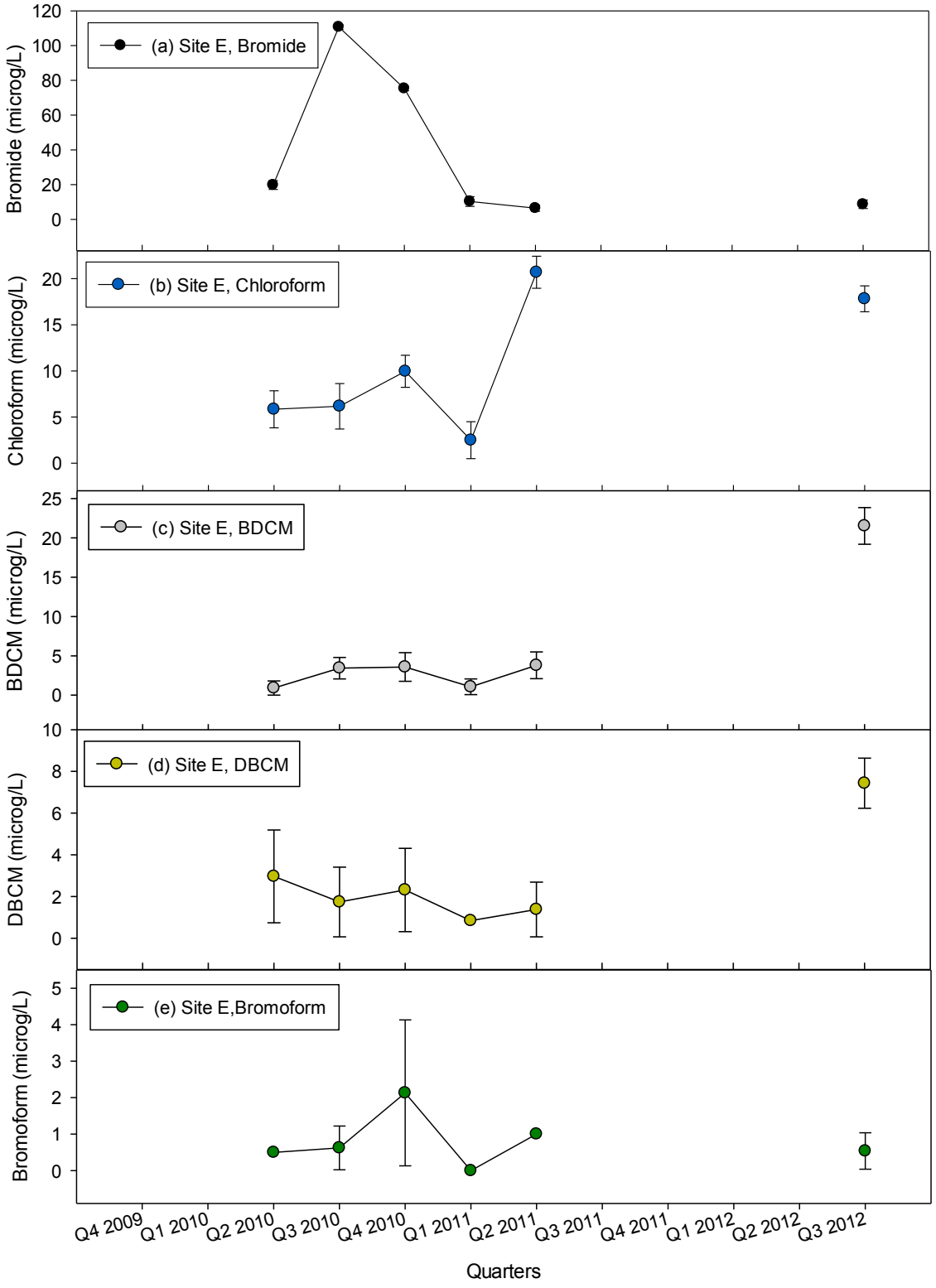

Figure C.4 Quarterly bromide concentrations and each THM levels in finished water at Site E.

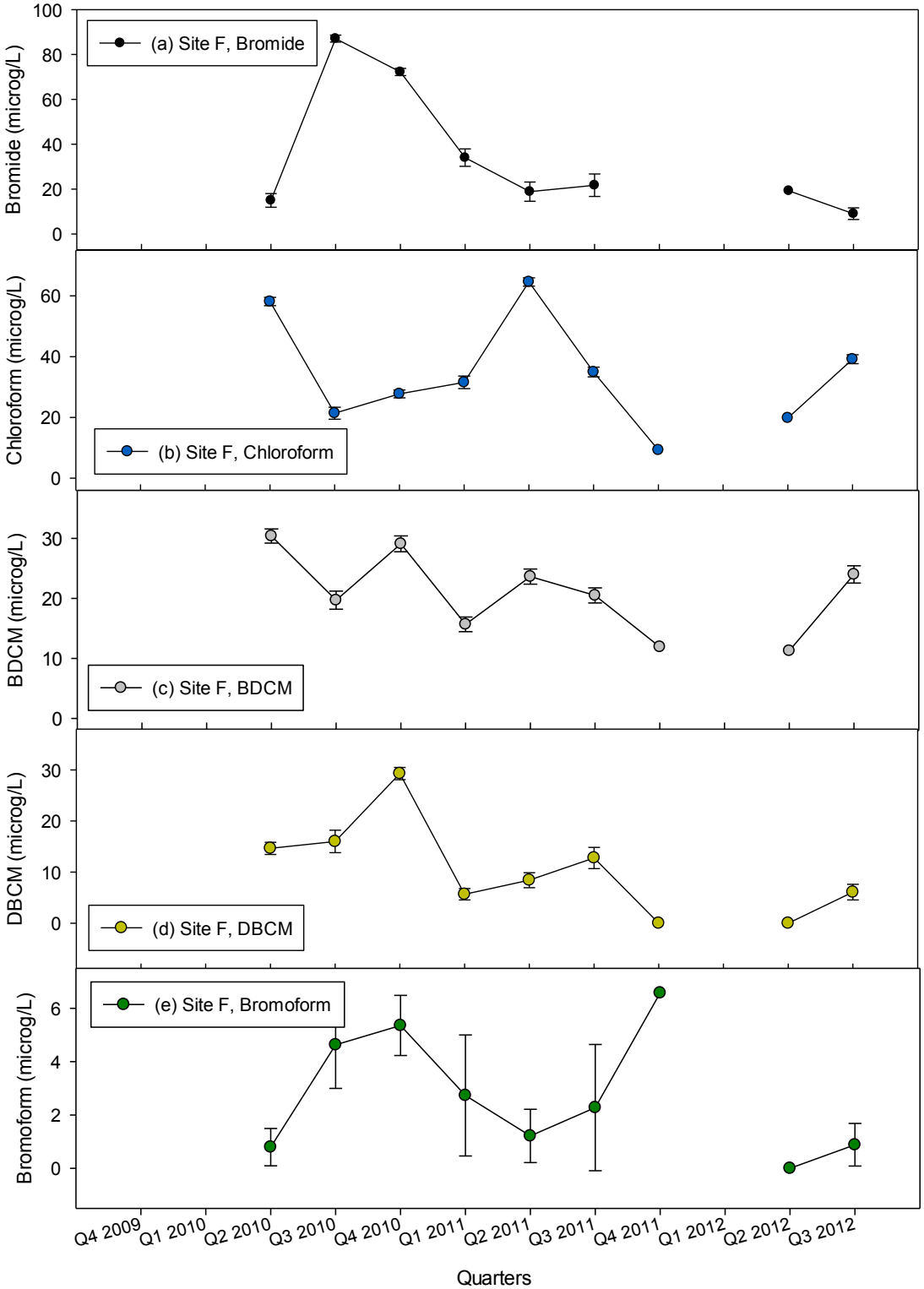

Figure C.5 Quarterly bromide concentrations and each THM levels in finished water at Site F.

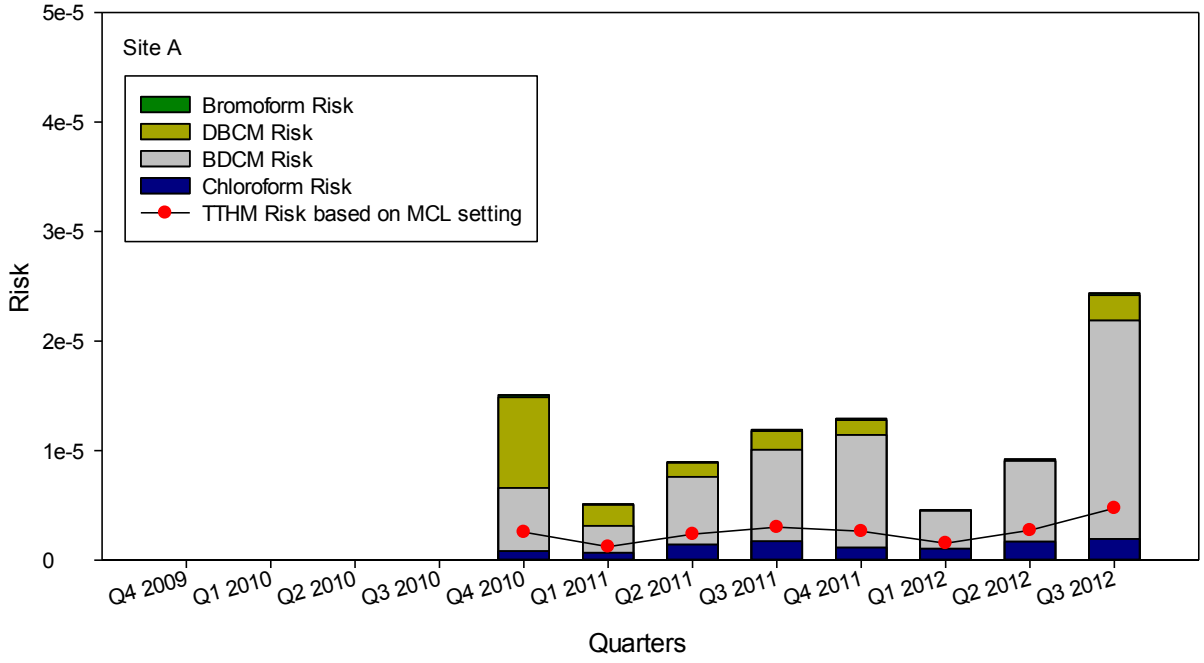

Figure 0.6 Risks of THM species at a quarterly basis of Site A.

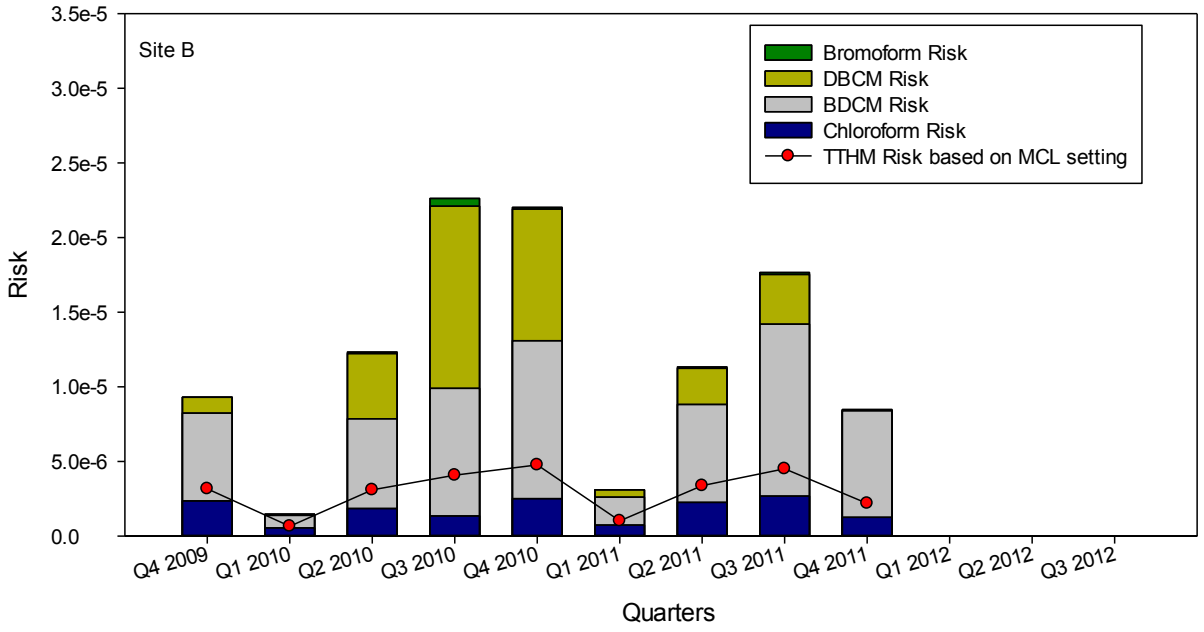

Figure C.7 Risks of THM species at a quarterly basis of Site B.

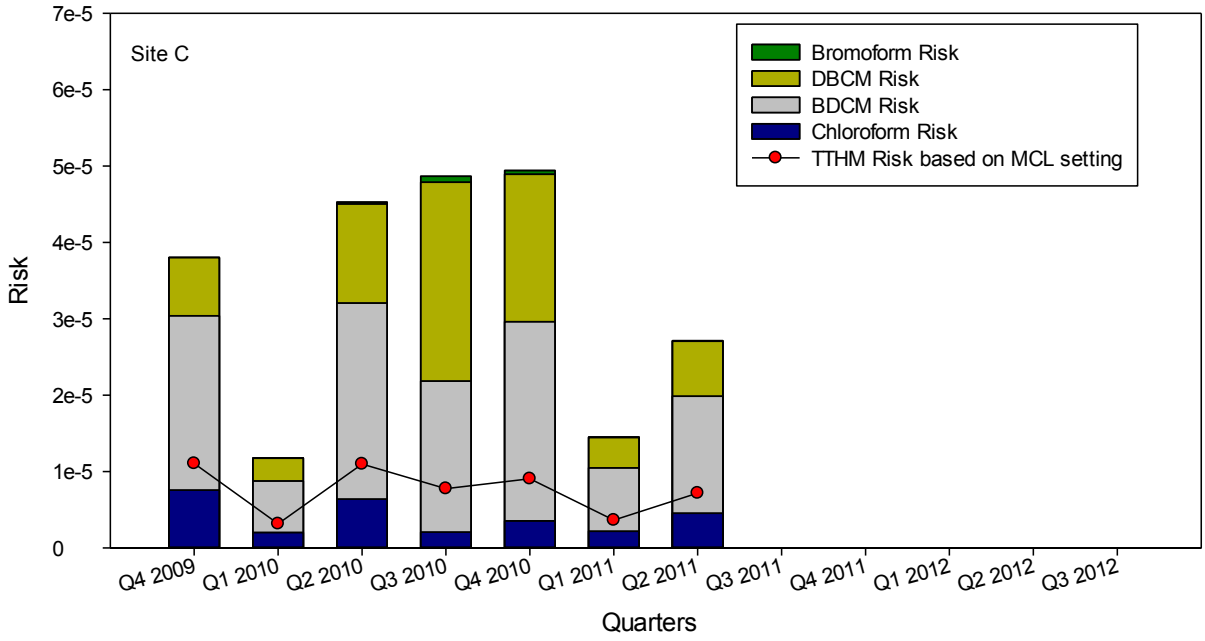

Figure C.8 Risks of THM species at a quarterly basis of Site C.

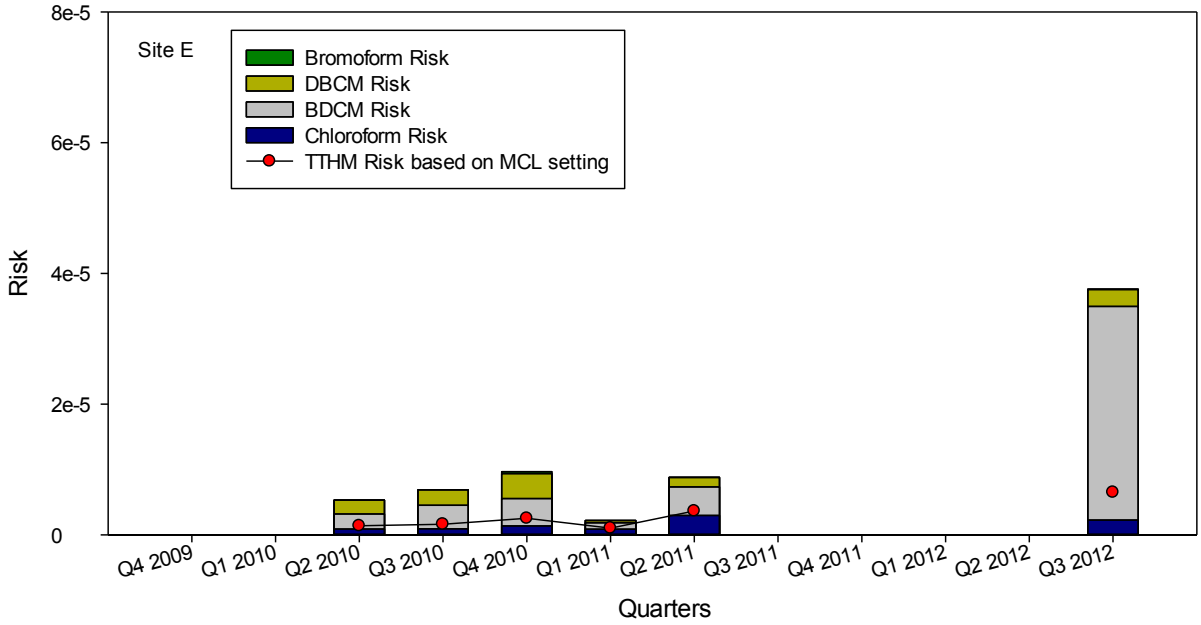

Figure C.9 Risks of THM species at a quarterly basis of Site E.

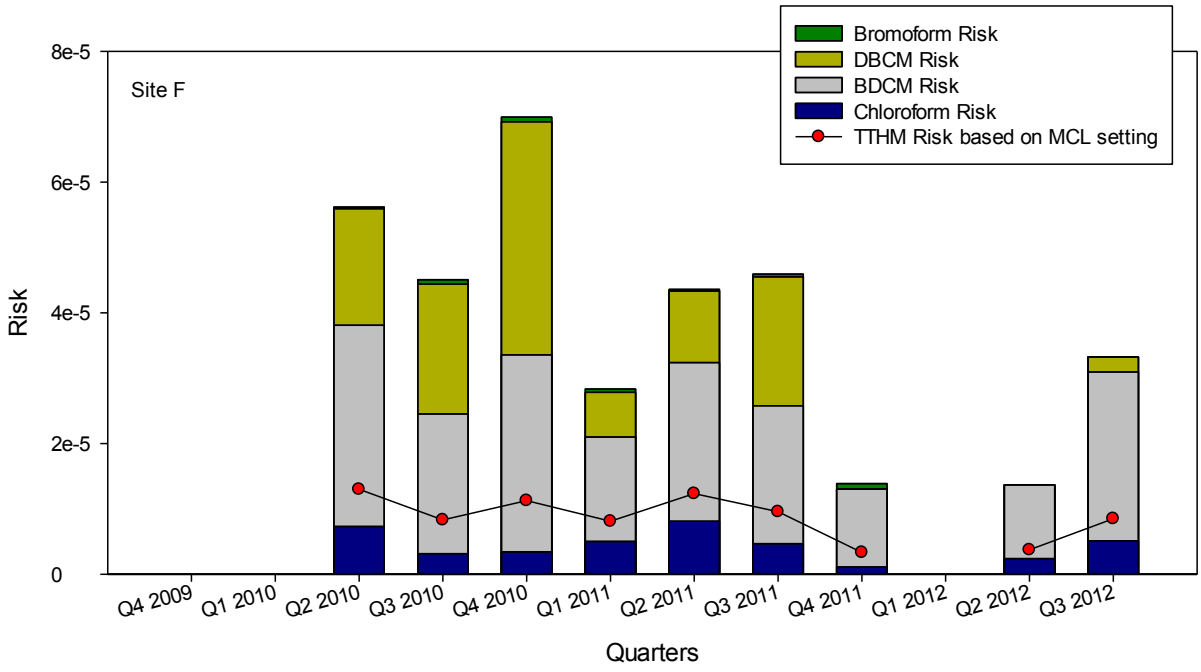

Figure C.10 Risks of THM species at a quarterly basis of Site F.

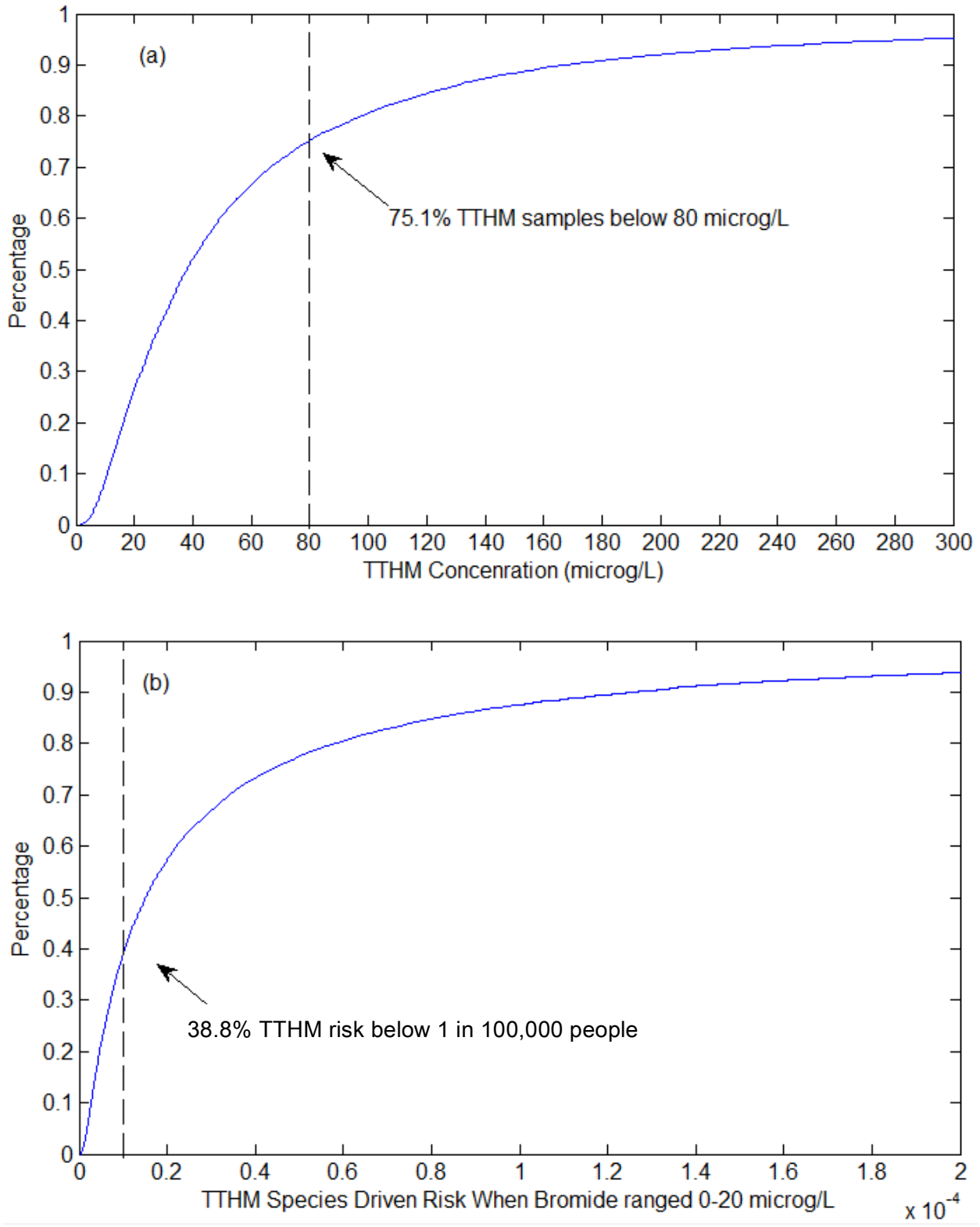

Figure C.11 Empirical CDF of TTHM concentration (panel a) and empirical CDF of TTHM species-specific risk (panel b) when bromdie ranges 0-20 µg/L.

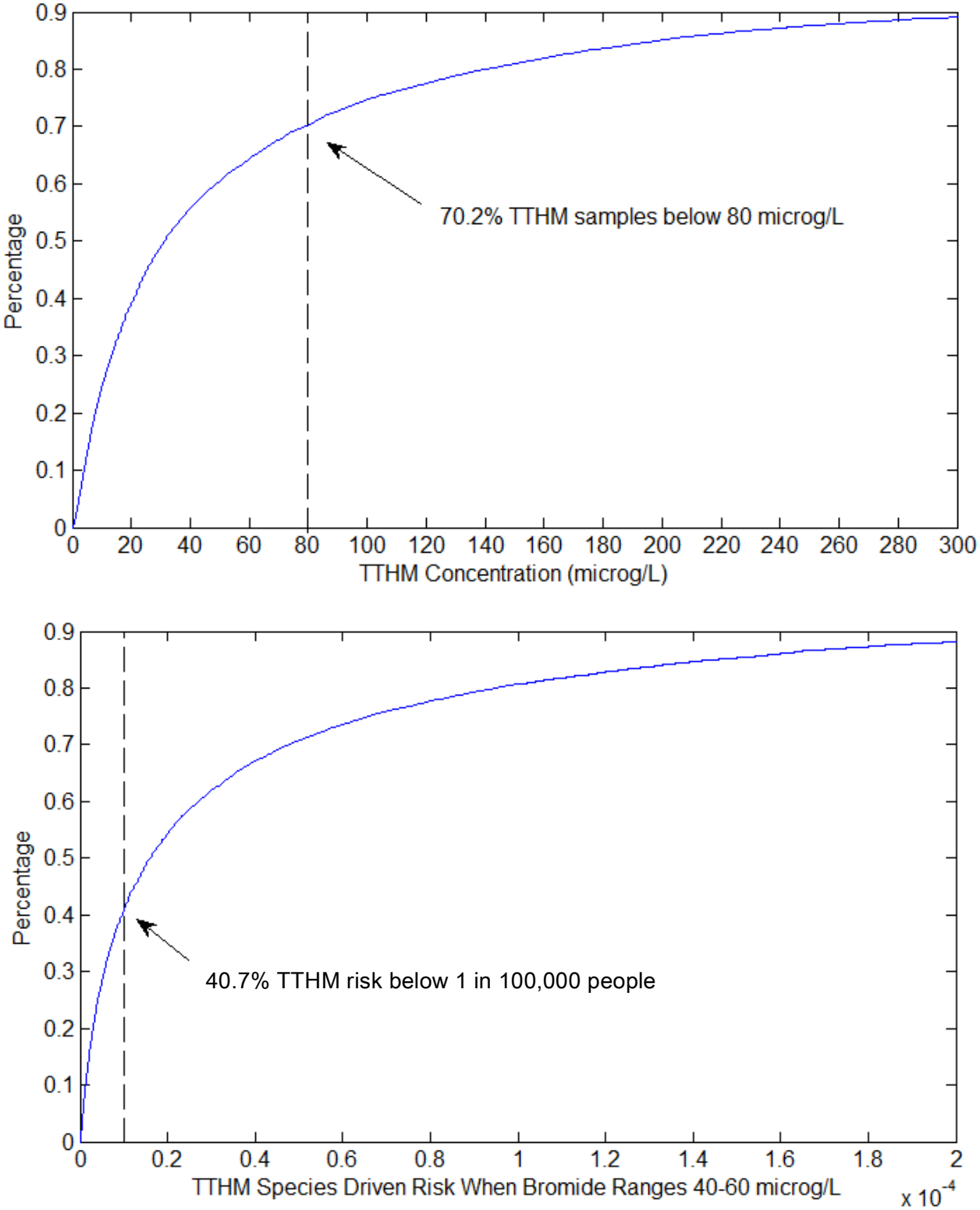

Figure C.12 Empirical CDF of TTHM concentration (panel a) and empirical CDF of TTHM species-specific risk (panel b) when bromide ranges 40-60 µg/L.

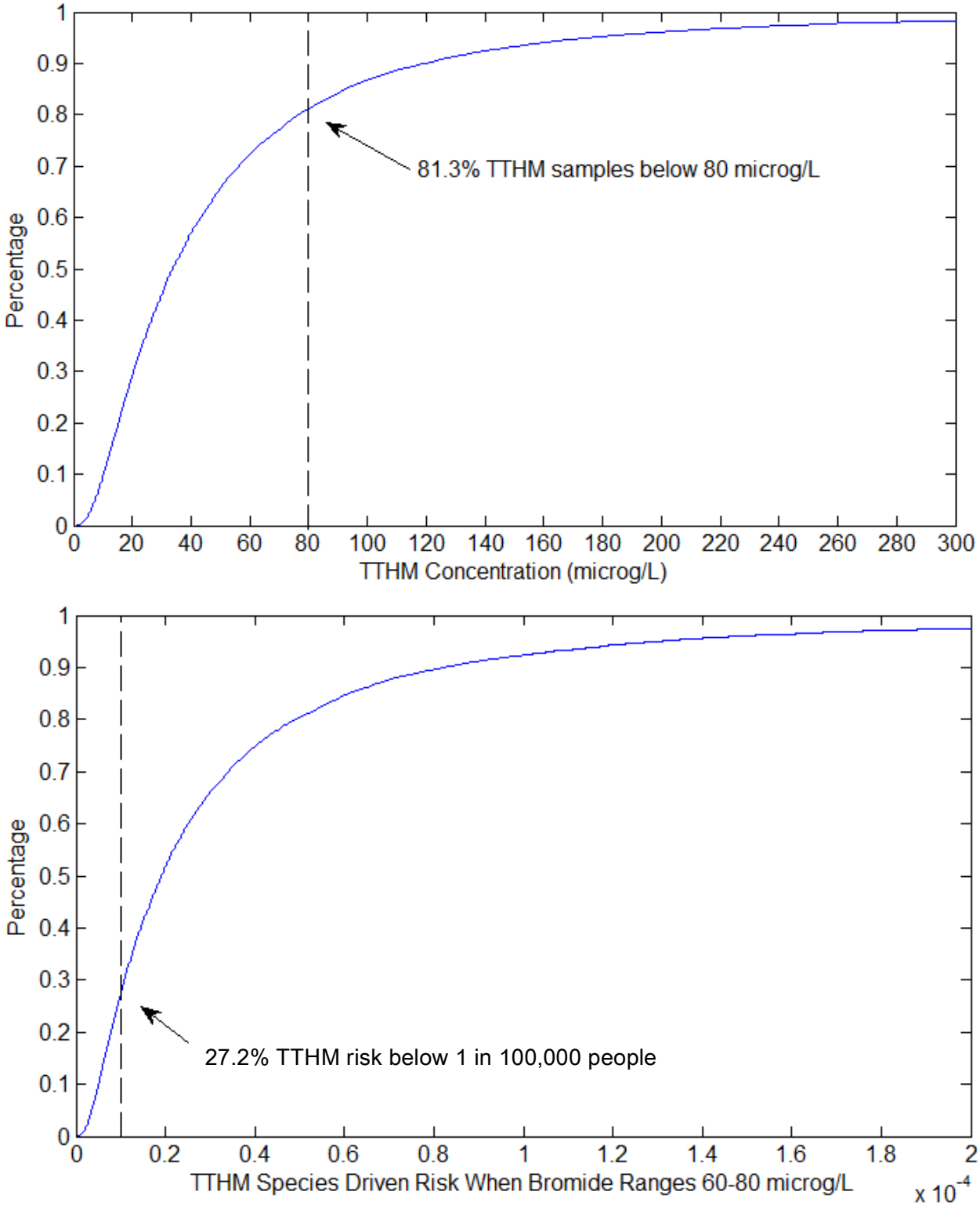

Figure C.13 Empirical CDF of TTHM concentration (panel a) and empirical CDF of TTHM species-specific risk (panel b) when bromide ranges 60-80 µg/L.

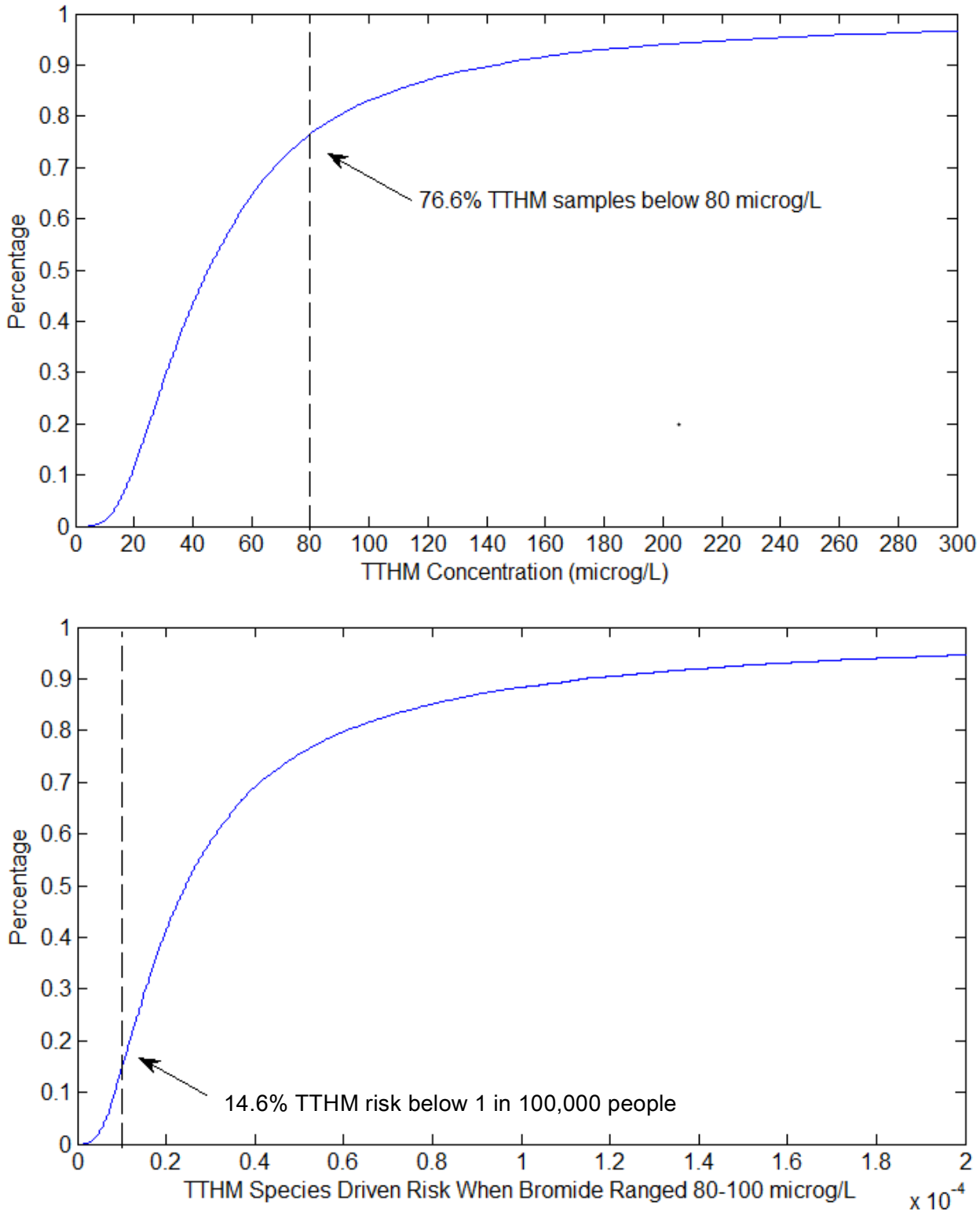

Figure C.14 Empirical CDF of TTHM concentration (panel a) and empirical CDF of TTHM species-specific risk (panel b) when bromide ranges 80-100 µg/L.

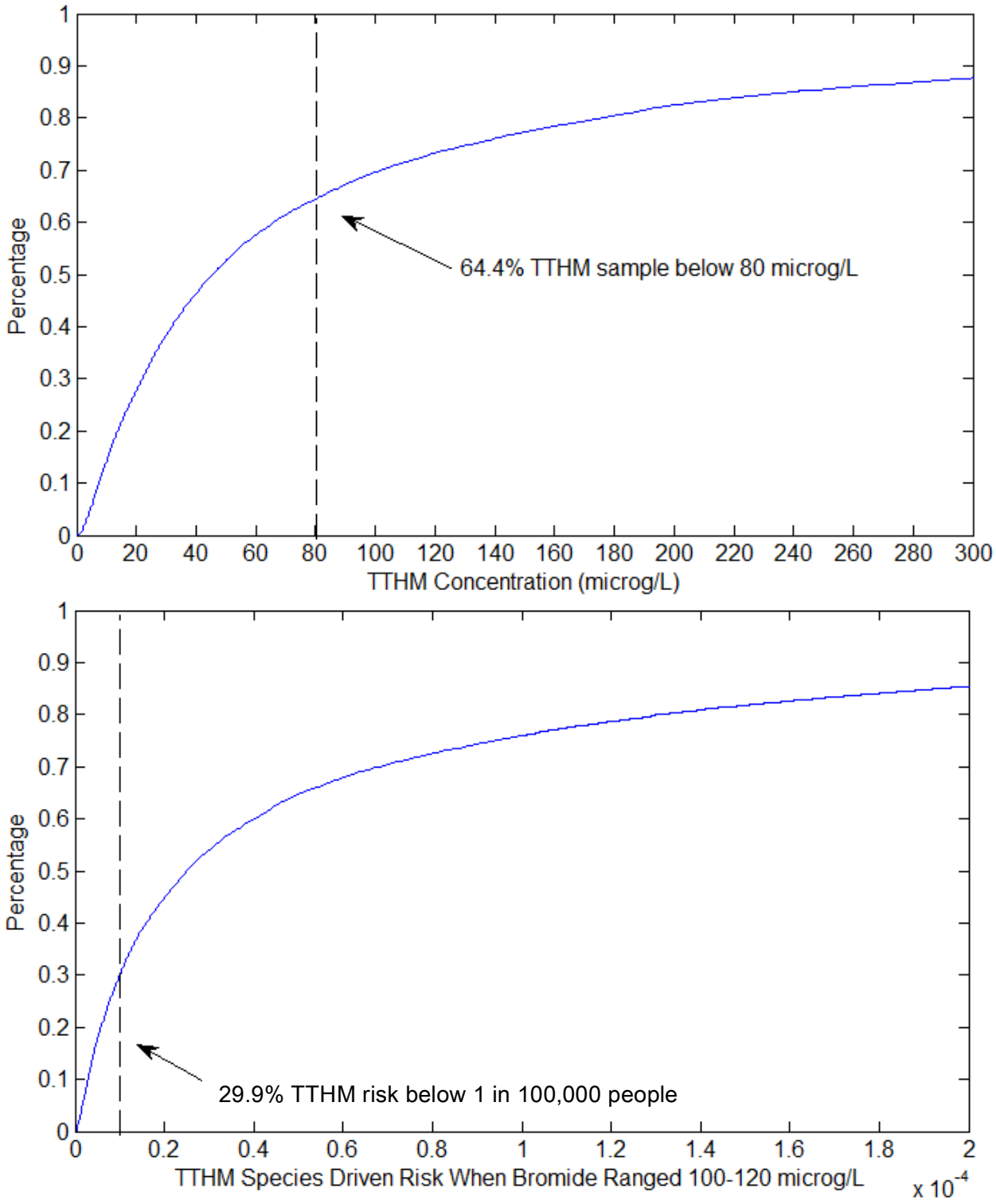

Figure C.15 Empirical CDF of TTHM concentration (panel a) and empirical CDF of TTHM species-specific risk (panel b) when bromide ranges 100-120 µg/L.

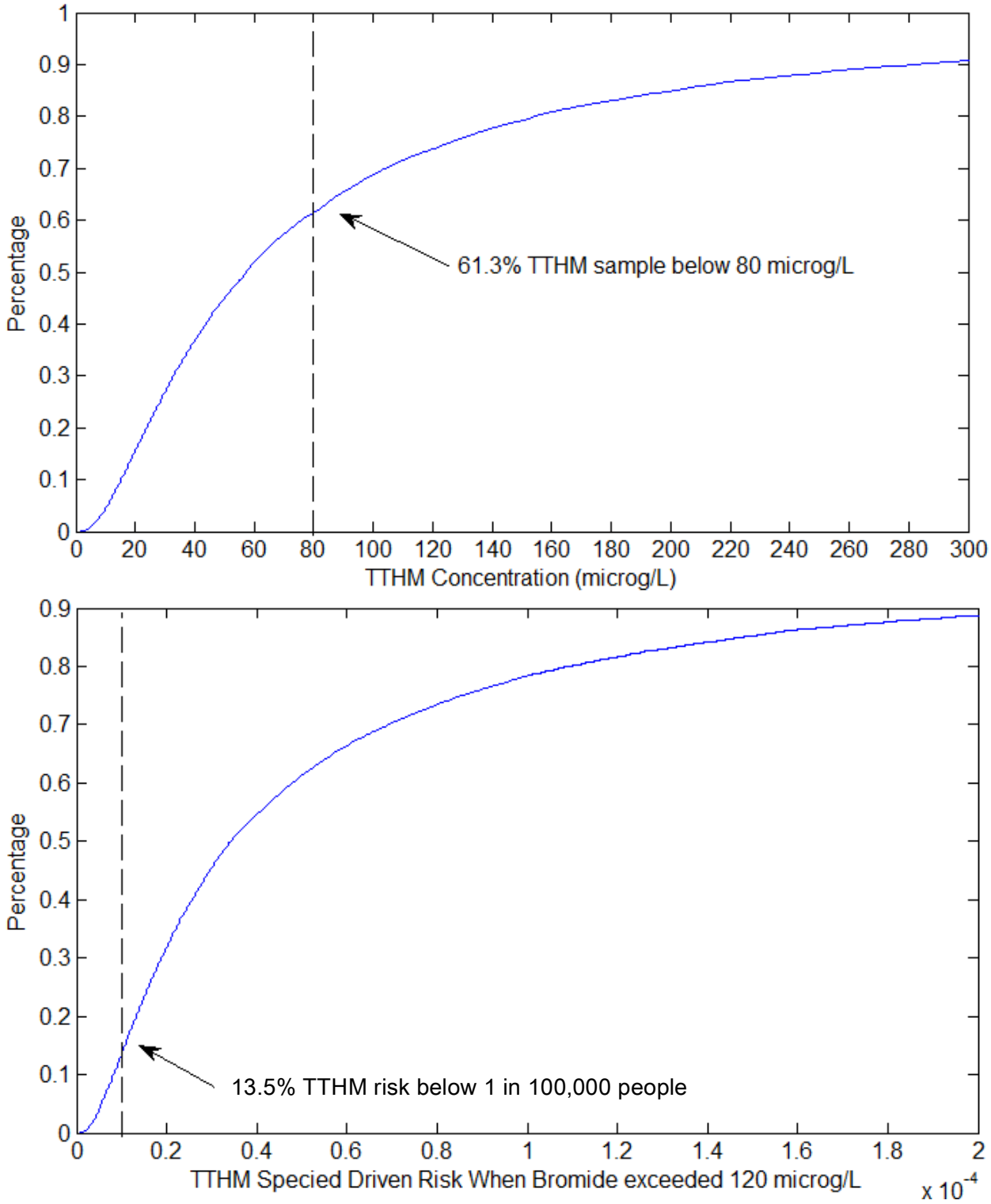

Figure C.16 Empirical CDF of TTHM concentration (panel a) and empirical CDF of TTHM species-specific risk (panel b) when bromide exceeds 120 µg/L.

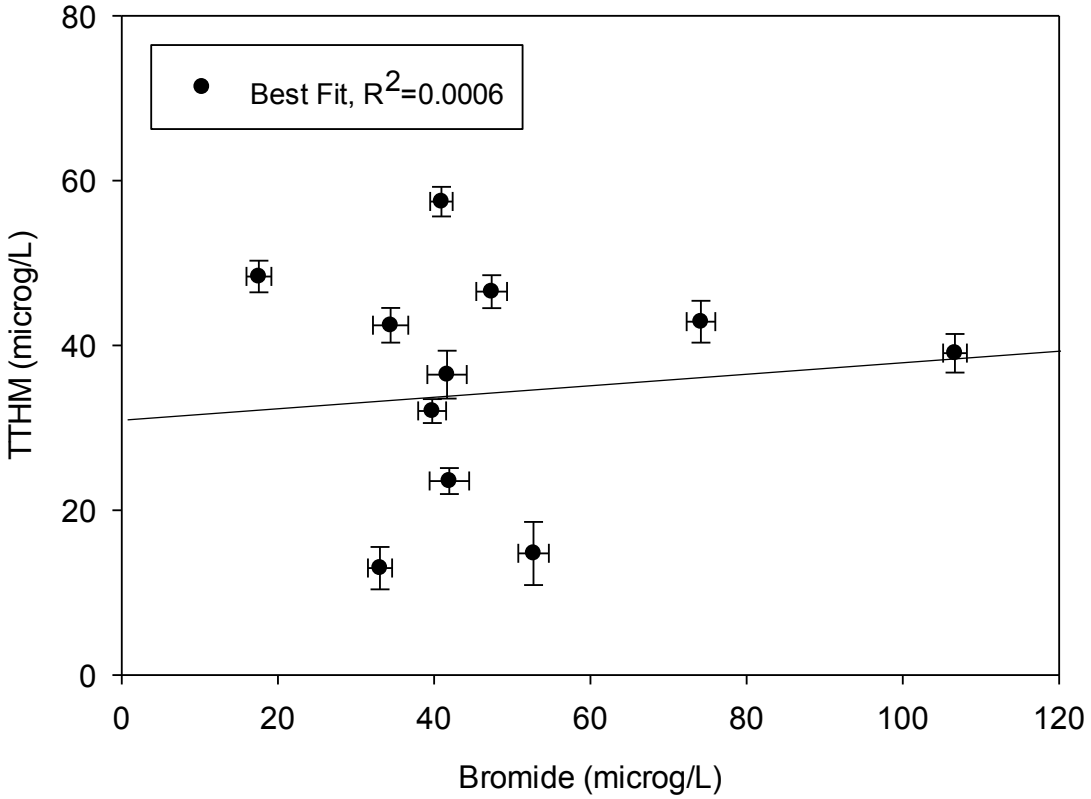

Figure C.17 Linear relationship between quarterly bromide and TTHM concentrations. The vertical error bar shows the standard deviation of TTHM. The horizonal error bar shows the standard deviation of bromide.

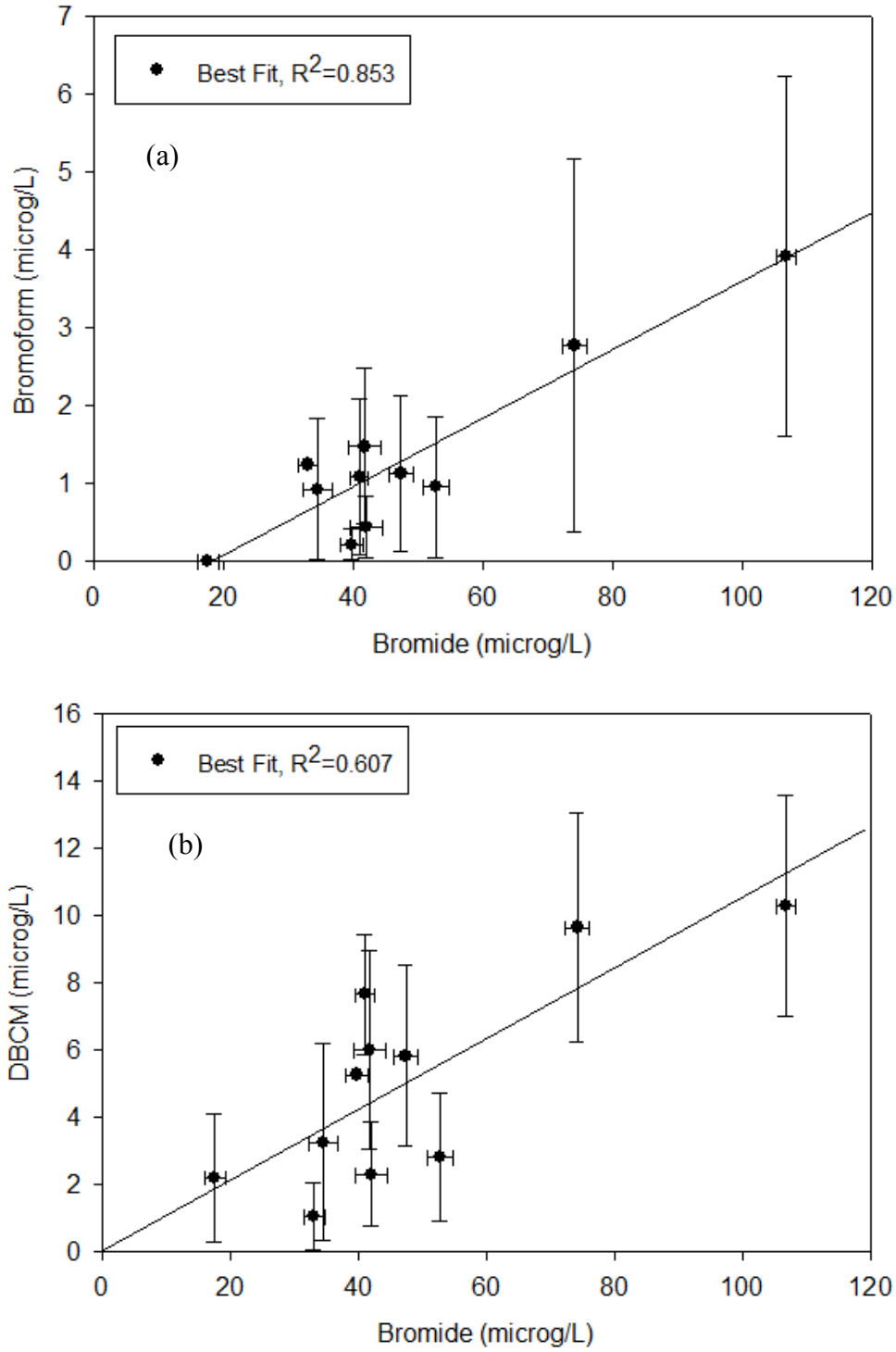

Figure C.18 Linear relationship between quarterly bromide and bromoform levels in panel (a); and DBCM levels in panel (b).

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